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**Single palladium sites supported on carbon capsules:
Synthesis, structure, and catalysis**

A thesis presented in fulfilment of the requirements of the degree of

Masters of Science

in

Chemistry

at Massey University, Manawatu, New Zealand

Nicholas Symon

2019

Abstract

This work investigates the impregnation of palladium into hollow carbon capsules through a novel synthesis method. This work investigates the feasibility of the method, improves on the method and suggests further improvements. The formation of palladium nanoparticles in hollow carbon capsules is investigated by varying the loading of palladium. This is further investigated by demonstrating the effect of other synthesis variables. The synthesized single palladium sites supported on hollow carbon capsules are then investigated for catalytic activity. These catalysts were found to be catalytically active for the Suzuki coupling reaction.

Contributions

Density functional theory calculations were performed by Omid Taheri. All other work in this thesis was completed by Nicholas Symon.

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Thank you to my loving partner Abbey Moore, my supervisor Shane Telfer, my Telfer group colleagues (in particular Subo Lee and Adil Alkas) and the mechanical workshop (especially the ever reliable Steve Denby).

Publications and thesis structure

Publications relevant to this thesis

No work has been published from this work.

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Chapter 1 Introduction

Introduction to Single Metal Atom Catalysts

Catalysts

A catalyst is any material that lowers the activation energy needed for a chemical reaction to occur that is not consumed in the reaction. This is shown graphically in Figure 1 below. Catalysts are used in almost every industry in which chemical reactions occur to minimise energy cost and processing time.

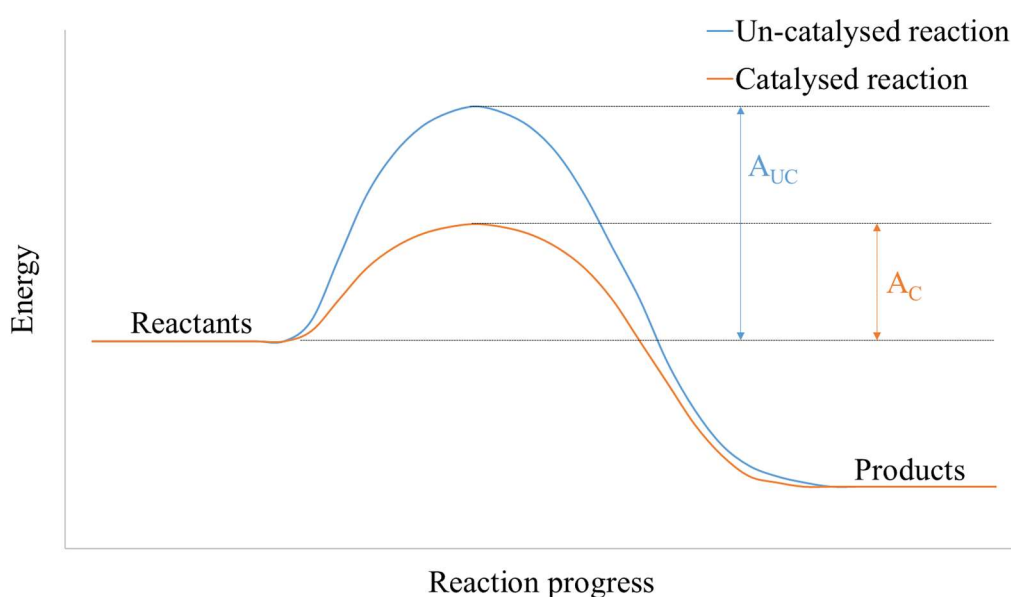


Figure 1 - Graph of the activation energy required compared between an un-catalysed and catalysed reaction. A_{UC} and A_C represents the activation energy required for the un-catalysed and catalysed reaction respectively.

Generally, catalysts affect the reaction by allowing the reactants to bind to a site where the catalyst then modifies them in some way (e.g. enhances the polarity of a key bond or breaks a bond in the reactant altogether). The reactant is then able to form the product via a pathway with a lower activation energy barrier than would otherwise be required. This is shown in Figure 1 above, as the activation energy for the catalysed reaction (A_C) is smaller than the activation energy required for the un-catalysed reaction (A_{UC}). It is important to note that every catalyst increases the kinetics of both the forward and reverse reactions, thereby increasing the rate of reaction, and does not affect the thermodynamic properties of the reaction such as the equilibrium point.

Homogeneous Catalysts and Heterogeneous Catalysts

Homogeneous catalysts are generally liquid catalysts present in a liquid reaction (homo: same, genos: kind). The mechanics of how they operate are well understood, meaning they are easily tailored to a reaction resulting in exceptional performance. However, homogeneous catalysts are generally difficult to separate from the solution of products and reactants and are therefore not easily recyclable. In contrast, heterogeneous catalysts are easily separated from the reactants and products once the desired reaction has taken place, but the mechanism of how the material catalyses the reaction is generally not as well understood. Also, heterogeneous catalysts are not as easily tailored by conventional synthetic chemistry. Therefore, it is difficult to optimise a heterogeneous catalyst toward a target reaction in a rational way. The difficulty in understanding the mechanics of how heterogeneous materials catalyse a reaction lies in the fact that, as a material in its solid state, a heterogeneous catalyst is a bulk material. As a bulk material, one can define the *average* or the *pristine* structure of the material, but it is often difficult to fully define the surface of a material and isolate the effect of each catalytic site. It is therefore difficult to tune a heterogeneous catalyst for a reaction, as although we can see the overall effect of the material on the reaction, we cannot determine the effect of each surface site.

Single Metal Atom Catalysts

In the case of bulk metal catalysts, the metals are not perfect crystals, and the defects on the surface of the material such as ridges or holes/vacancies present on the atomic scale of the metal lattice generally operate as the catalytic site. Another way to look at this is that not every atom in a bulk metal material can serve as a catalytic site. This is important as when we try to maximise the efficiency of the metal used in a catalyst by imbedding or adsorbing the metal on a supporting material, we see that the metal atoms tend to aggregate into nanoparticles. This restricts the efficiency of the catalyst as each nanoparticle can contain hundreds of metal atoms and yet serves as a few catalytic sites at most, as shown below in Figure 2. A simple way to visualise this is the chocolate inside an M&M – you can't taste the chocolate until you have stripped away the coloured layer. Here we are looking to use as many metal atoms possible as catalytic sites – but many of them are trapped beneath the surface.

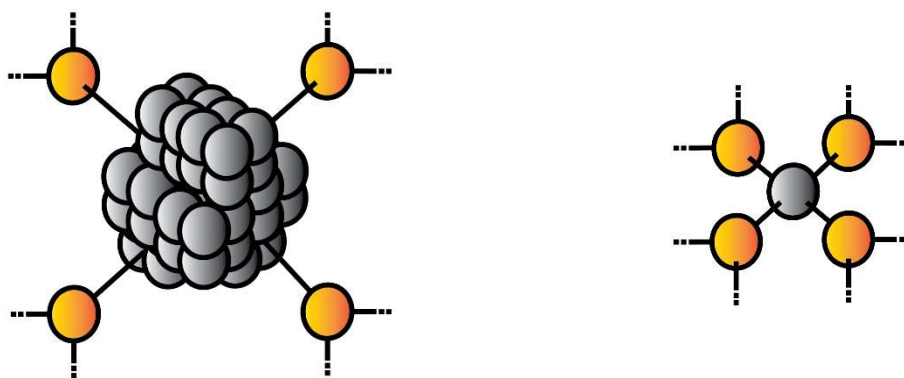


Figure 2 – Comparison between nanoparticle (left) and single metal atom sites (right) that are bound to a support material. Metal atoms are coloured grey and support atoms are orange.

Single metal atom catalysts are catalysts that use a single metal atom as the catalytic site. Single metal atoms must be bound to a support material to prevent aggregation into larger clusters. These materials have been of particular interest recently^[1-6], due to their high catalytic activity, ability to provide insight into the mechanisms of catalysis and their high efficiency of metal usage. Supported single metal atoms have extremely important qualities as catalysts. They often have higher catalytic activity per metal than their nanoparticle counterparts^[7] and can even outperform homogeneous catalysts^[8]. However, without strong interactions with the support the atoms tend to aggregate into larger particles to reduce surface energy. The support used has also been found to strongly influence the catalytic properties of the material^[9-10].

Adsorbed Single Metal Atom Catalyst

Adsorbed single metal atoms are metal atoms that have bonded to the surface of the support but have not integrated into the structure of the support. Examples of common support materials are metal oxides^[11-12] and carbon^[13-14]. These single metal atom materials differ from others in that they are directly bonded to the surface of the support but are not integrated into it. This means that the single metal site is more exposed than in other materials – which has its positives and negatives. One positive is that sites cannot be embedded deep within the material, and are therefore all available as catalytic sites. Conversely, each site is at increased risk of poisoning^[14-15] and harsh conditions (or even mechanical stress) could remove the metal from the surface.

Like any single metal atom catalyst, it is difficult to avoid agglomeration of the metal atoms. Adsorbed single metal atom catalysts are generally made through processes such as atomic

layer deposition^[13-14]. Through self-limiting reactions only a single metal atom will bond to the surface of the support. Other methods require extreme conditions to bond the single metal atoms to the support surface^[12].

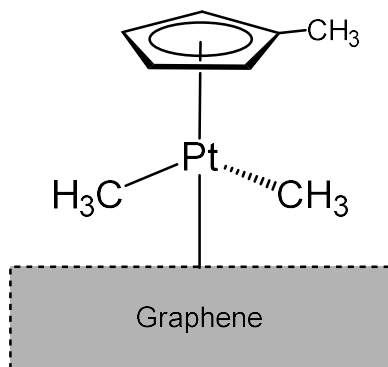


Figure 3 – Reproduced schematic^[14] of an adsorbed single metal atom catalyst.

The loading of the metal is generally quite low for these types of single metal atom catalysts, as higher loadings increase the likelihood of the metal atoms aggregating into nanoparticles. This is possibly because the bonding of the metal atom to the support is generally not as strong as the bonding that occurs in other types of single metal atom catalysts.

Organic Single Metal Atom Catalysts

Single metal atoms are often achieved by bonding the metal to an organic molecule^[16-18]. This can occur in living organisms, such as the well-known example of iron bonding to the porphyrin in heme^[19-20], or by utilising functional group in synthesized chemicals. Organic single metal atom catalysts feature all the benefits of conventional organic chemistry in that they are able to be designed and tailored.

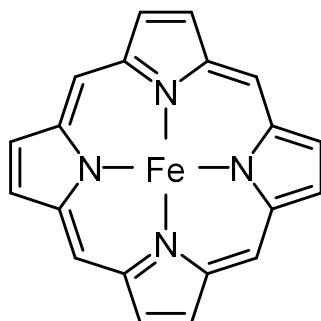


Figure 4 – Schematic of heme.

Organic single metal atom catalysts are traditionally homogeneous catalysts, but are included here as they can be bonded to supporting structures (such as MOF^[16]) to become heterogeneous. In this way, organic single metal atom catalysts can be thought of as a bridge between homogeneous and heterogeneous catalysts. Depending on the application, it may be desirable for the catalyst to be homogeneous, lowering mass transfer complications, or heterogeneous, lowering product contamination and aiding catalyst recyclability.

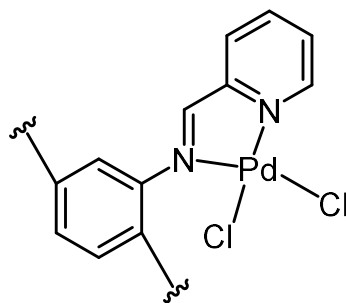


Figure 5 - Reproduced schematic of a single palladium atom bound to a coordinating group, shown without the support^[16].

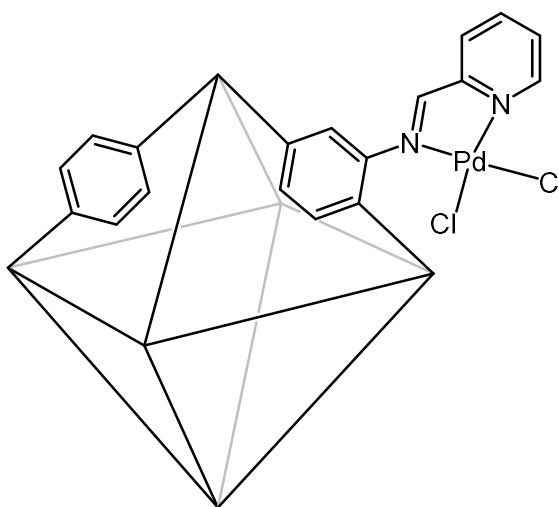


Figure 6 - Reproduced schematic of a single palladium atom bound to a coordinating group, shown with the support^[16].

These single metal atom materials differ from adsorbed single metal atom catalysts in that they utilise the activity of the functional groups contained on the organic molecule to bind to the support. Similar to adsorbed single metal atoms, they are not stable under harsh conditions, as the organic components of the material will decompose when exposed to high heat or acidity.

Doped Single Metal Atom Catalysts

Doped single metal atom catalysts are materials that feature single metal atoms throughout the structure of a support material. These materials vary widely, implementing metals such as cobalt^[21-22], nickel^[23], palladium^[8], platinum^[24], gold^[25], silver^[9], iridium^[26] and niobium^[27] on support materials, generally graphene or metal oxides. These materials are often synthesized through pyrolysis^[21, 28-34], but can also be synthesized through techniques such as photochemical methods^[35-36], wet-impregnation^[37] and ball-milling^[38].

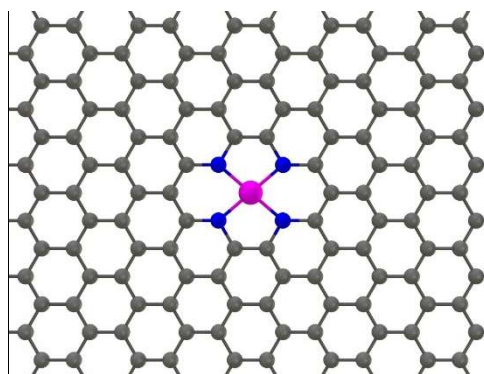


Figure 7 - Reproduced image^[38] of doped single metal atom catalysts.

As the metal atoms present in these materials are embedded into the supporting material, they are generally very stable and do not deteriorate easily. This is especially true of materials formed through extreme conditions such as pyrolysis. Conversely, the major downside of this type of single metal atom catalyst is that the metal atoms are not only embedded into the surface layer of the support, but throughout it. This creates complications in utilising the metal atoms fully, as some metal sites may be embedded deep in the material and have layers of support material covering the site, restricting access to the site. This can be counteracted somewhat by minimizing the thickness of the support, but this can be extremely difficult and create complications of its own as the support loses its structural integrity.

The loss of active sites due to the sites being embedded in deep layers of the support material is not as prominent in materials that feature pores at the atomic scale due to disorder in the layering structure. These pores allow reactants to penetrate into the catalyst support, accessing the embedded metal sites that are on deeper layers of the support. However, these sites will still suffer from mass transfer limitations and will therefore not be able to reach catalytic activities as high as metal atoms embedded on the surface of the support.

Carbon Doped Single Metal Atom Catalysts

Carbon doped single metal atom catalysts are catalytically active materials that feature single metal atoms embedded into a carbon support. The carbon support consists of graphene layers, often formed during pyrolysis and with the single metal atoms embedded during the process, but can also be pre-made and simply impregnated with the desired metal atoms. These graphene layers can be well-ordered, resulting in a dense graphite-like structure, or disordered, causing porosity.

In contrast to metal oxides, single metal atom materials that utilise carbon as a support generally utilise a binding agent to account for the lattice requirements of the support. While direct metal to carbon bonds are certainly possible, intermediary species such as sulphur^[37], nitrogen^[38] or oxygen^[13] are often utilized to integrate the metal into the support lattice. This can affect how stable the metal is, and therefore how resistant it is to agglomeration, as well as its catalytic performance^[4]. While metal oxides can also influence the catalytic activity of the single metal atom site, the binding mechanism of single metal atoms into graphene is of interest as there are many variables that can be utilised to optimise the catalytic activity of the single metal atom site.

Binding Mechanism of Nitrogen in a Graphene Lattice

The mechanism behind nitrogen as a binding agent is of particular interest in this work as nitrogen is readily available using the synthesis method in this work. There are 3 ways nitrogen can integrate into a graphene layer. These are graphitic nitrogen, pyridinic nitrogen, and pyrrolic nitrogen, as shown below in Figure 8. Graphitic nitrogen directly replaces a carbon atom in the graphene lattice. These are of interest when manipulating the electronic properties of graphene^[39], however, when binding palladium to the carbon support these graphitic nitrogen sites interact with palladium by a covalent bond without any charge redistribution. This results in the electronic state of the palladium corresponding to metallic palladium nanoparticles electronically modified by the interaction with the support^[40]. This suggests that graphitic nitrogen allows adsorption of palladium nanoparticles to the graphene surface, but does not integrate the palladium into the lattice of the graphene. This is largely proven by the lack of defects in the lattice surrounding graphitic nitrogen. Without defects there is no space to fit the palladium into the lattice. Pyridinic nitrogen bonds with two

carbon atoms at the edges or defects of graphene and contributes one p electron to the p system, whereas pyrrolic nitrogen refers to nitrogen that breaks the graphene lattice and contributes two p electrons to the π system^[41].

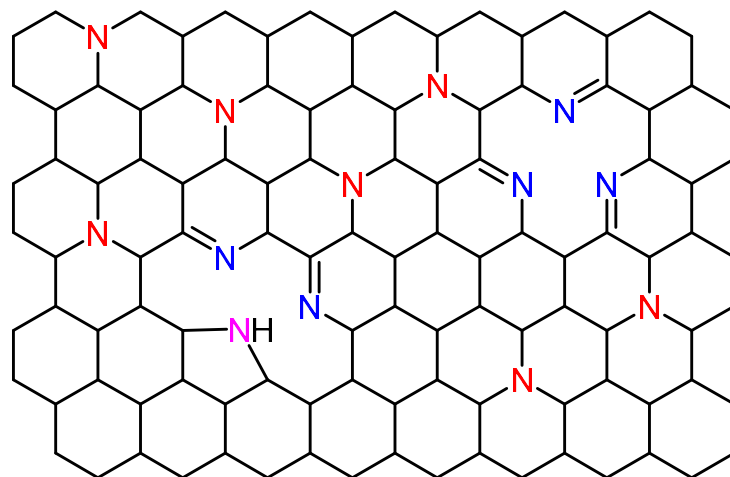


Figure 8 - Reproduced schematic representation of the N-doped graphene^[39]. The red, blue, and pink N's represent the “graphitic” N, “pyridinic” N, and “pyrrolic” N atoms in the N-doped graphene, respectively.

Pyridinic nitrogen can also form extended structures in graphitic carbon nitrides. These structures are referred to as triazine-based and heptazine-based layers^[42], shown below in Figure 9. It is likely that for the purposes of binding a metal atom into the lattice, triazine-based layers do not feature large enough vacancies in the lattice (shown by the red circle in Figure 9). Heptazine-based layers, however, have much larger vacancies, and have been shown to integrate palladium single metal atoms into the lattice extremely well^[8]. This type of binding site is likely difficult to synthesize through a pyrolysis-based nitrogen-doped graphene synthesis method due to the structures complexity, but is useful for comparison.

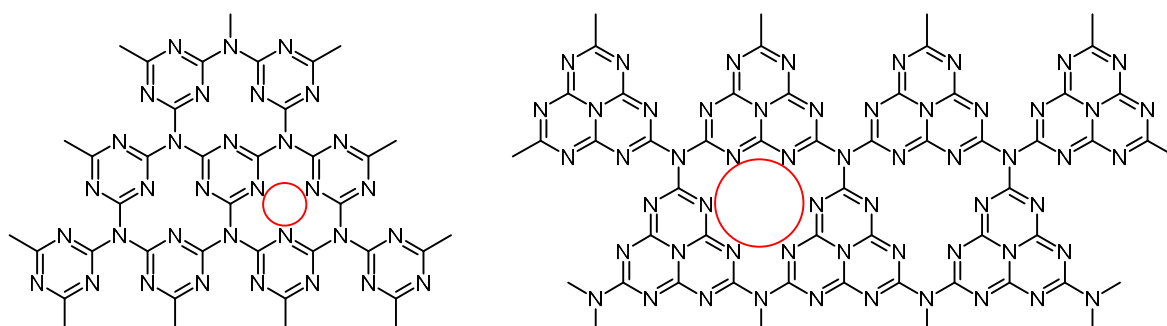
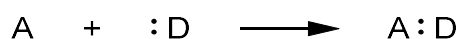


Figure 9 - Reproduced schematic of triazine-based (left) and heptazine-based (right) layers^[42]. Red circles highlight the vacancies in the lattice inherent to the structures.

Introduction to Coordination Chemistry

Coordination Complexes

Coordination complexes (also called coordination compounds or simply complexes) are molecules that are bonded by a coordination bond. A coordination bond is formed when one atom donates both electrons to form the bond between the two atoms^[43]. This is represented by Equation 1 below. Generally, coordination complexes are made up of charged metal centres (A) and organic linkers called ligands (D). In this bond formation the metal centres are electron acceptors and each of the electron-pair donors are ligands. Multiple ligands are usually present for each metal centre.



Equation 1 - Coordination bond formation using Lewis dot structure

Coordination Polymers

Coordination polymers are coordination complexes with repeating coordination entities in one, two or three dimensions^[44]. Coordination polymers can be both crystalline and amorphous. As with all polymers, coordination polymers feature repeating units called monomers. As opposed to conventional organic polymers that only polymerise in one dimension, coordination polymers can exhibit a much higher degree of polymerisation. For example, polyethylene can contain up to 200,000 repeating units, which is very high for an organic polymer but pales in comparison to the 10^{15} repeating units that may be present in a 0.1 mm cubic crystal of a coordination polymer^[45]. While this may seem dramatic, it is important to note that this is due to the difference in the dimensions that organic and coordination polymers extend in. Coordination polymers are not necessarily advantageous or disadvantageous in comparison to organic polymers but are a completely different material, with the common feature of consisting of repeating units.

Coordination Network

Coordination polymers are coordination complexes with repeating coordination entities in two or three dimensions^[44]. Coordination networks are a subset of coordination polymers.

Metal-Organic Frameworks (MOFs)

Metal-organic frameworks (MOFs) are a subset of coordination networks with the key property of containing potential voids. MOFs are often extremely porous with surface areas of up to $3000 \text{ m}^2/\text{g}$ ^[46]. The term metal-organic framework was coined by Yaghi in 1995^[47], and has since been defined by the IUPAC due to confusion between the use of the term MOF and others such as porous coordination network (PCN)^[44]. MOFs have a large variety of applications such as chemical sensing^[48], electronics^[49-50], biological and medical^[51-54], gas storage and separation^[55-58] and luminescence^[59].

In MOFs, metal clusters, rather than single metal ions, are used to provide the structure with rigidity^[60]. Without these, the structure would be flexible and prone to collapse. These clusters typically consist of metal ions bridged by oxygen and/or nitrogen donors. An example is shown in Figure 11 below as light blue Zn^{2+} polyhedral that cluster into Zn_4O vertices in MOF-5, IRMOF-3 and IRMOF-10.

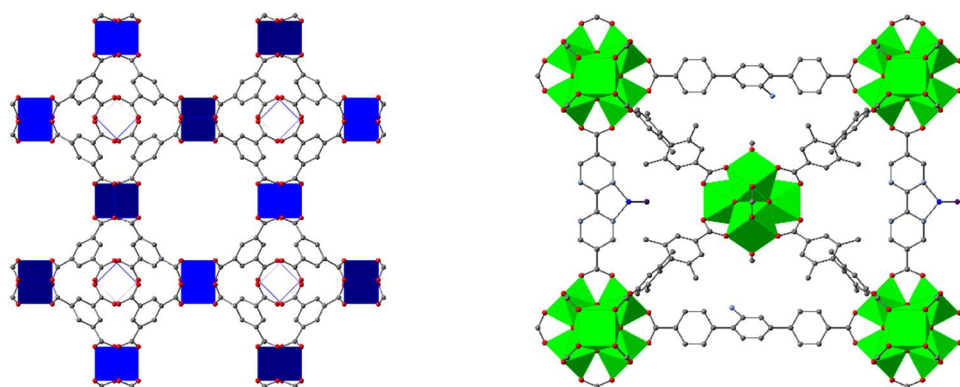


Figure 10 - Two examples of metal organic frameworks, HKUST1 (left) and LIFM-80 (right).

Each MOF is defined by its structure. MOF structures can vary immensely, forming almost any structure imaginable. This is important in the potential applications of MOFs, as they can be designed to fit an intended purpose. Another key aspect of MOFs is the interchangeability of the ligands in the structure. The length of the ligand determines the size of the unit cell and therefore the porosity of the MOF. This can be tuned to trap specific molecules within the structure or to sieve molecules and separate mixtures. The chemical properties of the MOF can also be tuned as functional groups on the ligand can be added, modified or removed as required. This is shown below in Figure 11, as MOF-5 can be formed without functional groups (left), with functional groups (middle) or with extended ligands (right). Excitingly, MOFs can even be synthesized with one structure and be post-

synthetically modified using methods such as ligand exchange to achieve properties otherwise impossible^[61].

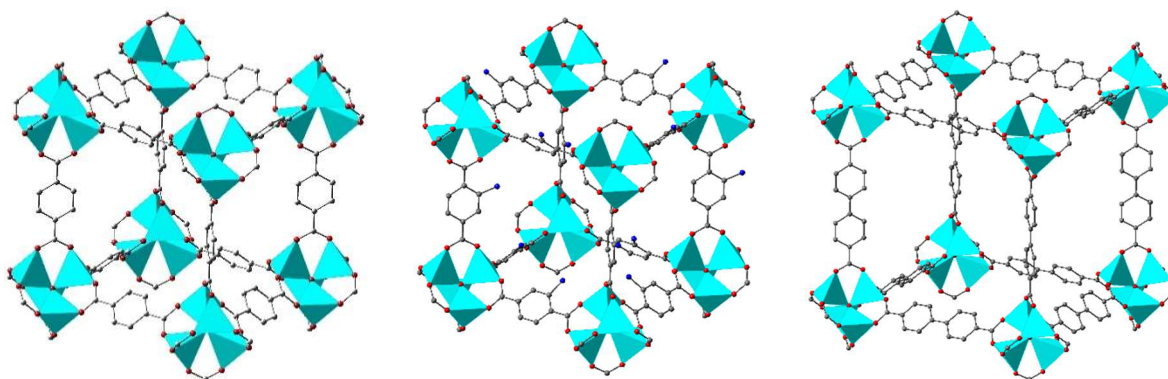


Figure 11 - MOF-5 (left), IRMOF-3 (middle) and IRMOF-10 (right) structures. Grey, red, dark blue and light blue represent carbon, oxygen, nitrogen and zinc respectively.

MOFs are often compared to zeolites due to the shared property of extremely high porosity. Zeolites are often better catalysts or molecular sieves (two of the main applications of MOFs) and are more thermally stable as MOFs cannot survive high temperatures. Despite this, MOFs are an extremely enticing subset of materials due to their designable nature.

Zeolitic Imidazolate Frameworks (ZIFs)

Zeolitic imidazolate frameworks are a subset of MOFs that are composed of imidazolate linkers and metal ions with similar structures to aluminosilicate zeolites^[62]. The structure mimics aluminosilicate zeolites structure in that the M-Im-M (M stands for Co or Zn cation, Im stands for the imidazolate linker) bridges that make up the framework have an angle of $\sim 145^\circ$. In comparison to zeolites, the metal cations of ZIFs replace the silicon in zeolites and the imidazolate anions replace oxygen.

ZIFs have a plethora of enticing properties as they feature many of the benefits of MOFs as well as high stability. For this work, the properties to note are the high nitrogen content of ZIFs (due to the imidazolate linker), high stability and high crystallinity.

Materials in this Work

This work builds on a synthesis method developed in our research group by a former postdoctoral fellow, Hui Yang^[63]. This method synthesizes a MOF, coats it in a coordination polymer, and exchanges metal atoms of interest into the coordination polymer and then the material is pyrolyzed under argon to generate a novel doped single metal atom catalyst.

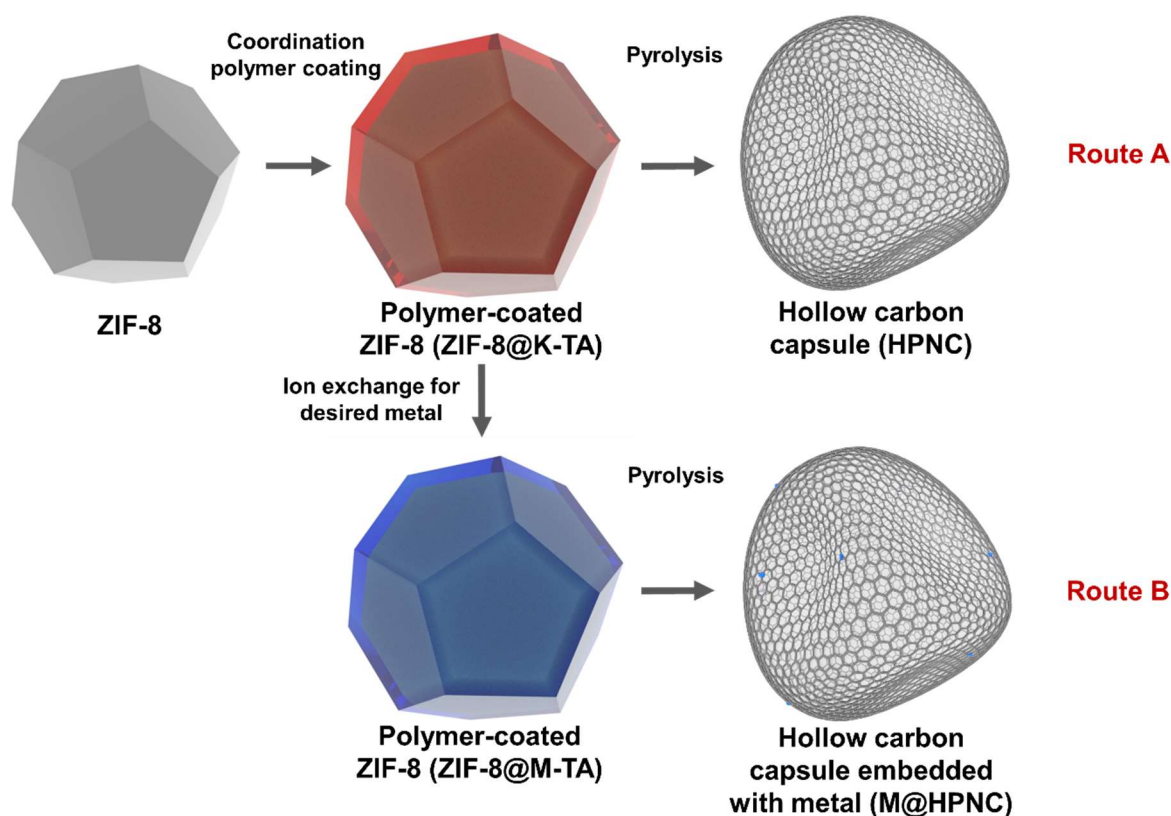


Figure 12 - Synthesis route for hollow porous nitrogen-doped capsules (HPNC) and metal impregnated HPNC (M@HPNC).

ZIF-8

The MOF used in this work was chosen to be ZIF-8 as it is cheap to synthesize, well-researched, easily size-controlled^[64-65], has Zn^{2+} centres that will be reduced and evaporate at relatively low temperatures and is a good nitrogen source during pyrolysis. Nitrogen that is released during pyrolysis may provide a binding mechanism allowing single metal atoms to bind to a carbon lattice^[38]. ZIF-8 is a very thermodynamically stable material and synthesis is extremely facile.

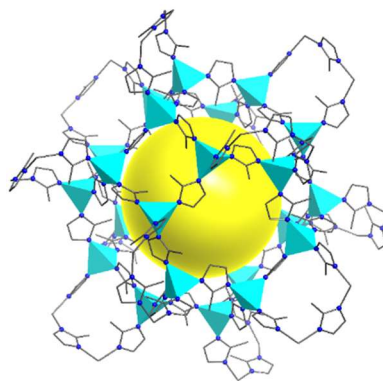


Figure 13 - ZIF-8 structure. Grey, dark blue, light blue and yellow represent carbon, nitrogen, zinc and the crystal pore respectively.

Tannic Acid

Tannic acid (TA) is a large organic molecule consisting of a glucose core covalently bonded to 3 to 5 gallic acid (3,4,5-trihydroxyl benzoic acid) residues through ester bonds (shown below in Figure 15). This is often misrepresented as a decagalloyl glucose (shown below in Figure 14).

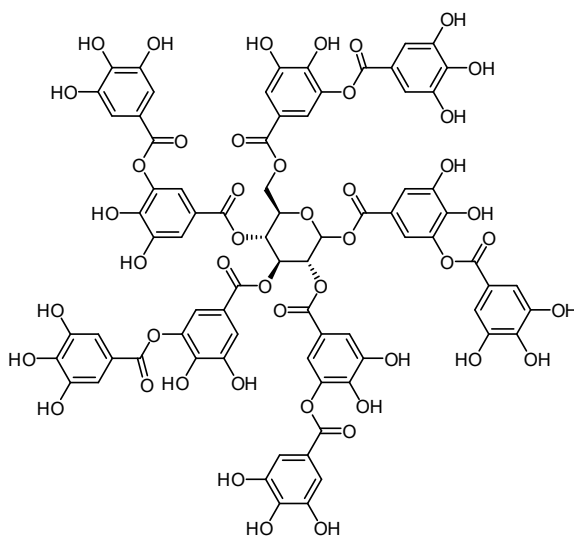


Figure 14 - The common representation of tannic acid as a decagalloyl glucose.

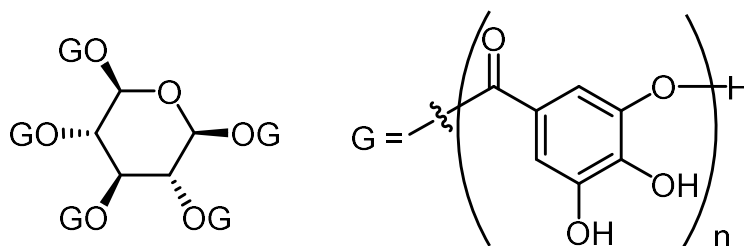


Figure 15 - Chemical structure of tannic acid (CAS 1401–55-4, C₇₆H₅₂O₄₆). TA consists of a glucose core, which covalently connects to 3–5 gallic acid (3,4,5-trihydroxyl benzoic acid) residues through ester bonds. Each gallate residue can covalently link to other gallic acid molecules. Thus, TA is referred to as a glucoside polymer of gallic acid^[66].

Metal-Impregnated Hollow Porous Nitrogen-Doped Carbon Capsules (M@HPNC)

A well-established technique of forming doped single metal atom catalysts is through the pyrolysis of coordination polymers^[28-29]. Recently, a novel method of pyrolyzing coordination polymers to synthesize a doped single metal atom catalyst, called metal-impregnated hollow porous nitrogen-doped carbon capsules (M@HPNC), has been developed by Hui Yang in the Telfer research group^[63]. This method adds the highly tuneable nature of MOFs to the process, allowing much greater control of the catalyst synthesized. This allows the size control of the resulting carbon capsules that are embedded with single metal atoms. The MOF is also a uniformly distributed nitrogen source, which may be key to embedding the metal atoms in the carbon lattice^[38].

Characterization

Arguably, the most important stage of any research is proving your results. In synthesis fields, this involves providing evidence for the characteristics of the material you have produced. In this work it is necessary to show the existence, morphology and elemental composition of the synthesized ZIF-8, ZIF-8@K-TA, HPNC and metals within the HPNC. Powder X-ray diffraction (PXRD), energy-dispersive X-ray spectroscopy (EDXS) and transmission electron microscopy (TEM) are key characterisation techniques used to examine materials synthesized in this work.

Powder X-ray Diffraction (PXRD)

PXRD has been one of the most valuable and frequently used characterization techniques available in this work. X-ray diffraction is caused by the regular lattice of a crystal acting as a diffraction grating. Once X-rays enter a crystal, the layers within the crystal will cause the

X-rays to diverge from their original path at an angle defined by the distance between the crystal lattice layers (as defined by Bragg's diffraction law).

$$n\lambda = 2d\sin\theta$$

Equation 2 - Bragg's diffraction law

Every crystalline material has a unique assortment of layers within the crystal and therefore gives a unique X-ray diffraction pattern. By matching the pattern obtained from a sample with a known pattern of a material it is possible to determine if the scanned sample contains the material in question. PXRD is very simple and relies on the premise that within the powder scanned there is a large number of different orientations of the same crystal. My work has used PXRD to confirm the existence (and lack thereof) of the MOF scaffold throughout the synthesis process.

Scanning Electron Microscopy (SEM)

SEM is a microscopy technique that allows the surface of a material to be viewed by firing electrons at the sample and measuring the secondary electrons that are emitted by the sample's surface. This is interpreted as an image. The sample stub surface must be conductive to avoid arcing. Arcing occurs when the charge on the surface becomes energized from the bombardment of electrons, resulting in an electrical arc of plasma that discharges the energy. This is seen in SEM as a bright flash on the viewing screen, corresponding to the high concentration of electrons. To avoid arcing the stub is generally coated in either carbon or gold. This conductive coating allows charge to be dissipated to an earth. A carbon coating is generally better for EDXS (discussed below) and a gold coating is generally better for capturing high-resolution images using SEM.

Transmission Electron Microscopy (TEM)

TEM is an imaging technique in which electrons are transmitted (hence 'transmission electron microscopy') through the sample and interactions between the electrons and the sample form an image of the sample. This characterization technique is used because electrons have a much shorter wavelength than photons, and we are therefore able to generate images at a higher resolution using this technique than is possible with optical microscopes.

In this work TEM has been useful in determining both the quality of the coordination polymer coating on the MOF and imaging the final M@HPNC catalyst.

Energy-Dispersive X-ray Spectroscopy (EDXS)

EDXS is a very quick, facile and non-destructive technique for obtaining an approximation of the elemental composition of a sample. As with all spectrometry, EDXS operates under the principle that each atom has a unique atomic structure. X-rays are focused on the sample and this energy causes electrons to become excited, rising out of their ground state to a higher energy level and then falling back, emitting an X-ray unique to the element. This is represented in the obtained spectrum as a peak. This technique was available as an attachment on the SEM during my research project, and was extremely valuable. EDXS allowed confirmation that the desired metal ions had been exchanged into the coordination polymer, and that the same metals were present in the final carbon capsule.

When deciding what material to coat the sample stub with to avoid arcing, it is important to consider what materials are expected in the EDXS. For instance, if EDXS is being used to test for gold, it will render the test redundant if the stub is coated with gold to avoid arcing. In this work, carbon coatings were chosen as any gold peaks seen in the EDXS spectrum could overshadow other important peaks, due to gold's location on the EDXS spectrum. Unfortunately, this may have resulted in being unable to see nitrogen peaks, as nitrogen is located very close to carbon on the EDXS spectrum. However, it is likely this would have occurred regardless, as the synthesized HPNC largely consists of carbon.

Chapter 2 Modifying the Synthesis Method

Introduction

The goal of this work is to first replicate Yang's work^[63], find the loading of metal required to form single metal atom sites with no nanoparticle formation for chosen metals and then test their catalytic activity. Synthesis of the catalyst is a 4-step process, whereby: 1) ZIF-8 nanocrystals are synthesized, 2) the nanocrystals are coated in a potassium tannic acid coordination polymer (K-TA), 3) K^+ ions in the coordination polymer are exchanged with a desired metal, and 4) the coated ZIF-8 is pyrolyzed to produce M@HPNC. This is shown below in Figure 16 as 'Route B'.

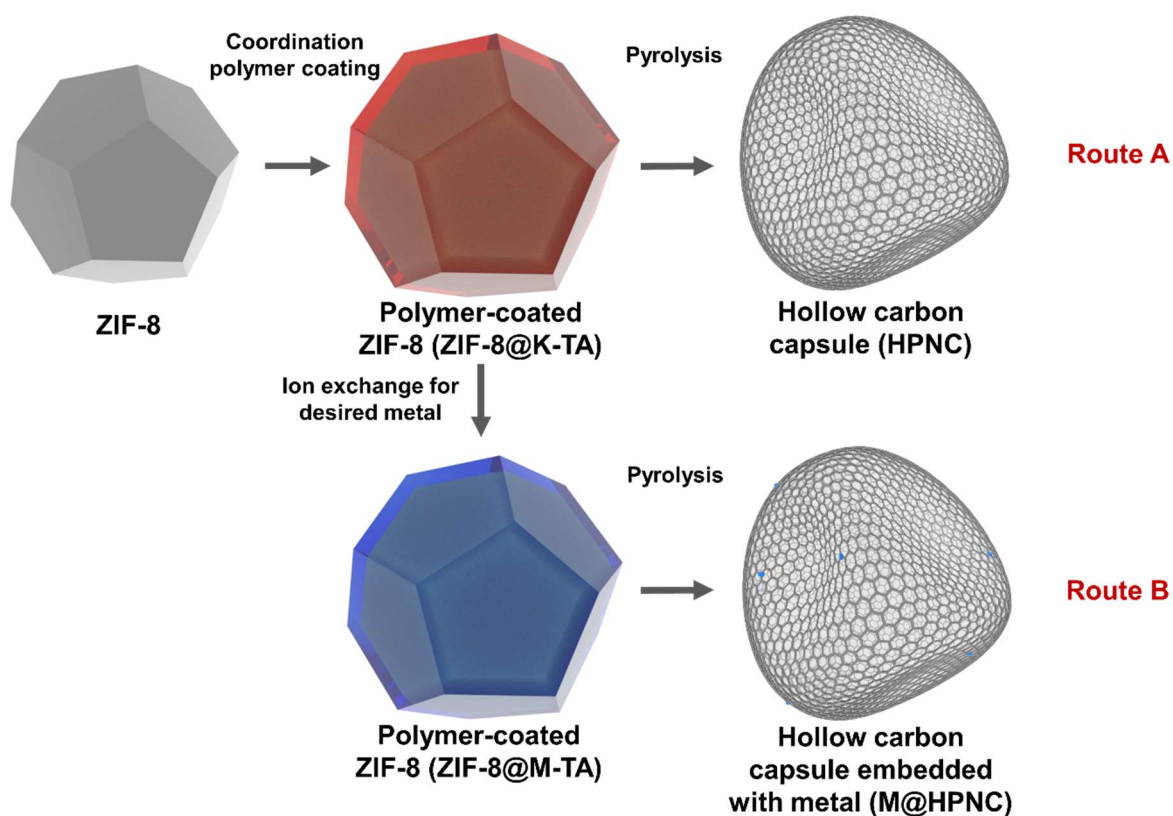


Figure 16 - Synthesis route for hollow porous nitrogen-doped capsules (HPNC) and metal impregnated HPNC (M@HPNC).

Key Concepts

In this method, ZIF-8 acts as a nucleation site for the coordination polymer (K-TA) growth and a scaffold and carbon and nitrogen source for the final carbon capsule (HPNC) support. The zinc ions that form the base of the ZIF-8 structure evaporate during the pyrolysis process, ideally meaning no zinc is left in the finished M@HPNC catalyst. As ZIF-8 is both

a scaffold for this M@HPNC catalyst synthesis method and is easily size controlled^[64-65], this allows the size of the resulting carbon capsules to also be controlled. The resulting carbon capsule is a hollow sphere made up of a thin layer of carbon. The thickness of this carbon is likely determined by the thickness of the K-TA layer formed during coating, which can be influenced by time and pH (and likely ratio of precursors). Ideally, this layer would be as thin as possible. This would allow maximum catalytic site access to all single metal atoms embedded in the carbon.

ZIF-8 Synthesis

ZIF-8 was synthesized using the method given by Yang^[63]. The reactants, zinc nitrate and 2-methylimidazole in methanol, are mixed and stirred for one hour. This is to generate even nucleation of the crystals throughout the solution. The solution is then left to incubate for 24 hours. This allows the ZIF-8 crystals to grow and settle in the bottom of the vessel (later the top layer can be discarded). The temperature of the vessel is not controlled and therefore the size of the resulting ZIF-8 crystals is only roughly controlled. The product was confirmed to be ZIF-8 by PXRD and TEM, as shown in Figure 17. SEM images can be found under ‘ns000’ in the ZIF-8 synthesis section of the supporting information (SI). The average ZIF-8 nanocrystal is approximately 150 nm in diameter using this method.

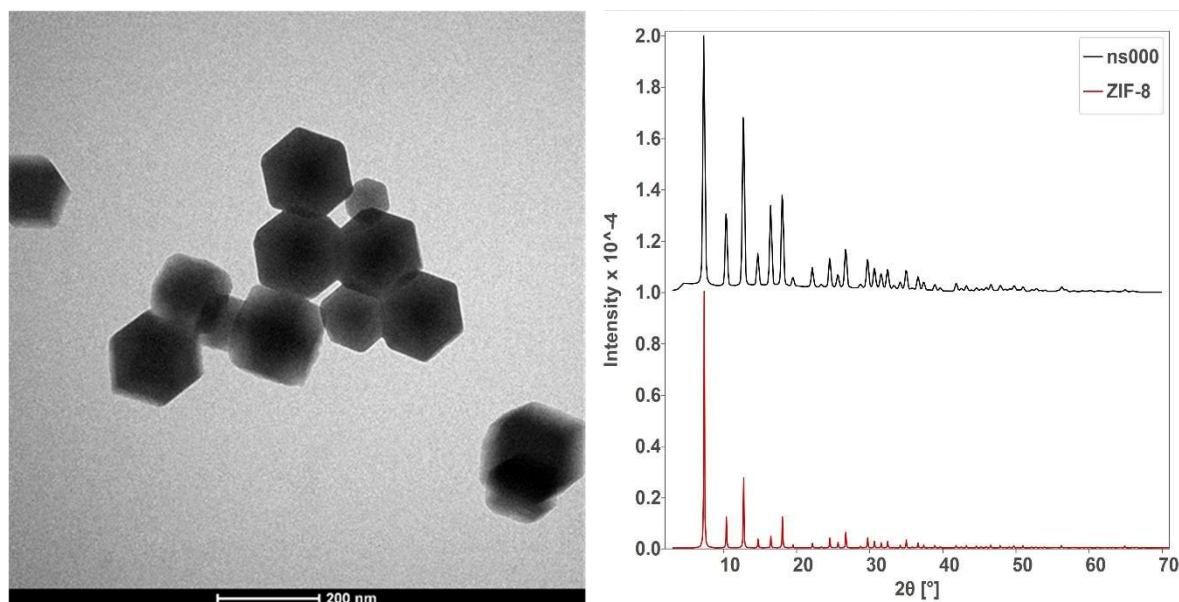


Figure 17 - TEM image (left) and PXRD pattern (right) of ns000, ZIF-8 synthesized at ¼ scale of Yang’s method^[63].

K-TA Coating

The previously synthesized ZIF-8 was then coated in a coordination polymer derived from potassium hydroxide and tannic acid (K-TA). The coordination polymer must be synthesized separately from the ZIF-8 as the ZIF-8 is extremely sensitive to acidic conditions^[67]. Yang's method disperses ZIF-8 (previously dried under vacuum) into water, and then mixes this with the tannic acid solution that has been adjusted to pH 8 with KOH. After 5 minutes of stirring, the solution is centrifuged to separate the ZIF-8 coated with K-TA (ZIF-8@K-TA). This was then washed several times with methanol before drying under vacuum^[63]. The product was confirmed to contain ZIF-8 by PXRD and images were obtained by TEM, as shown below in Figure 18. SEM images can be found under 'ns000c' in the ZIF-8@K-TA synthesis section of the SI.

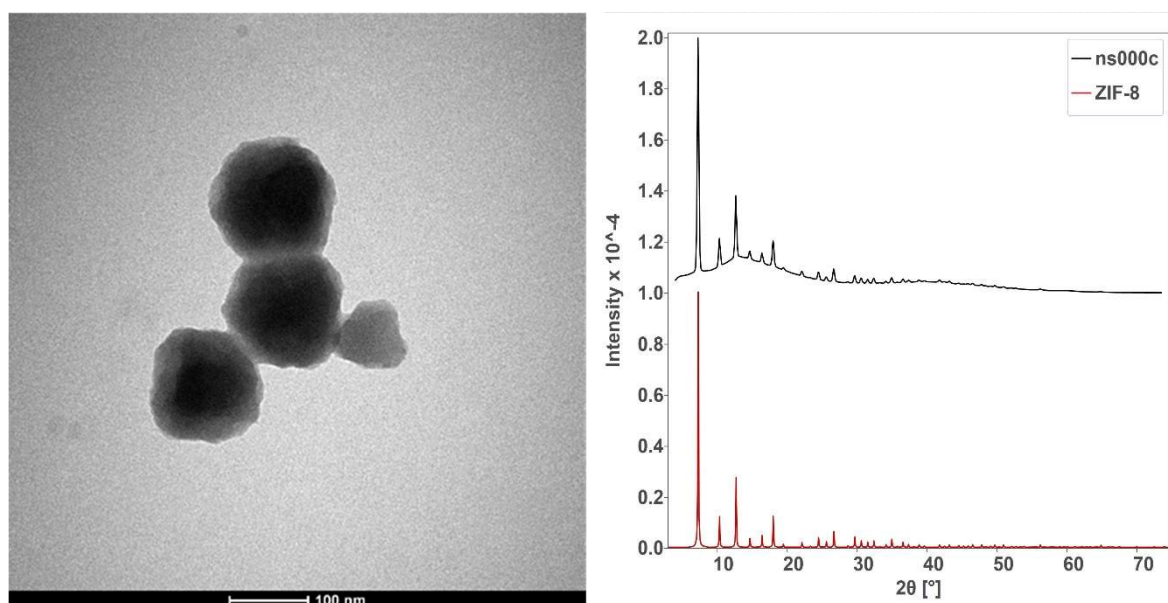


Figure 18 - TEM image (left) and PXRD pattern (right) of ns000c, ZIF-8@K-TA synthesized at ¼ scale of Yang's method^[63].

Ion Exchange (for ZIF-8@Fe-TA)

According to Yang's method^[63], the ZIF-8@K-TA that was dried in the previous step is then soaked in a methanolic solution containing the desired metal ion. This metal ion will be exchanged with the potassium in the K-TA layer. After stirring for two hours the solution is centrifuged to remove the product, washed several times with methanol and dried overnight under vacuum. A TEM image of ZIF-8@Fe-TA synthesized using this method is shown

below in Figure 19, next to a PXRD pattern of the same ZIF-8@Fe-TA confirming the presence of ZIF-8.

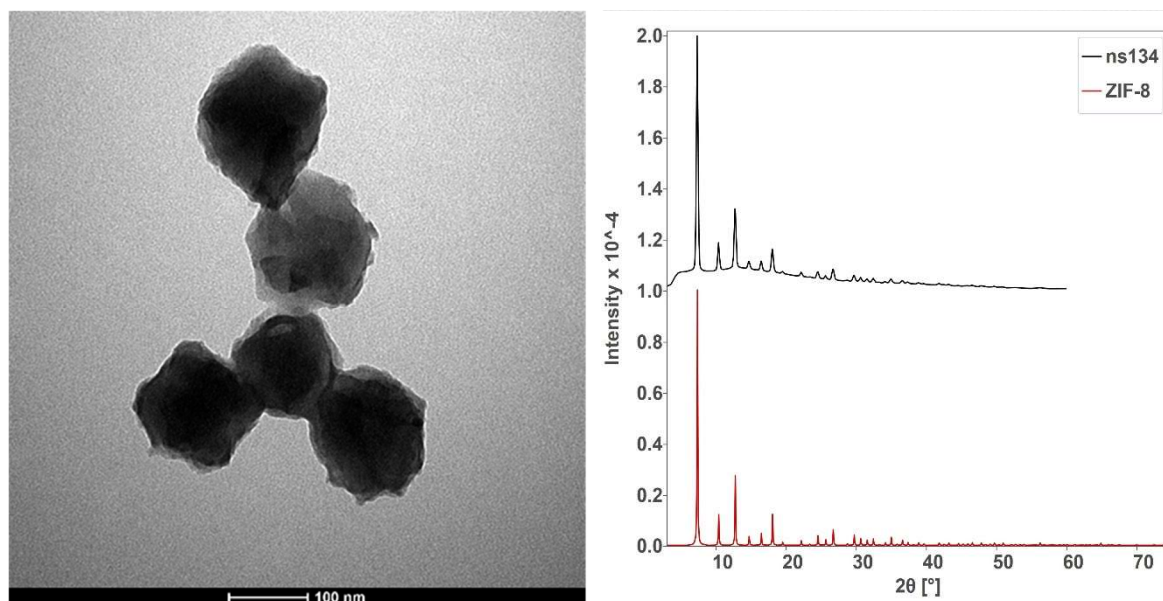


Figure 19 - TEM image (left) and PXRD pattern (right) of ns134, ZIF-8@Fe-TA synthesized using Yang's method^[63].

Pyrolysis

Pyrolysis is the process by which a material is thermally decomposed under a controlled atmosphere. A controlled atmosphere is critical, as any oxygen present will cause the combustion of carbon materials at elevated temperatures.

Following Yang's method^[63], ZIF-8@Fe-TA is then transferred into a ceramic crucible, placed in a furnace under a dry nitrogen flow, and heated from room temperature to 900 °C over a period of 900 min. After reaching the target temperature, the sample is pyrolyzed for a further two hours at 900 °C then cooled to room temperature to give hollow porous nitrogen-doped carbon capsules with embedded iron (Fe@HPNC). This method was followed with the exception of using argon instead of nitrogen as the inert atmosphere. A TEM image and PXRD pattern of the synthesized Fe@HPNC is shown below in Figure 20.

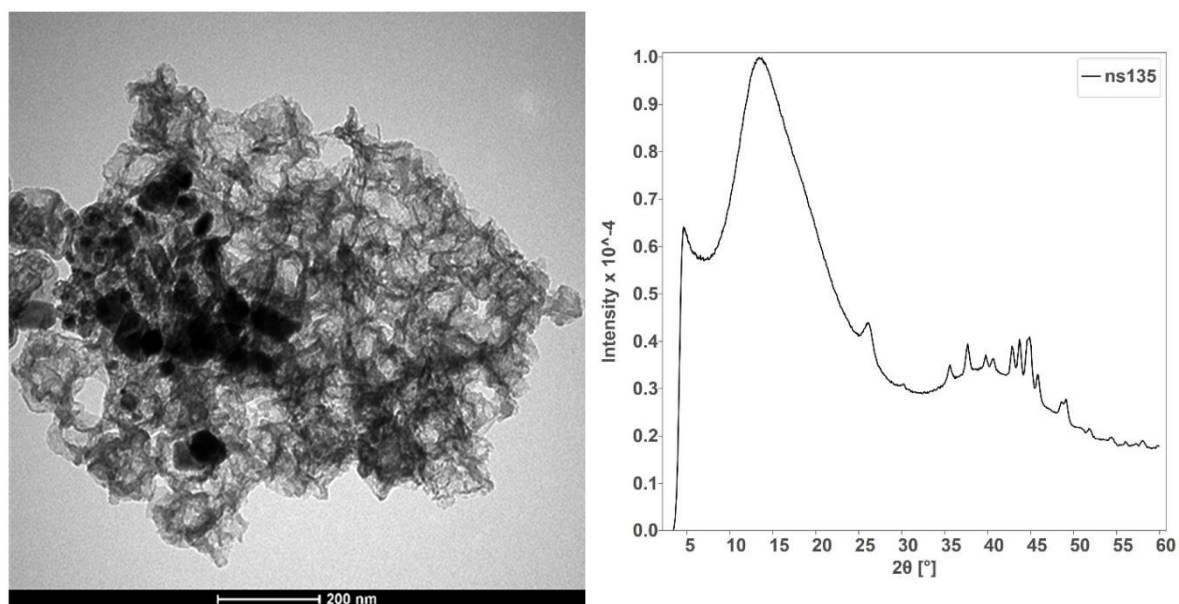


Figure 20 - TEM image (left) and PXRD pattern (right) of ns135, Fe@HPNC synthesized by Yang's method^[63].

Method Revision

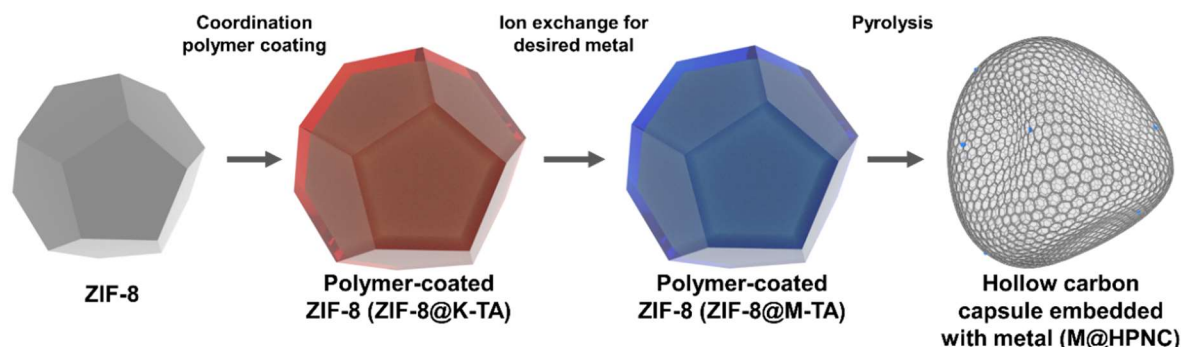


Figure 21 - General synthetic scheme for the synthesis of metal impregnated hollow porous nitrogen-doped carbon capsules.

Yang's method was modified to decrease processing time and increase consistency. This was done by keeping the material in solvent throughout the process until the material was ready for pyrolysis. This lowered the time needed to produce the final product from 5 days to 3 days. This change also avoided the difficulties and inconsistencies created when attempting re-disperse the materials. Several key aspects of the synthesis method were also investigated in order to better control the synthesis process. This work focused on controlling the coordination polymer coating as this process showed inconsistencies and by-products. The method was also scaled up to avoid inconsistency between batches. This was done by directly multiplying amounts used by a set value. This allowed generation of a considerable amount of M@HPNC catalyst once the method was perfected.

A Method Comparison

As is the case with most single metal atom materials achieved through pyrolysis^[3], Yang allowed metal nanoparticles to form by aggregation of metal atoms during pyrolysis and then removed them by washing with dilute acid and then re-pyrolyzed to achieve pure single metal atom materials^[68]. This work aims to circumvent this process by lowering the concentration of metal introduced during ion exchange, to the point that nanoparticles do not form during pyrolysis. Yang's work achieves very similar materials as this work in a much simpler manner, but is wasteful. In Yang's work the amount of metal introduced to the ZIF-8@K-TA does not need to be as rigorously controlled as in this work, as washing with acid intrinsically lowers the amount of metal present in the material to below the concentration at which nanoparticles form. This also has the added benefit of increased accuracy (or loading). This is because in this work it is necessary to account for error when trying to

introduce the exact amount of metal to the measured amount of ZIF-8@K-TA to achieve single metal atoms with no nanoparticles. In other words, Yang's method always achieves near 100% of the possible single metal atom loading without forming nanoparticles while the method developed in this work can only ever reliably achieve a much lower loading. If the same loadings were attempted using the method described in this work nanoparticles would form a significant amount of the time due to the intrinsic error that arises during measurement.

However, Yang's method has two disadvantages. One, it requires the re-pyrolysis of his material. This is energy intensive. Two, more importantly, it does not utilize 100% of the metal introduced. When considering the future of science and technology on Earth it is important to understand that there is a limited amount of resources. Precious metals, such as palladium used in this work, are (as one might be able to tell by the name) scarce. By only loading the carbon capsules with metal that will be used as catalytic sites, this work avoids the loss of precious metals. Arguably, these metals could be recovered, but reprocessing of this waste is a definite downside to be considered. In summary, which method is more suitable comes down to the purpose of the material. If high metal loadings are important and the metal is earth abundant, Yang's method is likely a better choice, and *vice versa*.

ZIF-8 Synthesis

The ZIF-8 was left to grow for 24 hours, during which the crystals settle to the bottom. The solution therefore separates into two layers – the bottom layer is a white solid consisting of ZIF-8 and the top layer is methanol and precursors. This separation allows the top layer, consisting of methanol and precursors, to be decanted. An important practical consideration here is to leave the vessel on an angle during these 24 hours. The angle should be such that any further angling of the vessel will begin pouring the contents out. This means that when it comes to decanting the material settled on the bottom is not disturbed as much as it would otherwise be. This means that less of the material is dispersed back into solution, and therefore more of the top layer can be decanted off without losing product. This is especially important at larger scales of synthesis.



Figure 22 - Image taken of vessel left on angle during 24 hours that ZIF-8 is left to incubate at room temperature. The white solid ZIF-8 has settled at the bottom of the vessel and the remaining solution is ready to pour off.

The amount of washes that should be done on ZIF-8 after it is synthesized is not specified in the literature^[63]. A systematic study was performed by synthesizing ZIF-8 and taking small aliquots from the product after synthesis and each wash. It was first washed two times with an equal parts water and methanol mixture and then two further times with pure methanol. The resulting TEM images (Shown in Figures S6 to S10 in the SI) suggest that minimal washing should be done as this deteriorates the quality of the crystal and does not clear away contamination (in fact it seems to add more from the solvent). The residual reactant in the mixture should not create issues as the material will be washed after the coordination polymer is coated. The amount of solvent used during ZIF-8 synthesis was also investigated because at large scales the amount of methanol used became inconvenient. It was found, however, that the amount of solvent used is proportional to the yield (see Table 1 below) and therefore the amount of solvent cannot be lowered.

A major change that was made to the method is that ZIF-8 is not dried out under vacuum after synthesis. Drying out ZIF-8 created an issue in re-dispersing the ZIF-8 crystals in solution for the coordination polymer coating. This is because large pores of ZIF-8, as with all MOFs, become filled with gas once dried out. Introducing water back into these pores is difficult due to the surface tension of water, and usually results in large agglomerates of ZIF-8 floating on top of the water (as their pores are filled with air). This can be circumvented somewhat by first dissolving the ZIF-8 in a small amount of methanol and then introducing the water (after which the methanol can be dried off), but this is time-intensive, complicated and unnecessary.

Table 1 - Effect of scale and solvent scale on yield of ZIF-8 synthesis. 2-MIM represents 2-methylimidazole, $\text{Zn}(\text{NO}_3)_2$ represents $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and MeOH represents methanol. Scale is relative to method given by Yang^[63].

Sample	Scale	Solvent scale	2-MIM (g)	MeOH (L)	$\text{Zn}(\text{NO}_3)_2$ (g)	MeOH (L)	ZIF-8 (g)	Yield	
								Mass	Molar
ns187a	1/2	1	1.97	0.030	0.839	0.010	0.238	8%	37%
ns187b	1/2	1/2	2.04	0.015	0.85	0.005	0.098	3%	15%
ns187c	1/2	1/4	2.03	0.008	0.85	0.003	0.085	3%	13%
ns188a	5	1	20.05	0.300	8.38	0.100	2.746	10%	42%
ns188b	5	1/2	20.02	0.150	8.41	0.050	1.38	5%	21%
ns188c	5	1/4	20.04	0.075	8.43	0.025	1.056	4%	16%
ns196	15	1	60.15	0.900	25.14	0.300	6.62	8%	34%
ns200	60	1	240.6	3.600	100.56	1.200	28	8%	36%

By keeping the material in solvent, it is ensured that the material is well-dispersed throughout the solution and therefore any processes will affect the material uniformly. To move from ZIF-8 synthesis to K-TA coating, the ZIF-8 is washed once with methanol and the resulting solid is dispersed in distilled water. This does allow the methanol that is contained within the pores of the ZIF-8 to be introduced to the K-TA coating step but it does not seem to affect the coating step significantly.

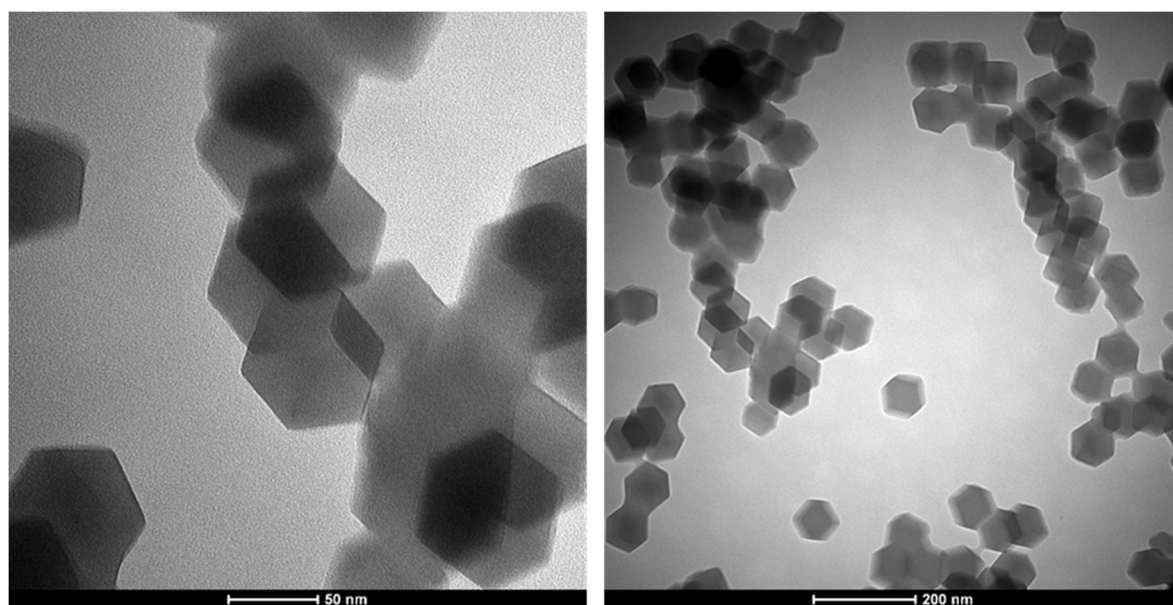


Figure 23 - TEM images ns262, ZIF-8 synthesized at 15x the scale given by Yang.

This work makes no attempt to control ZIF-8 crystal size, and simply repeats the same synthesis method throughout the work. This creates a small degree of uncertainty throughout

the method, as there is batch to batch variation. Initial experiments directly following Yang's method^[63] resulted in ZIF-8 crystals with a diameter of ~ 180 nm. By the end of my project ZIF-8 was being synthesized at scales 15 times that of Yang's method (all volumes and masses linearly scaled up). The average size of ZIF-8 crystals produced from these scaled up syntheses is ~ 95 nm, but can vary to ~ 85 nm and ~ 110 nm. The dramatically smaller crystals obtained do not appear to affect this work significantly and were therefore ignored. Changes in ZIF-8 size also occur while the crystals are stored in solvent. Since this was observed, the time that ZIF-8 spends stored in solvent before the K-TA coating was kept to a minimum.

K-TA Coating

K-TA Synthesis

K-TA is a coordination polymer formed between free K^+ ions and tannic acid (see 'Tannic Acid' on page 13 for more on tannic acid). Basic conditions are required for tannic acid to form a coordination polymer. This is because the phenol groups of the tannic acid must be deprotonated before a coordination bond can form with the metal ion^[69]. This is shown below in Figure 24. The potassium forms coordination bonds with multiple phenol groups, each from a different tannic acid molecule. As tannic acid is a large and complicated molecule with many potential binding sites, the polymerisation of K-TA is likely to be extremely complicated.

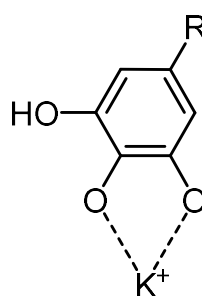


Figure 24 - Bonding mechanism of potassium to the deprotonated phenol group of tannic acid.

This work has shown that K-TA self-nucleates, and that this occurs fastest at pH 8.0. Even slight deviations in pH to 7.5 or 8.5 causes a significant decrease in K-TA nucleation speed. This is shown below by Figure 25 and Figure 26 which depict images taken of K-TA

solutions made at a variety of pH levels, ~10 minutes and ~1 hour after KOH addition respectively.



Figure 25 - Picture taken of solutions made during ns241. The right number written on the vial is the amount of KOH (6.011 M) added in μL and the left number is the resulting pH. These solutions were made in order of left to right. The picture was taken ~10 minutes after the last vial was made. The contrast in the cloudiness of the solutions shows that solutions closer to pH 8.00 form the K-TA coordination polymer much faster and that a difference of 0.5 in pH has a significant effect on K-TA formation.



Figure 26 - Picture taken of solutions made during ns241. This picture was taken ~1 hour after the picture taken in Figure 25. This shows that a pH varying 0.5 from 8.0 (i.e. 7.5 and 8.0) will still form K-TA, albeit much slower than it would at a pH of 8.0. The centre vial (at a pH of 8.38) also shows signs of a green phase forming on top of the solution. This green phase is an undesired by-product that forms faster at higher pH.

This work has also shown the occurrence of a secondary phase of K-TA that is green, lighter than water, forms faster at higher pH and forms after the desired phase of K-TA has formed. In Figure 29 above, it can be seen that only the middle vial has formed this phase, showing that this secondary phase forms faster at higher pH. Figure S14 in the SI shows that after 12h (overnight) this phase is formed in all solutions. This shows that pH affects the rate of formation of this by-product but is not the reason for its formation, as it will form at lower pH given enough time. Further investigation into this phase would be beneficial and interesting, but for the purposes of this work this phase was avoided.

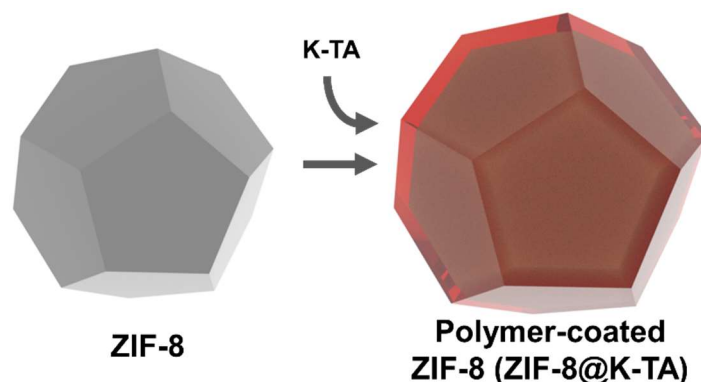
K-TA Coating

Figure 27 - Illustration of the coating of ZIF-8 with the coordination polymer K-TA.

The largest change made to the K-TA coating process is that ZIF-8 was not dried out after synthesis and was instead directly suspended in distilled water after washing once. As explained above, drying out ZIF-8 created an issue in re-dispersing the ZIF-8 crystals in solution for the coordination polymer coating. This is because large pores of ZIF-8, as with all MOFs, become filled with gas once dried out. Introducing water back into these pores is difficult due to the surface tension of water, and usually results in large agglomerates of ZIF-8 floating on top of the water (as their pores are filled with air). By keeping the material in solvent, it is ensured that the material is well-dispersed throughout the solution and therefore any processes will affect the material uniformly. This became increasingly important when scaling up the process. As a reasonable amount of the final product will be required to characterise the material as well as perform catalysis experiments, it is important that the K-TA coating process can be done on a large enough scale to allow for the required amount of final product after processing. If the product of the coating step is inconsistent due to difficulties in re-dispersing the ZIF-8, this will result in a significant amount of potentially redundant material at later stages of the synthesis process.

Consistent with similar thin-film coating of a tannic acid-based coordination polymers found in literature^[69], this work has shown that K-TA is nucleated by ZIF-8. This clarifies why ZIF-8 is so well coated by K-TA, as the K-TA is therefore grown on the surface of the ZIF-8 crystal and does not form independent structures. This is shown below in Figure 28, as the K-TA solutions (inner vials) have not yet become cloudy (a sign of K-TA formation), while the solutions containing ZIF-8 (outer vials) have already turned green. This green hue is a

sign of the formation of the by-product of K-TA discussed earlier, and therefore is an indicator that K-TA formation has reached its final stages.



Figure 28 - Pictures showing K-TA solutions (inner vials) compared to the ZIF-8 solutions to which the K-TA was added (outer vials). The pictures were taken ~15 minutes after the K-TA solution was added to the ZIF-8 solutions.

Understanding this is key to creating a synthesis method that results in a homogenous mixture of purely ZIF-8@K-TA. K-TA self nucleates over approximately 15 minutes (shown in Figure S11 of the SI). The addition of ZIF-8 accelerates the K-TA nucleation to the point that K-TA added to ZIF-8 will over polymerise to the point of forming the undesired by-product (identifiable by the characteristic green colour) before the K-TA would have even begun to significantly self-nucleate. This is shown again by Figure 28 in the SI. Therefore, while adjusting the pH of the K-TA solution it is necessary to be careful to not take so long that K-TA begins to self-nucleate, but once the K-TA is added to the ZIF-8 mixture it is important to not leave the ZIF-8 and K-TA together for too long.

As ZIF-8 is extremely sensitive to low pH^[67], care must be taken to adjust the pH of the coordination polymer to sufficiently basic conditions to avoid the etching of ZIF-8. Though some etching is not concerning and slightly etched batches of ZIF-8@K-TA were even used to synthesize the final M@HPNC catalysts in this work (shown below in Figure 29), the more that ZIF-8 is etched the less nitrogen is available during pyrolysis for metal to bind into the carbon lattice. It is therefore important to ensure the K-TA is adjusted to pH 8.0 at the minimum (as was the case in Figure 29 below).

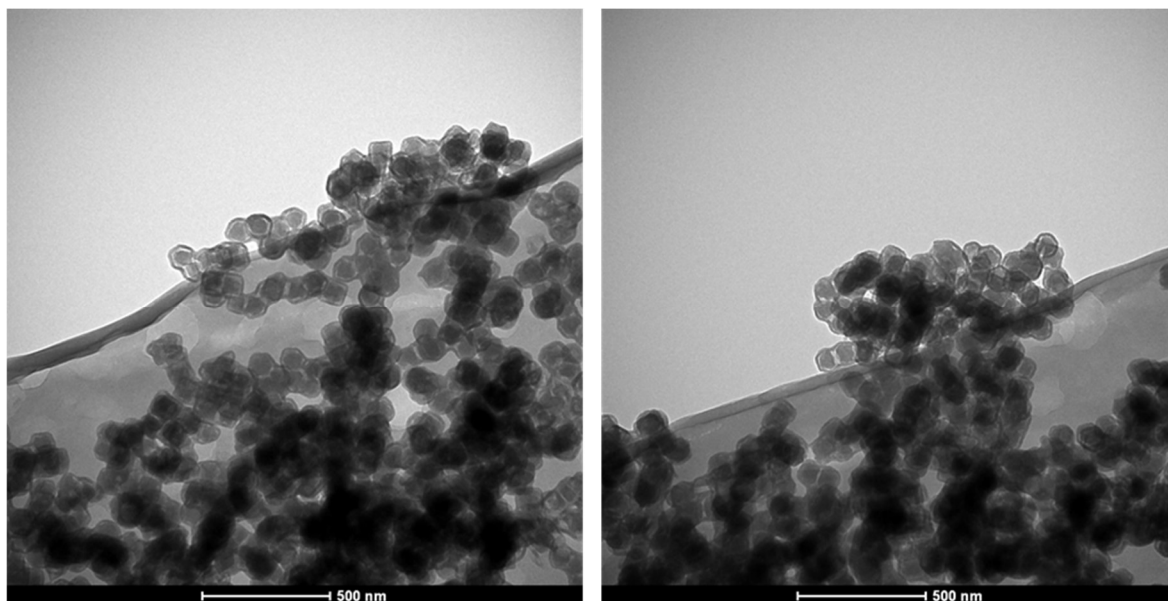


Figure 29 - TEM images of ns264, ZIF-8@K-TA synthesized using the revised method. There is consistent etching of the outer surface of the ZIF-8 crystal throughout the sample.

As etching of ZIF-8 was a consistent issue despite care taken in adjusting the pH of the K-TA precursor solution before mixing with ZIF-8, a small study was undertaken. This study focused on the time that the K-TA precursor solution was allowed to mix after adjusting the pH before mixing with ZIF-8. This was done by adjusting the pH of the K-TA solution and then adding aliquots of this solution to prepared samples of ZIF-8 after measured amounts of time. Unfortunately, the K-TA began to self-nucleate before the first addition to ZIF-8 due to the time taken to carefully adjust the pH of the K-TA solution to pH 8.0. Perhaps as a result of this, the resulting TEM images (shown in Figure S23 to S25 in the SI) all show no etching of the ZIF-8. This suggests that the etching of ZIF-8 is caused by free acidic groups on the tannic acid, and some time is needed before these groups are deprotonated by the basic conditions of the solution.

Figure 19 above on page 20 shows TEM images of ZIF-8@Fe-TA synthesized using the original method. Although these images are of post-ion exchanged material, they highlight a key issue with the coating method. The control of pH in the given method is not accurate enough to produce consistent results. The specified pH of 8 allows an error of ± 0.5 ^[63]. The images in Figure 19 show that the K-TA layer produced at pH levels ~ 8.5 become rough and inconsistent. To remedy this, in this work the pH was controlled to 8.0 ± 0.1 . Consistent with findings in the K-TA Synthesis section above on page 26, this circumvented the formation of the green K-TA by-product within the processing time-frame.

Using a more dilute KOH solution would allow a more consistent pH adjustment with a single measured aliquot, which would likely be an improvement to the method as this would significantly decrease the time taken to adjust the pH of the K-TA precursor solution. With the current 6 M KOH solution, a pH curve can be made with the 24 mM TA solution (shown above), but this curve is not enough to reliably control the final pH with a single aliquot as the concentration of the 6 M KOH solution can change significantly from solvent lost to the environment over time. Reliably controlling the pH using 6 M KOH solution would require either making a fresh batch of KOH and/or making a 24 mM TA versus 6 M KOH pH curve every time a K-TA coating is required. Conversely, if a significantly more dilute KOH solution was used (e.g. 0.6 M) the solvent lost from the stock solution of KOH would not significantly affect the concentration. Therefore this dilute KOH solution would be much more reliable and would allow a consistent single aliquot addition of KOH to the TA to adjust the pH to 8.0.

It was of interest to see the growth of K-TA over time in order to quantify its effects and determine the required accuracy. The resulting TEM images of this study can be seen in Figures S18 to S21 in the SI. Surprisingly, the thickness of the K-TA coating does not grow much more after 5 minutes, though in Figure S20 of the SI (showing ZIF-8@K-TA left in the K-TA solution for 30 minutes) there are some crystals that show slightly larger K-TA coatings (in particular, the right-most crystal in the left image). Perhaps more interesting is the observation that the ZIF-8 shows noticeably increased etching over the hour (shown in Figure S21 of the SI).

Ion Exchange

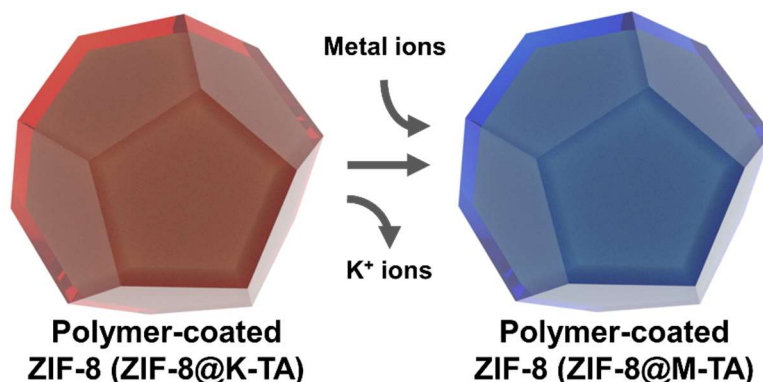


Figure 30 - Illustration of the ion exchange process, during which desired metal ions are exchanged with potassium ions that are present within the K-TA coordination polymer.

The catalytic site on the final M@HPNC catalyst must be introduced to the coated coordination polymer prior to pyrolysis. This is done via ion exchange, where the desired metal is introduced in a solvent in its ionised form and will naturally exchange with the K^+ ions present in the coordination polymer. In this way coordination polymers provide an ideal mechanism to allow single metal atoms to be spread evenly across a material^[28, 70].

This work has used a slightly modified method compared to the method provided by Yang^[63]. The premise still remains that the metal ion desired for the final M@HPNC catalyst is exchanged with the K^+ present in ZIF-8@K-TA. However, the precursor to this step (ZIF-8@K-TA) is not dried after coating the coordination polymer and washing. This means that instead of a porous solid there is a solution of suspended precursor to work with. As explained above in the ZIF-8 synthesis and K-TA coating method revision sections, this is to avoid the ZIF-8 pores being filled with air and becoming difficult to disperse in solution.

During ion exchange, the solution containing ZIF-8@K-TA is stirred in a large vessel while the metal ion-containing solution is added slowly. This allows the most even coating possible. For example, if the precursor was instead added to the metal ion-containing solution, the first few crystals may be introduced to more metal ions than the last crystals to reach the solution. Comparatively, the method that is used allows the amount of metal introduced to the precursor to slowly increase in a turbulent environment.

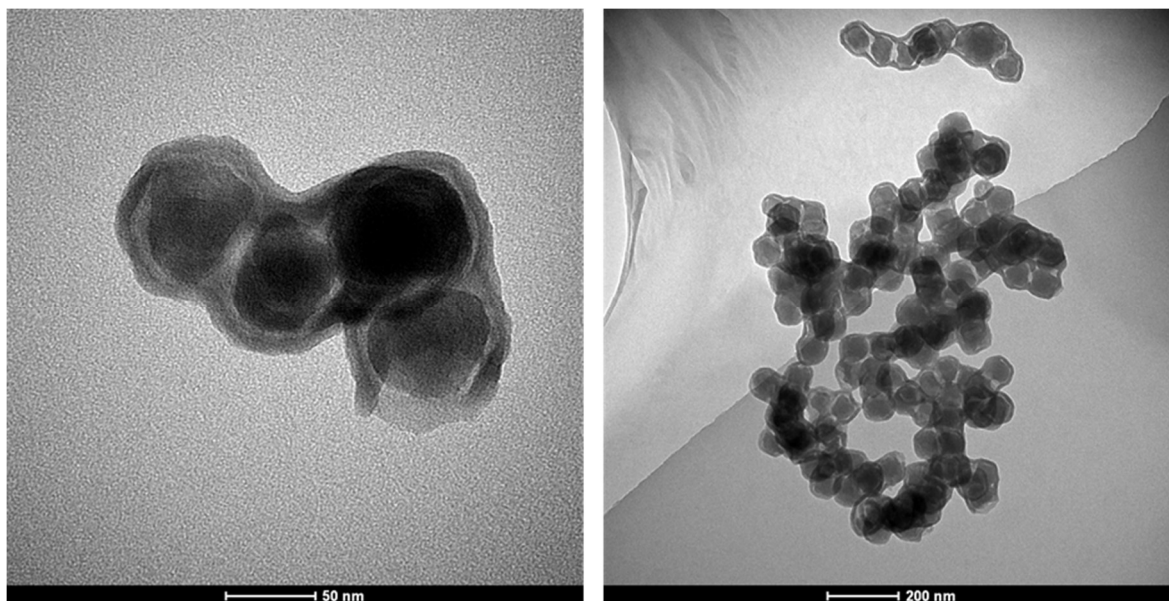


Figure 31 - TEM images of ns266, ZIF-8@Pd-TA synthesized using the revised method.

Diluting the metal salt containing solution sufficiently before it is added to the precursor (ZIF-8@K-TA) solution is extremely important as it prevents a high concentration of metal being exchanged into the ZIF-8@K-TA in close proximity to each other. The result of not diluting the metal salt solution sufficiently and/or adding the ZIF-8@K-TA to the metal salt solution will be a clustering of metal ions in close proximity in the K-TA layer, whereas an even dispersion is desired. During pyrolysis, these clusters of metal ions will be more likely to form a nanoparticle. This is of the most concern when some capsules contain more metal than others, as the metal cannot transition from one capsule to another. The metal will spread throughout the sea of carbon during pyrolysis as single metal atoms, but if there is too much metal present, the metal will aggregate into a more thermodynamically stable nanoparticle. Therefore, as the aim of this work is to find concentrations at which nanoparticles form and to stay below these concentrations, it is important to note that the inconsistency during the ion exchange will result in nanoparticles at metal concentrations below what would otherwise cause nanoparticles to form.

The change to the method also provides an added benefit in time efficiency, as to dry out the precursor sufficiently the material must be left overnight under vacuum. This restricts the processing flow, meaning that the coordination polymer coating and the ion exchange must be carried out over two days. With the modified method that is used in this work, both of these processes can be carried out on the same day, dramatically decreasing processing time.

Consistent with Yang's method, during ion exchange the solutions are left for two hours to allow the system to reach equilibrium and eliminate kinetic effects.

Metals Chosen

Cobalt, nickel, palladium and platinum were the 4 metals originally chosen for investigation. However, no attempts at synthesis of ZIF-8@Pt-TA were made during this work due to the unavailability of a suitable platinum salt. Platinum salts are both scarce and extremely expensive. Work on implementing single platinum sites in HPNC should be done in the future when more platinum salts become commercially available (such as platinum acetate, which is likely to be the optimal salt for this application when considering palladium acetates success – see 'Palladium Reduction' in Chapter 3).

Pyrolysis

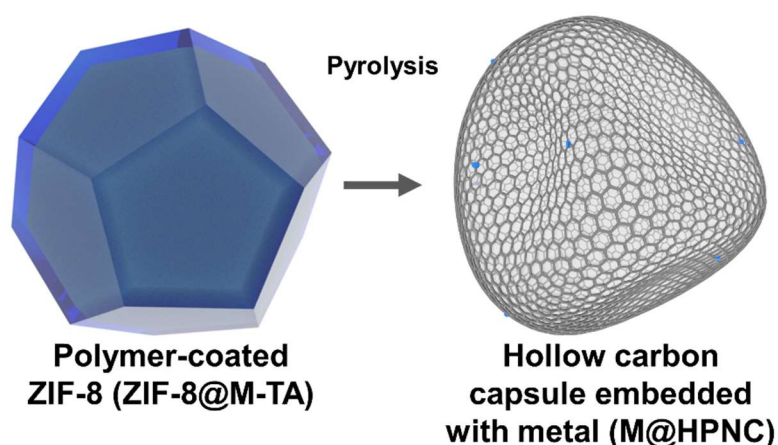


Figure 32 - Illustration of the precursor and product of the pyrolysis process to synthesize M@HPNC. Note that the pyrolysis process is held consistent regardless of the presence of metal atoms, and therefore the same method is used to produce HPNC (hollow porous nitrogen-doped carbon capsules without metal sites).

The pyrolysis process was modified compared to Yang's method simply to save time. Raising the temperature to 900°C over 900 minutes means that only one sample can be pyrolyzed per day. Instead, a pyrolysis procedure was developed that both purged the instrument and processed the sample in a timely yet controllable manner. Once quartz tubes had arrived (see 'Tube Furnaces' in the SI), the atmosphere in the instrument was able to be rapidly adjusted to an inert atmosphere by vacuum pumping the instrument to low pressures and subsequently pressurizing the vessel with inert gas, which can be cycled repeatedly for an increasingly pure atmosphere. This also allows crude monitoring of the purity of the

atmosphere as lower pressures reached during vacuum pumping suggest less interactions between gas molecules in the vessel, insinuating a larger presence of noble gases. Therefore, the lower the pressure reached during vacuum pumping the better the purity of the atmosphere.

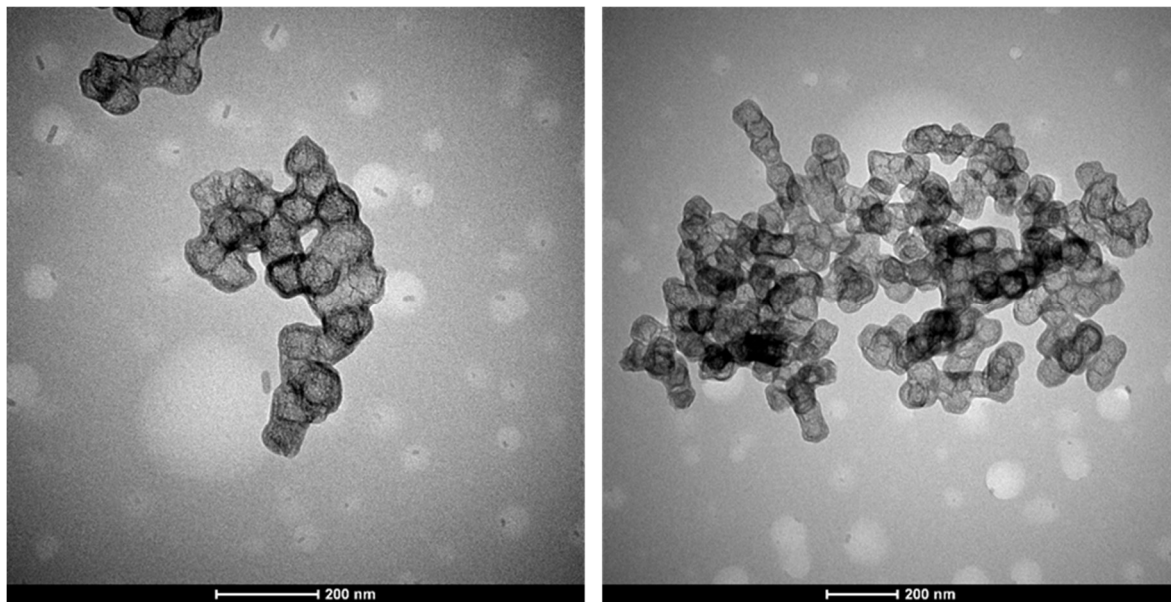


Figure 33 - TEM images of ns264p_X_7/9, HPNC synthesized using the new general method. Sample ns264 was used as the precursor ZIF-8@K-TA. This follows ‘route A’ of the synthesis method as shown in Figure 16.

The pyrolysis process was kept consistent for all samples except when specified. Note that the pyrolysis process is held consistent regardless of the presence of metal atoms, and therefore the same method is used to produce HPNC (hollow porous nitrogen-doped carbon capsules) as well as M@HPNC (metal impregnated HPNC). The temperature was raised at a rate of 5°C/minute to 900°C. Consistent with Yang’s method, the temperature was held at 900°C for 2 hours before lowering to ambient temperature. Accounting for the time taken for the instrument to cool, this allowed 2 pyrolysis runs per day. The products obtained using this ramp rate were satisfactory (shown above in Figure 33). The heating rate was not tested at faster rates because the added time efficiency drops significantly past this point and the furnaces control over the temperature drops with increased heating rate. For example, this change saved 12 hours, whereas multiplying the heating rate by 5 again only saves 2.7 hours. The furnaces control over the temperature is performed by a PID (proportional, integral, differential) controller. The faster the temperature is increased, the more the temperature will overshoot the set temperature and problems such as ringing will occur. At a heating rate of

5°C/minute the temperature of the furnace was observed to be well-controlled and did not overshoot the desired 900°C by more than 3°C.

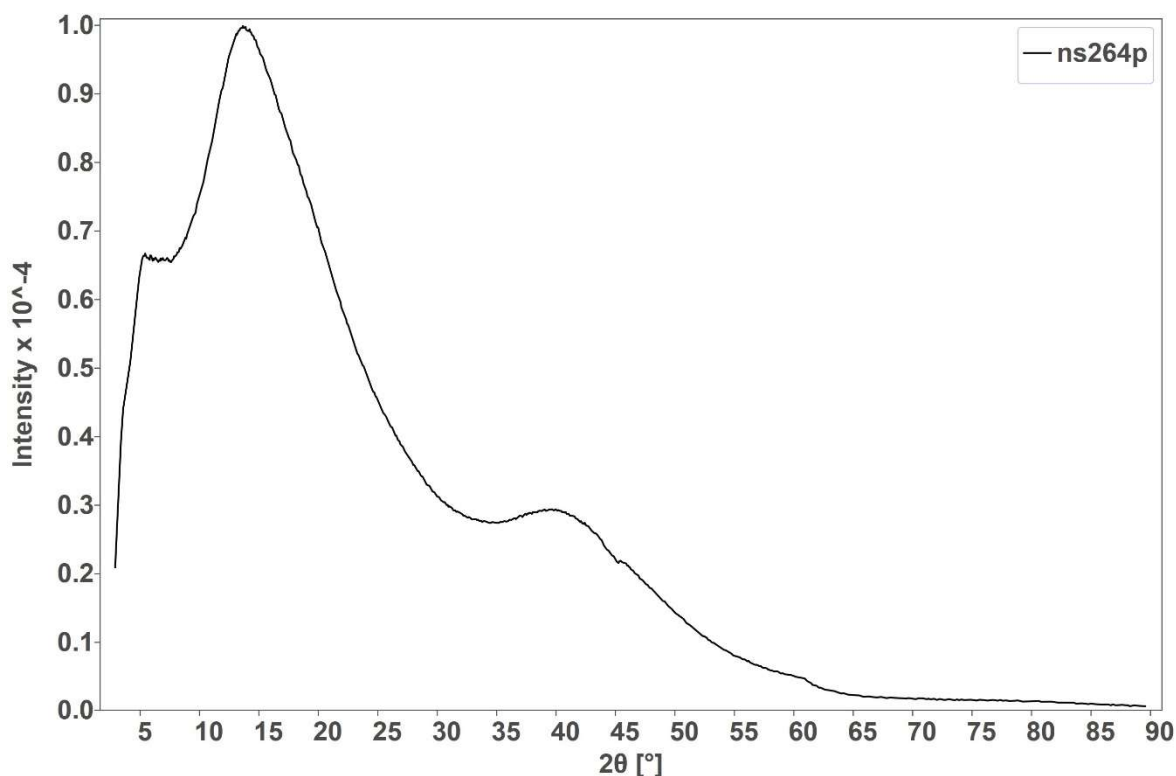


Figure 34 - PXRD pattern of ns264p_X_7/9, HPNC synthesized using the new general method. Sample ns264 was used as the precursor ZIF-8@K-TA. This follows 'route A' of the synthesis method as shown in Figure 16.

TEM images and a PXRD pattern taken of the HPNC resulting from this method are shown above in Figure 33 and Figure 34 respectively. The TEM images show that the material has low electron density through the centre of each capsule and has high electron density at the edges, characteristic of a hollow structure. It was also confirmed that the capsules were hollow by rotating the sample inside the TEM, but unfortunately this is unable to be shown. The capsules are slightly warped but all walls of the capsules are intact. Some capsules are larger structures, caused by agglomerated ZIF-8 crystals during the K-TA coating process. The broad peaks in the PXRD pattern at 15° and 40° result from the graphitic features of the carbon support^[68]. The PXRD patterns are otherwise amorphous. There is an artefact in the PXRD pattern between 44° and 45° caused by the instrument. An EDX spectrum obtained from the HPNC synthesized in this work is shown below in Figure 35. The sample mostly consists of carbon, but has trace oxygen and zinc (discussed later). Trace silicon is also

shown, but this is likely due to the tape required to stick the sample to the stub in the SEM. It is also highly likely that nitrogen is also present due to the nitrogen released from ZIF-8 during pyrolysis. The nitrogen peak is not identifiable as the large carbon peak present at 0.277 keV overshadows any potential nitrogen peak at 0.392 keV^[71].

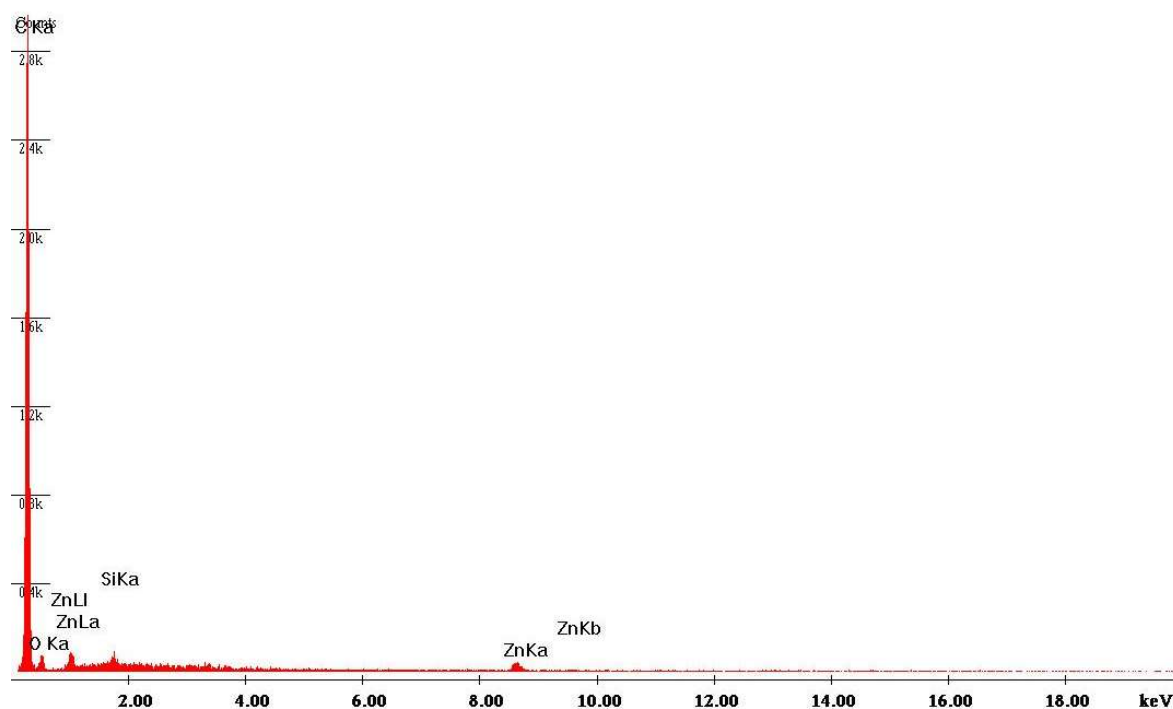


Figure 35 - EDX spectrum of ns264p_X_7/9, HPNC synthesized using the new general method. Sample ns264 was used as the precursor ZIF-8@K-TA. This follows ‘route A’ of the synthesis method as shown in Figure 16.

It is also worth noting that it can be seen from the TEM images above that the carbon walls of the HPNC produced in this work are considerably thick at ~10 nm. Assuming that the distance between layers is the same as bulk graphite^[72], there is ~30 layers of carbon present in each HPNC. This is important for the catalytic activity of the material as much of the palladium may be in the inner layers of the carbon wall, and may not be exposed as a catalytic site if the wall is densely packed like graphite.

Zinc Contamination

A noticeable contamination in all EDX spectra of HPNC synthesized using an inert argon atmosphere was the presence of small zinc peaks, as shown above in Figure 35. This is due to zinc oxide formation, as zinc oxide decomposes at 1,974°C^[73], far above the 904.5°C

boiling point of zinc^[74]. A reducing atmosphere prevents this by reducing the zinc oxide back to zinc, which will then gradually evaporate off at the pyrolysis temperature of 900°C (in the same way that water will gradually evaporate off at a temperature of 90°C, also below its boiling point). A reducing atmosphere is easily achieved by introducing a small amount of hydrogen gas, however, single metal atoms supported on carbon tend to aggregate into nanoparticles under a reducing atmosphere^[75]. This is explored further in ‘Reducing Atmosphere’ later in the text.

Single Cobalt and Nickel Sites

Attempts at synthesizing single metal atom cobalt and nickel sites without formation of nanoparticles were successful. These results are tabulated below in Table 2 and Table 3, for cobalt and nickel respectively.

Table 2 - Pyrolysis results of a single ZIF-8@K-TA source (ns243) that were impregnated with varying amounts of cobalt. Arranged in chronological order. Cells for PXRD results that were amorphous are omitted for clarity.

Sample	ns244pa	ns244pb	ns252p	ns255c	ns255d	ns255e
mol Co²⁺/ mg ZIF-8@K-TA	5.78E-08	8.67E-08	14.3E-08	45.8E-08	51.5E-08	57.3E-08
ZIF-8@K-TA (mg)	60	60	60	30	30	30
Volume MeOH (mL)	80	80	80	40	40	40
PXRD				NP present	NP present	NP present

Table 3 - Pyrolysis results of a single ZIF-8@K-TA source (ns243) that were impregnated with varying amounts of nickel. Arranged in chronological order. Cells for PXRD results that were amorphous are omitted for clarity.

Sample	ns245pa	ns245pb	ns253p	ns256pa	ns256pc	ns256pd	ns256pe
mol Ni²⁺/ mg ZIF-8@K-TA	6.00E-08	8.40E-08	14.3E-08	34.4E-08	45.8E-08	51.5E-08	57.3E-08
ZIF-8@K-TA (mg)	60	60	60	30	30	30	30
Volume MeOH (mL)	80	80	80	40	40	40	40
PXRD			NP present	NP present	NP present	NP present	NP present

The lack of nanoparticles was confirmed only by PXRD, and not checked extensively with TEM. Therefore, these results are tentative and further investigation is required to confirm these results. The PXRD pattern obtained for ns252p, the highest loading of cobalt on HPNC

without nanoparticle formation, is shown below in Figure 36 on the left (the sample code suffix ‘_X_25/6’ simply refers to the furnace ‘X’ and the date of the pyrolysis). Correspondingly for nickel, the PXRD pattern of ns245pb is also shown in Figure 36 on the right.

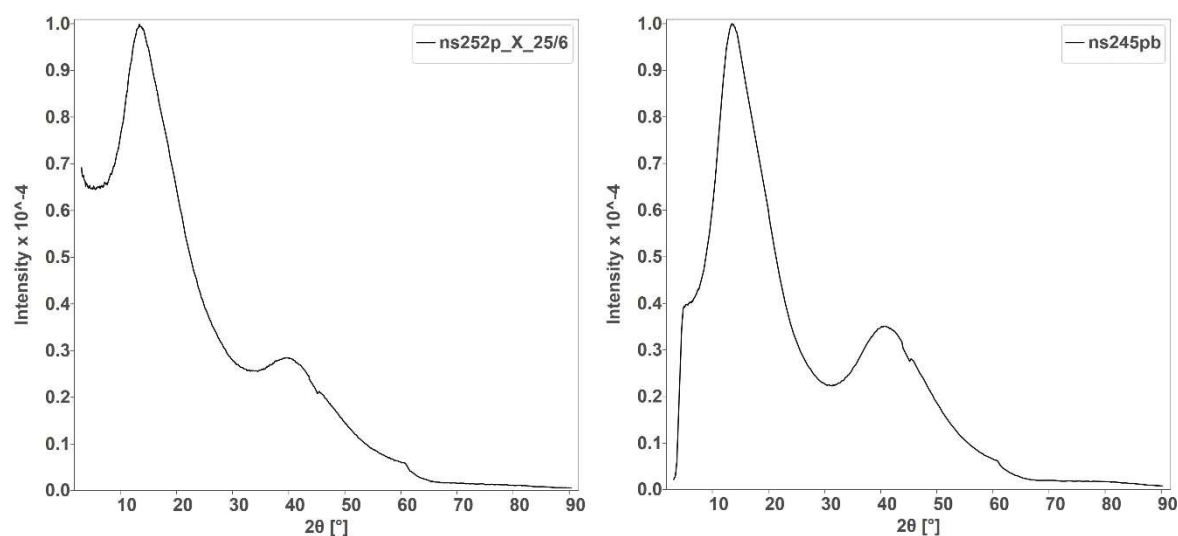


Figure 36 - PXRD pattern of ns252p_X_25/6 (Co@HPNC) and ns245pb (Ni@HPNC) on the left and right respectively. Both samples are completely amorphous.

It should be noted that the diffraction peaks seen in ns253p were very difficult to distinguish, as shown in Figure 37 below, and higher loadings were attempted to confirm the presence of nanoparticles. Despite this difficulty, the presence of nanoparticles in nickel exchanged samples (ns253p) at a metal concentration during ion exchange (14.3×10^{-8} mol metal ion/mg ZIF-8@K-TA) that did not cause nanoparticles in cobalt (ns252p) is of interest. This shows that either more nickel exchanged into the K-TA layer during ion exchange or nickel is more susceptible to aggregation during pyrolysis (or both).

Although these results were not investigated further due to oxide formation (discussed below), the presence of nickel was confirmed in ns245pa by EDX and TEM was used to confirm no nanoparticles were present in the sample, as shown in Figure 38 below.

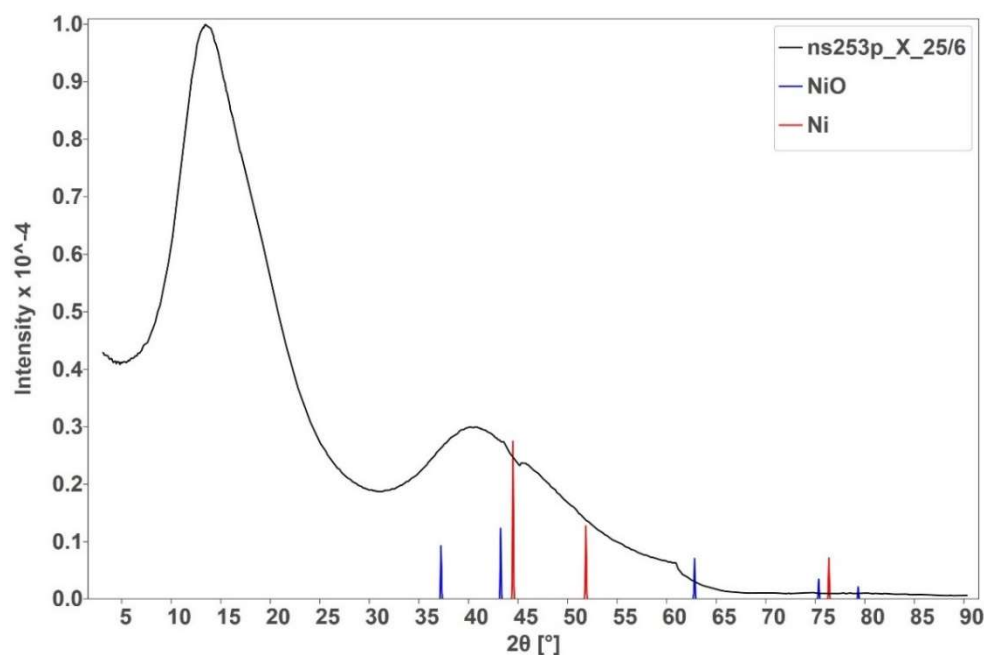


Figure 37 - PXRD pattern of ns253p_X_25/6 (Ni@HPNC). Pattern has peak coinciding with nickel oxide at $\sim 43^\circ$. This is difficult to identify due to the artefact in the measurement that causes a drop in the pattern between 42° and 45° , but can be compared to amorphous patterns for reference.

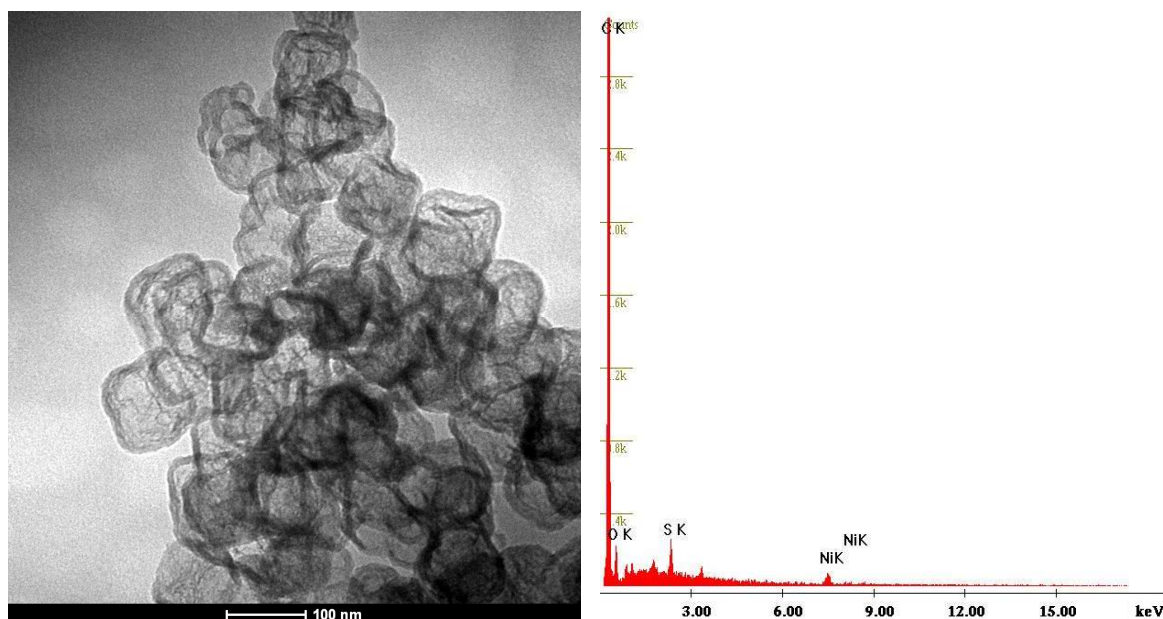


Figure 38 - TEM images (left) and EDX spectrum (right) of ns245pa (Ni@HPNC).

Oxide Formation

Despite success in forming HPNC with purely single metal atom sites for both cobalt and nickel, difficulties arose when investigating the concentration at which nanoparticles form for these metals. This was due to metal *oxide* nanoparticle formation instead of the expected

metal nanoparticle formation. Evidence of metal oxide formation is shown clearly by PXRD, as shown below in Figure 39 and (albeit much less clearly) Figure 37.

These figures also show why metal oxide nanoparticle formation (rather than pure metal nanoparticle formation) creates difficulty in determining the concentration at which nanoparticles form. This is because sample ns252p_X_23/6 (shown below to have oxide nanoparticles) is pyrolyzed from the same precursor (ns252) as ns252p_X_25/6 (shown in Figure 36 to be amorphous). The only difference between these samples and their corresponding amorphous samples was in how the tube (of the tube furnace) was purged before pyrolysis began (full methods described in SI). This means that the presence of oxygen (caused here by inadequate atmosphere control) induces oxide nanoparticle formation in samples that would otherwise be amorphous.

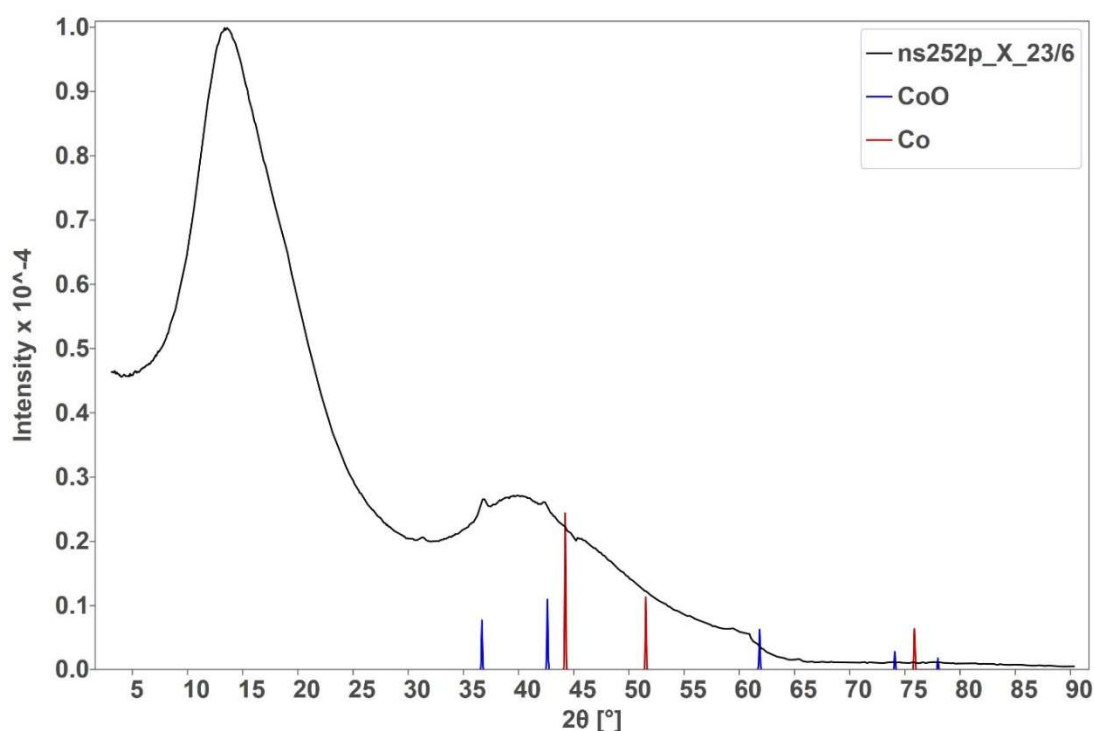


Figure 39 - PXRD pattern of ns252p_X_23/6 compared to simulated cobalt oxide (CoO)^[76] and cobalt metal (Co)^[77]. Crystalline peaks are apparent in the PXRD pattern of ns252p_X_23/6.

These results are extremely important as if the conditions inside the tube furnace are not ideal (e.g. a leak occurred or purging was not complete) this would cause more oxide formation than would otherwise occur. This would affect the loading at which there are no nanoparticles, and as such, it is difficult to confidently report findings around this. To prevent

oxygen being introduced to the sample during pyrolysis, much effort was made to identify and seal leaks in the gas line. Despite this, no samples were able to be formed without oxide peaks observed by PXRD.

Therefore, it is likely that the formation of oxide nanoparticles in many of the samples is due to the intrinsic oxygen contained within tannic acid. This oxygen is released at a temperature at which cobalt and nickel oxidize readily. Even at room temperature cobalt^[78] and nickel^[79] will form a small surface layer of their corresponding oxide. As the amount of metal present as metallic cobalt or nickel is so small, almost the entire metal present will convert into the oxide. It is also worth noting that the K-TA layer begins carbonisation at 250°C^[80], above which oxygen from the tannic acid will begin to be released. As CoO and NiO layer growth rates increase with temperature^[78-79], this provides strong evidence that the intrinsic oxygen contained with the tannic acid layer is the cause of oxide formation. Many experiments were performed varying the pyrolysis method to attempt to eliminate the influence of the intrinsic oxygen contained within the tannic acid, yet none of these were able to completely eliminate oxide peaks in the produced HPNCs PXRD pattern. These are detailed in the SI. It should also be noted that it is possible that as cobalt and nickel form a surface layer of their corresponding oxide at room temperature the oxide consistently found during these experiments was simply due to the materials exposure to oxygen present in the air when transferring from the furnace to the diffractometer. This could be investigated by using a reducing atmosphere during pyrolysis to ensure no oxide formation occurs in the furnace (discussed later), but due to time limitations was not investigated in this work.

In comparison, palladium does not oxidize as easily and did not have these issues. Therefore, the content of palladium was able to be lowered until no nanoparticles formed and therefore only single metal atom sites were present.

Chapter 3 Single Palladium Atoms Supported on HPNC

Introduction

Although the discovery of palladium was in 1802^[81], it wouldn't be until the late 1950's that palladium's catalytic activity would be unveiled with the discovery of the Wacker reaction^[82]. Further discoveries in 1967^[83] and 1970^[84] changed the landscape of organic chemistry by allowing direct carbon-carbon bond formation catalysed by palladium in a zero-valence state. Compared to nonprecious metal catalysts (such as Cu^[85], Ni^[86] or Fe^[87]), palladium may seem unrealistic for industrial catalysis due to its high cost and scarcity on earth - but palladium holds many advantages as an industrial catalyst due to its comparably higher catalytic activity. This increased catalytic activity enables conversion of less reactive substrates^[88], increased performance at room temperature^[89-90] and extremely high turnover numbers (TON, number of times each catalytic site completes a catalytic cycle) of up to 10^6 ^[91].

A key consideration when discussing palladium catalysts is product contamination. While palladium contamination in the product of reactions utilizing homogeneous catalysts can be significant with residual palladium levels of 40-80 ppm, previous studies have found that using palladium supported on carbon can reduce the contamination to <4-6 ppm^[92]. As shown in Table 4 below, the maximum acceptable concentration for residual palladium in oral pharmaceutical products is 5 ppm. Therefore, if the contamination can be lowered such that it is consistently below 5 ppm, there will be great incentive to trial the catalyst in industry.

While this work is certainly not the first to produce single palladium atoms bound to a carbon support^[8, 13, 93], the resulting Pd@HPNC catalyst is novel in its hollow capsule support shape and the method used to fabricate the catalyst is novel and has potential for scalability. If the Pd@HPNC catalyst synthesized in this work shows contamination levels below 5 ppm (as well as high catalytic activity) there will be great incentive to push the catalyst forwards as an industrial catalyst.

Table 4 - Maximum acceptable concentration limits for the residues of metal catalysts that can be present in pharmaceutical products^[94].

Metal	Maximum acceptable concentration limit in product (ppm)	
	Oral	Parenteral
Pd, Pt, Ir, Rh, Ru, Os	5	0.5
Mo, V, Ni, Cr	10	1.0
Cu, Mn	15	1.5
Zn, Fe	20	2.0

In order to carry out a systematic investigation of the relationship between palladium concentration during ion exchange and palladium nanoparticle formation it was necessary to ensure that all other variables were held constant. The most reliable method to achieve this is to use a single batch of ZIF-8@K-TA as precursor, as well as using the same pyrolysis conditions throughout the study. To achieve this, considerable effort was put into scaling up the ZIF-8 synthesis and K-TA coating procedures and tweaking these methods, as described earlier in Chapter 2. Detailed methods of each experiment are given in the SI.

Palladium Reduction

Impregnating the coated coordination polymer with palladium (to make ZIF-8@Pd-TA) via ion exchange requires first forming a solution with stable Pd^{2+} ions. Factors that can influence the Pd^{2+} ions stability in solution include the salt, solvent, temperature and light exposure^[95]. Strong stability under ambient light and room temperature provides a much more convenient lab procedure, and therefore it was desirable to find a palladium salt and solvent combination that was stable in these conditions. A table of the palladium salts and the solvents trialled can be seen below in Table 5.

Table 5 - Solubility and reactivity table of solvents and palladium salts. Reactivity refers to whether the solvent and salt react with each other. For solubility, ✓ means the salt is very soluble, ~ means the salt is somewhat soluble and/or requires sonication to dissolve and X means the salt is not noticeably soluble.

Solvent	Palladium Acetate			Palladium Nitrate			Palladium Chloride		
	Solubility	Reaction		Solubility	Reaction		Solubility	Reaction	
		Initial	After 2 days		Initial	After 2 days		Initial	After 2 days
Methanol	~	Yes	Yes	✓	Yes	Yes	x	No	No
Acetonitrile	~/✓	No	Yes	✓	No	Yes	x	No	No
THF	~	No	No	✓	No	Yes	x	No	No
Dioxane	~	No	Yes	✓	No	Yes	x	No	No
Nitromethane	~	No	Yes	✓	No	Yes	x	No	No

Palladium nitrate seemed like the ideal choice of salt due to its high solubility in all solvents tested. However, when palladium nitrate was used the Pd^{2+} were easily reduced by sunlight to palladium metal over two days. Palladium chloride was not sufficiently soluble even under sonication. Palladium acetate was not greatly soluble but upon sonication the salt dissolved readily. However, palladium acetate also allowed the reduction of the Pd^{2+} under light when in methanol, acetonitrile and dioxane, and formed a white flocculent solid in nitromethane. Palladium acetate in tetrahydrofuran (THF) was the only stable combination of palladium salt and solvent that was investigated. This combination of salt and solvent was therefore used in this work during ion exchange to introduce palladium into the coated coordination polymer. It is important to note that the precursor (ZIF-8@K-TA) was washed twice with THF and suspended in THF to remove methanol, as methanol has been shown to aid the reduction of the Pd^{2+} in solution.

Nanoparticle Formation by Varying Metal Loading

Theory

Single atoms are likely present in M@HPNC regardless of the formation of nanoparticles. Therefore, even if the loading of metal in a sample reaches the threshold at which nanoparticles begin to form, there are likely to be many single metal atoms still present.

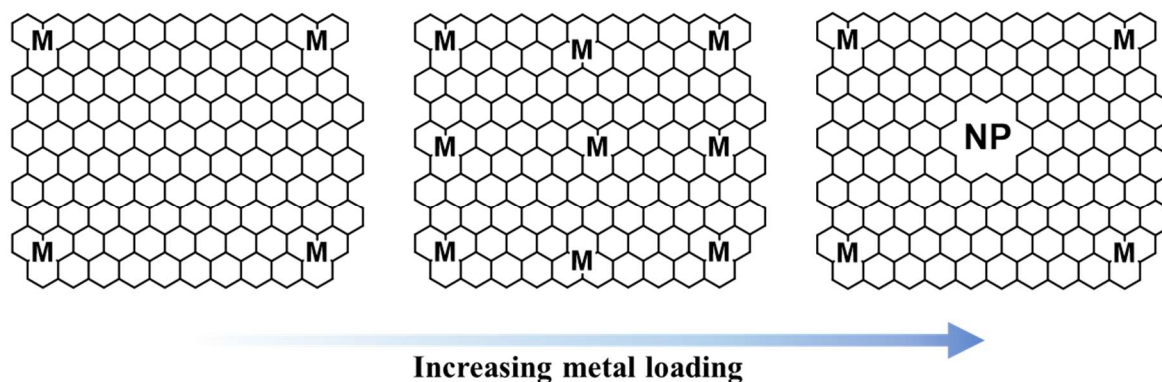


Figure 40 - Schematic depicting the effect of increased metal loading. Single metal atoms are represented with M and nanoparticles are represented with NP.

However, the formation of nanoparticles during pyrolysis is undesirable for the formation of an atomically disperse palladium catalyst. As previously discussed, this is because the palladium that is not exposed in nanoparticles is not available as a catalytic site. Any nanoparticles formed would need to be etched from the material using acid to contribute any found catalytic activity solely to the single metal atoms present. Therefore, palladium nanoparticle formation using this method needs to be understood so that it can be avoided. Assuming all other variables are held consistent (e.g. precursor ZIF-8@K-TA, pyrolysis temperature, pyrolysis atmosphere, etc.), palladium nanoparticle formation is influenced by the concentration of palladium that is impregnated into the coated coordination polymer. This is varied by changing the amount of palladium present during ion exchange.

Results from ZIF-8@K-TA Batch ns243

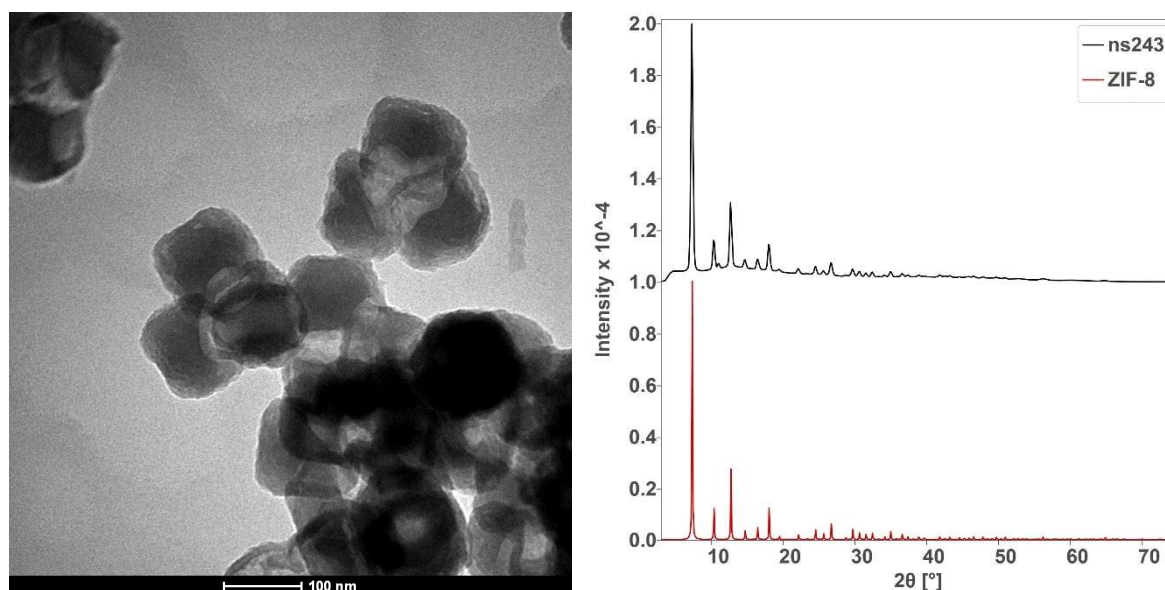


Figure 41 - TEM image (left) and PXRD pattern (right) of ns243 (a large scale batch of ZIF-8@K-TA). There is etching visible in the TEM image of the ZIF-8 crystals inside the K-TA coating. This is not ideal but is not a major concern because at this stage as it has served its purpose as a scaffold for K-TA.

Sample ns243 was the first large-scale batch of ZIF-8@K-TA that produced satisfactory results upon pyrolysis. Small aliquots of this batch of ZIF-8@K-TA underwent ion exchange with Pd^{2+} in tetrahydrofuran for 2 hours and after washing and drying were pyrolyzed. The resulting HPNC were characterised using PXRD and TEM to investigate the presence of palladium nanoparticles. The results of this process are shown in chronological order below in Table 6.

Table 6 - Ion exchange conditions and corresponding pyrolysis results of a single ZIF-8@K-TA source (ns243) that were impregnated with varying amounts of palladium. Arranged in chronological order. Cells for PXRD and TEM results that were amorphous are omitted for clarity.

Sample	ns251pa	ns251pb	ns254pa	ns254pb	ns258pa	ns258pb	ns260p
mol Pd^{2+} / mg ZIF-8@K-TA	6.68E-08	10.4E-08	1.05E-08	2.09E-08	1.55E-08	1.69E-08	1.69E-08
ZIF-8@K-TA (mg)	60	60	85.2	85.2	42.6	42.6	852
Volume THF (mL)	80	80	80	80	40	40	800
PXRD	Pd peaks	Pd peaks					Pd peaks
TEM	NP present	NP present		NP present			

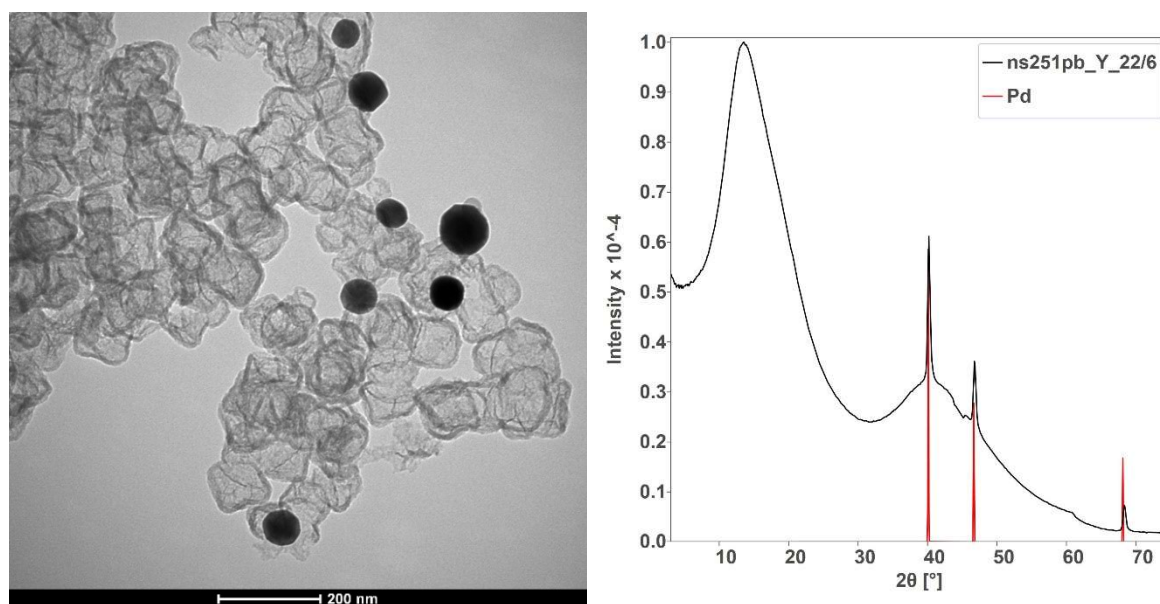


Figure 42 - TEM image (left) and PXRD pattern (right) of ns251pb_Y_22/6. TEM images show considerable nanoparticles and the PXRD pattern has crystalline peaks matching simulated palladium (Pd)^[77].

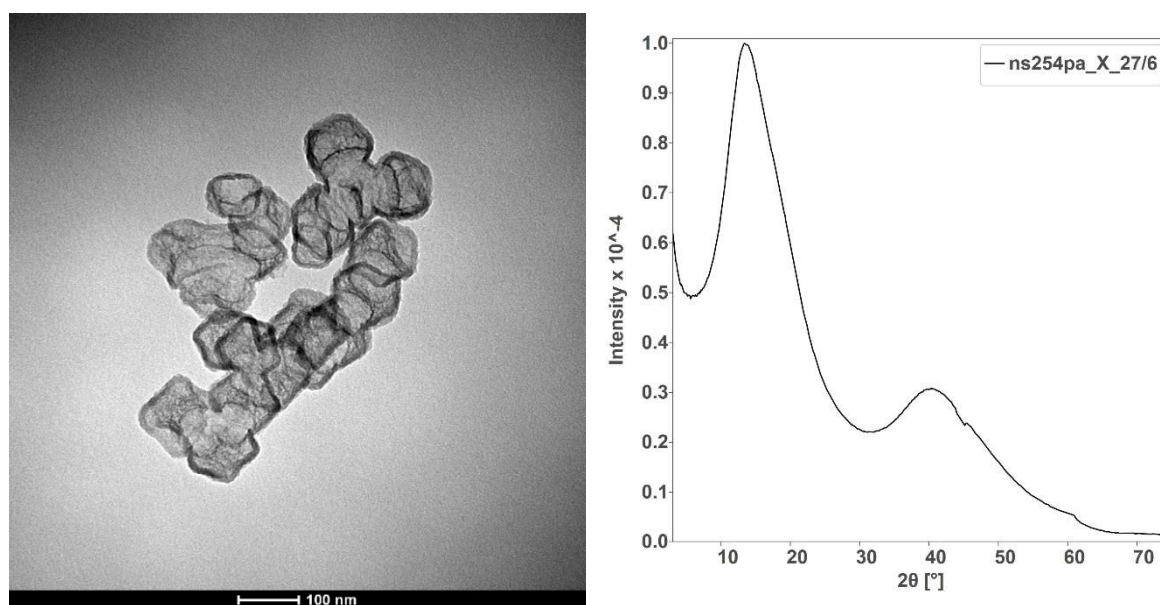


Figure 43 - TEM image (left) and PXRD pattern (right) of ns254pa_X_27/6. Both TEM image and PXRD pattern show sample to be completely amorphous.

It can be seen that the amount of palladium per ZIF-8@K-TA introduced during ion exchange was lowered until nanoparticles were no longer observed (ns254pa). The amount of palladium per ZIF-8@K-TA introduced during ion exchange was then pushed slightly to find the highest loading of palladium that could be introduced without nanoparticle formation (ns254pb, ns258pa and ns258pb). It was decided to use the highest ratio of

palladium per ZIF-8@K-TA that was found to not result in nanoparticles (ns258pb) when scaling up. The rest of the precursor ZIF-8@K-TA (ns243) was then exchanged with Pd²⁺ at a ratio of 1.69E-08 mol Pd²⁺ per mg ZIF-8@K-TA for sample ns260p. Unfortunately, the dispersion of palladium throughout K-TA is not perfect. This means that some patches of ZIF-8@Pd-TA, and therefore the resulting Pd@HPNC, have a higher concentration of palladium and the bulk of the material, and other areas have correspondingly lower concentration. At larger scales, this effect increases proportionally. This meant that at the palladium concentration that did not form nanoparticles at a small scale (ns258pb), nanoparticles were formed at the large scale (ns260p). This is shown in Figure 45 below by PXRD patterns taken of different samples of ns260p, some of which are amorphous and others which show palladium metal peaks. The results of Table 6 can be seen ordered from high to low palladium loadings below in Table 7.

Table 7 - Ion exchange conditions and corresponding pyrolysis results of a single ZIF-8@K-TA source (ns243) that were impregnated with varying amounts of palladium. Rearranged in order of highest concentration of palladium to lowest. Cells for PXRD and TEM results that were amorphous are omitted for clarity.

Sample	ns251pb	ns251pa	ns254pb	ns260p	ns258pb	ns258pa	ns254pa
mol Pd²⁺/ mg ZIF-8@K-TA	10.4E-08	6.68E-08	2.09E-08	1.69E-08	1.69E-08	1.55E-08	1.05E-08
ZIF-8@K-TA (mg)	60	60	85.2	852	42.6	42.6	85.2
Volume THF (mL)	80	80	80	800	40	40	80
PXRD	Pd peaks	Pd peaks		Pd peaks			
TEM	NP present	NP present	NP present				

It is important to consider the limitations of the characterisation techniques in this work. Noise in the PXRD patterns was largely mitigated by running all scans for 300 seconds instead of the conventional 60 seconds. Yet, as nanoparticles reduce in size (and number) as the concentration of the metal is lowered (eventually becoming single metal atom sites as shown earlier), the corresponding PXRD peaks become smaller and smaller. Although noise has been diminished greatly at the macro scale (when viewing a PXRD spectrum from 0° to 90°), when the PXRD pattern is expanded to focus on a specific area of interest it becomes difficult to identify peaks caused by nanoparticles amongst the noise. Unfortunately, as shown by ns254pb, as the size and amount of nanoparticles becomes small enough PXRD

patterns will not show peaks large enough to be attributed to palladium nanoparticles, yet nanoparticles were able to be identified using TEM.

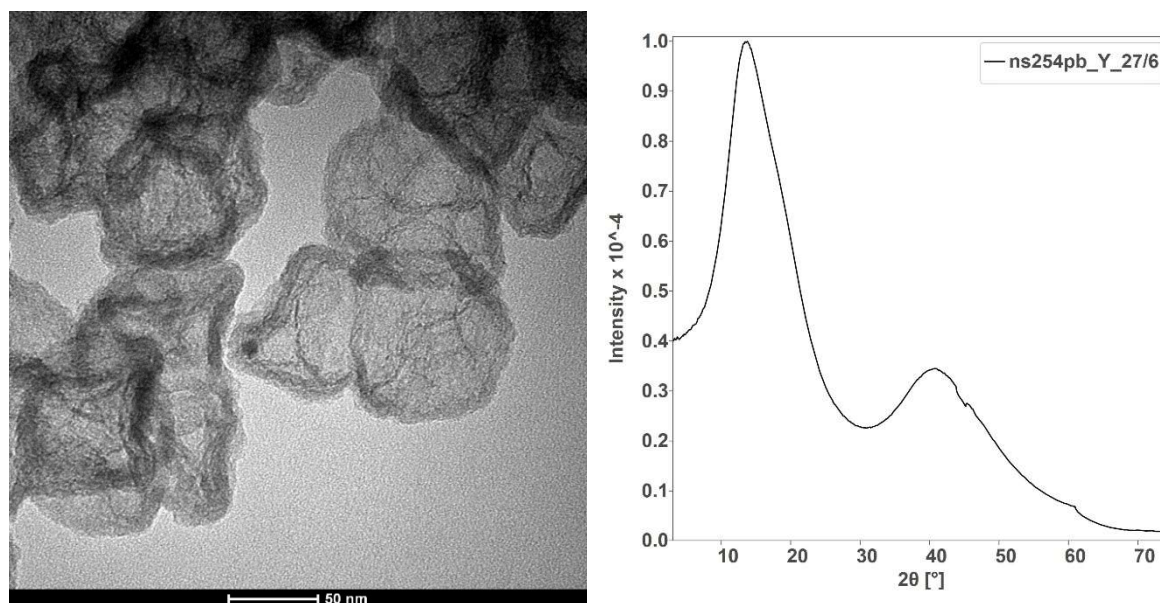


Figure 44 - TEM image (left) and PXRD pattern (right) of ns254pb_Y_27/6. TEM image shows a very small nanoparticle near the centre of the image, however the PXRD shows no obvious crystalline peaks.

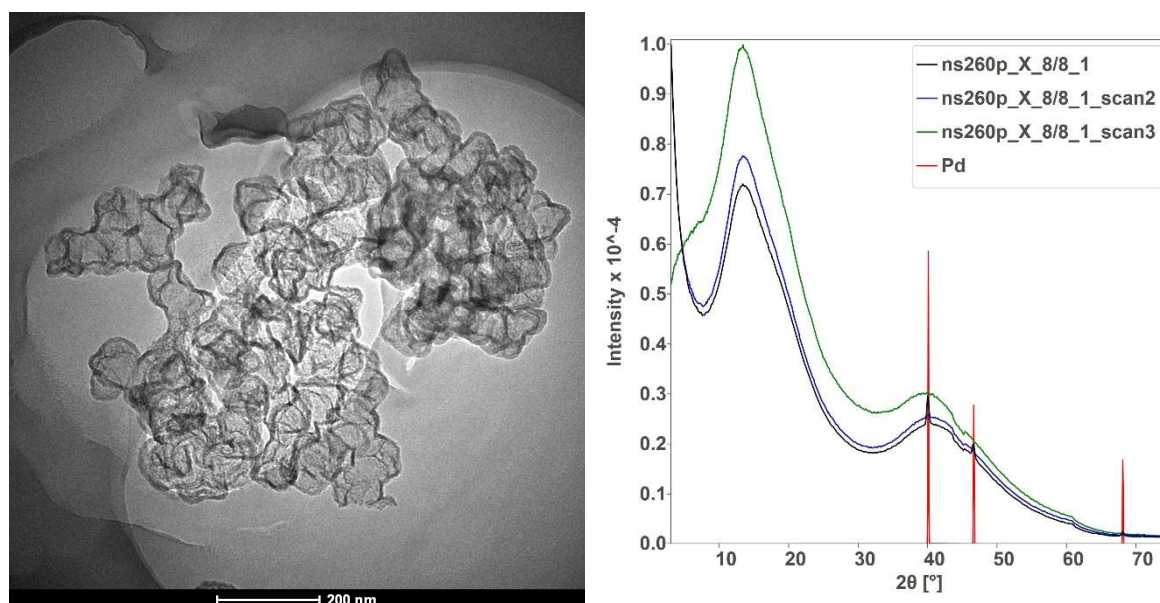


Figure 45 - TEM image (left) and PXRD pattern (right) of ns260p_X_8/8. No nanoparticles were seen by TEM whereas some PXRD scans had significant crystalline peaks. Other PXRD scans were seen to be amorphous. PXRD scans were compared to simulated palladium (Pd)^[77].

It is also important to consider the limitations of TEM. For instance, many hours can be spent screening the sample when searching for evidence of nanoparticles. During this time,

no nanoparticles may be found – yet this does not confirm that no nanoparticles are present in the sample as barely a fraction of a percentage of the sample has been observed. In this way, both PXRD and TEM are difficult techniques to use to identify the formation of very small and infrequent nanoparticle formation. Therefore, for this work, concentrations must be lowered significantly from a concentration at which nanoparticles form to completely avoid them.

Results from ZIF-8@K-TA Batch ns264

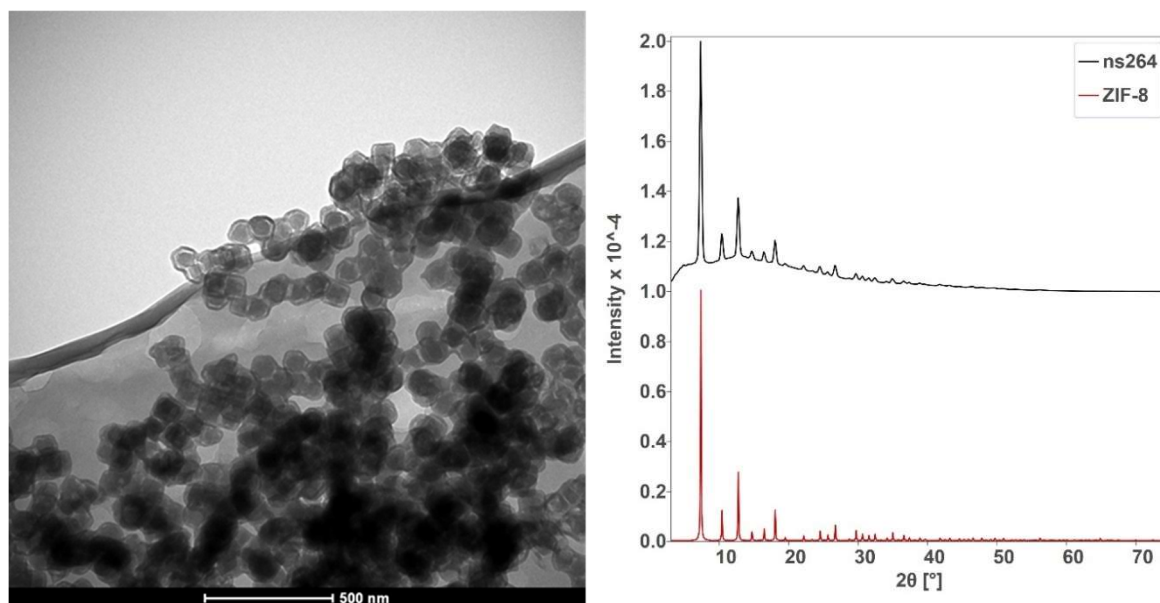


Figure 46 - TEM image (left) and PXRD pattern (right) of ns264 (a large scale batch of ZIF-8@K-TA).

As all of precursor ZIF-8@K-TA (ns243) was consumed in the initial scaled up Pd@HPNC synthesis ns260p, a new batch of ZIF-8@K-TA was synthesized (ns264). This new batch had to be investigated to ensure that similar palladium levels result in similar results as seen using ns243. Samples ns265pa and ns265pb were synthesized from the new batch of ZIF-8@K-TA and confirmed that it behaved similarly to the old batch (i.e. palladium levels above a certain value resulted in nanoparticles and levels below another value resulted in no nanoparticle formation).

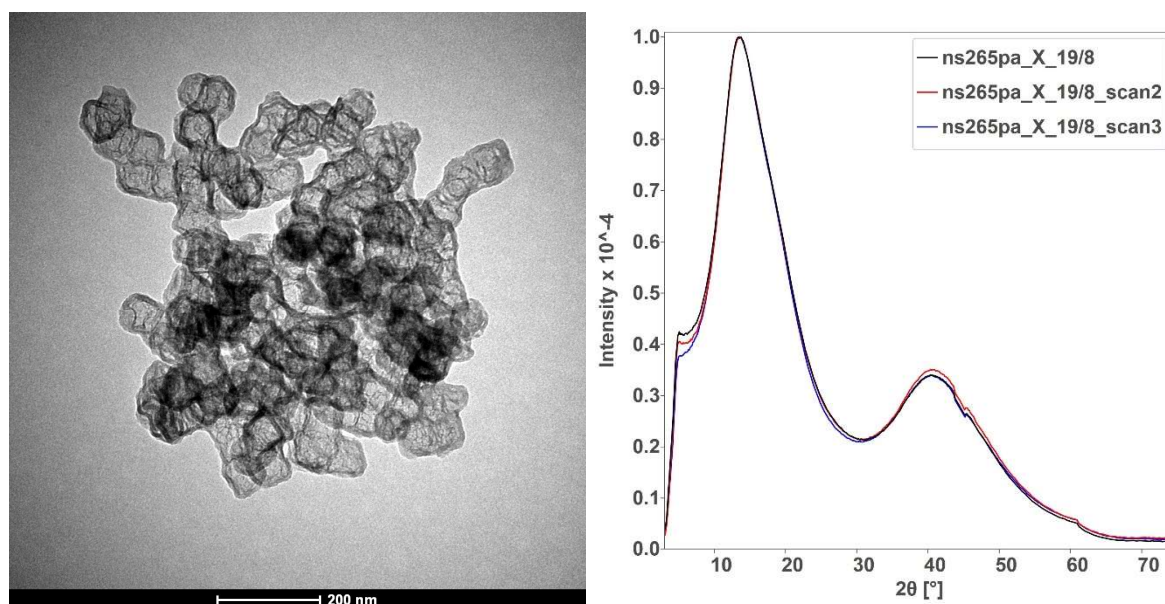


Figure 47 - TEM image (left) and PXRD pattern (right) of ns265pa_X_19/8 (Pd@HPNC). Sample is shown to be completely amorphous.

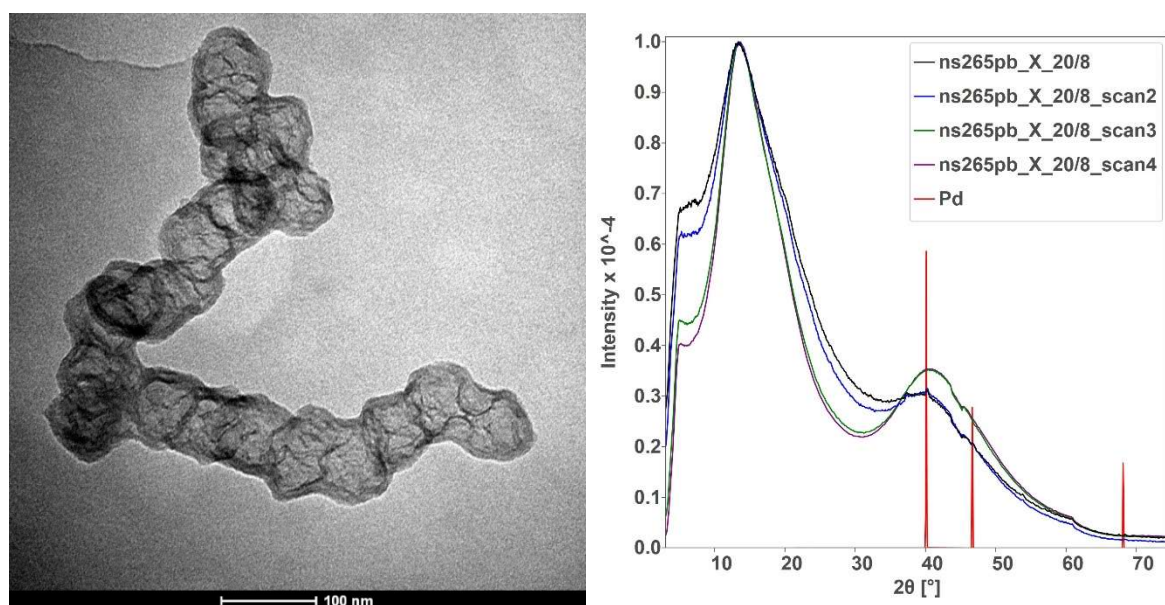


Figure 48 - TEM image (left) and PXRD pattern (right) of ns265pb_X_20/8. PXRD patterns of ns265pb_X_20/8 over multiple scans are compared to simulated palladium (Pd)^[77]. Crystalline peaks are apparent in the PXRD pattern of the initial scan and scan 2, but scan 3 and scan 4 are completely amorphous.

It was then attempted to scale up the ion exchange and pyrolysis processes to synthesize bulk Pd@HPNC from ZIF-8@K-TA source ns264. As previous attempts at scaling up had been brash (resulting in nanoparticle formation), ns266p erred on the side of caution and slightly lowered the amount of Pd²⁺ per ZIF-8@K-TA below what was found to result in no

nanoparticles, from 1.58E-08 to 1.50E-08. This scaled up synthesis of Pd@HPNC was successful and no nanoparticles were found using TEM or PXRD, as shown below in Figure 49. Many PXRD scans were done to confirm the lack of nanoparticles (these can be found in the SI under ‘ns266p’ in the pyrolysis section).

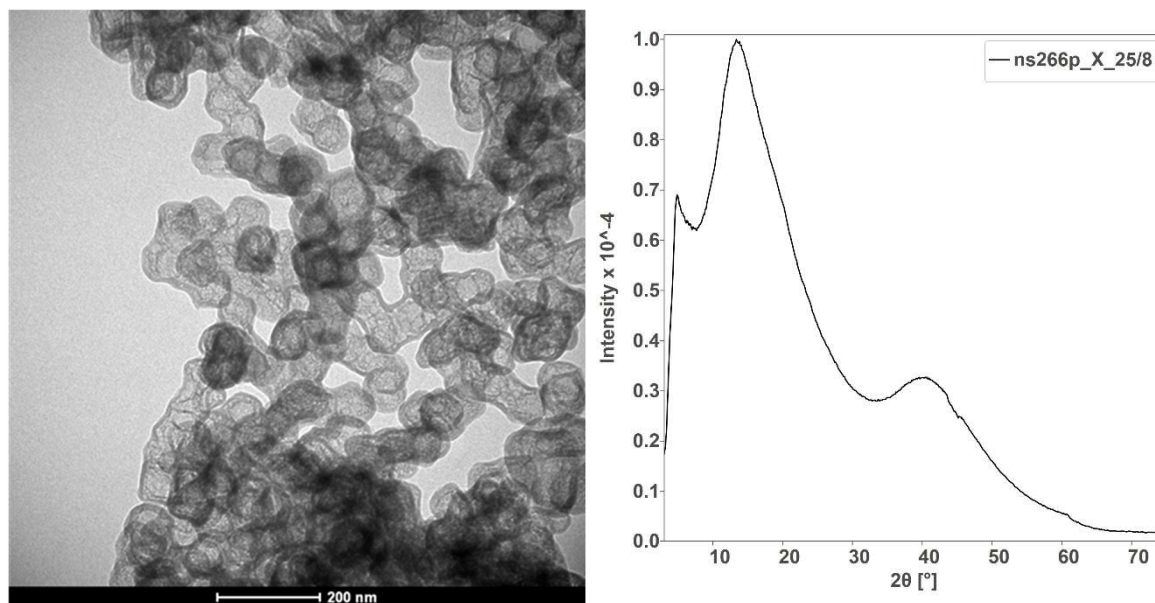


Figure 49 - TEM image (left) and PXRD pattern (right) of ns266p_X_25/8. Sample is shown to be completely amorphous.

To test repeatability, the conditions used in ns266p were repeated in ns269p. Synthesis of Pd@HPNC with no nanoparticles was again successful, as shown by the TEM image and PXRD pattern of ns269p shown in Figure 50 below. Both ns266p and ns269p show palladium in their respective EDX spectra (shown below in Figure 52), and have no signs of palladium nanoparticle formation by either TEM or PXRD. Therefore a reliable large scale synthesis for Pd@HPNC with no nanoparticle formation has been developed in this work. Although the term ‘large scale’ is used, only approximately 240 mg of Pd@HPNC is produced per batch. Despite this, the synthesis method developed has good potential for industrial scale production, should the material have sufficient catalytic performance.

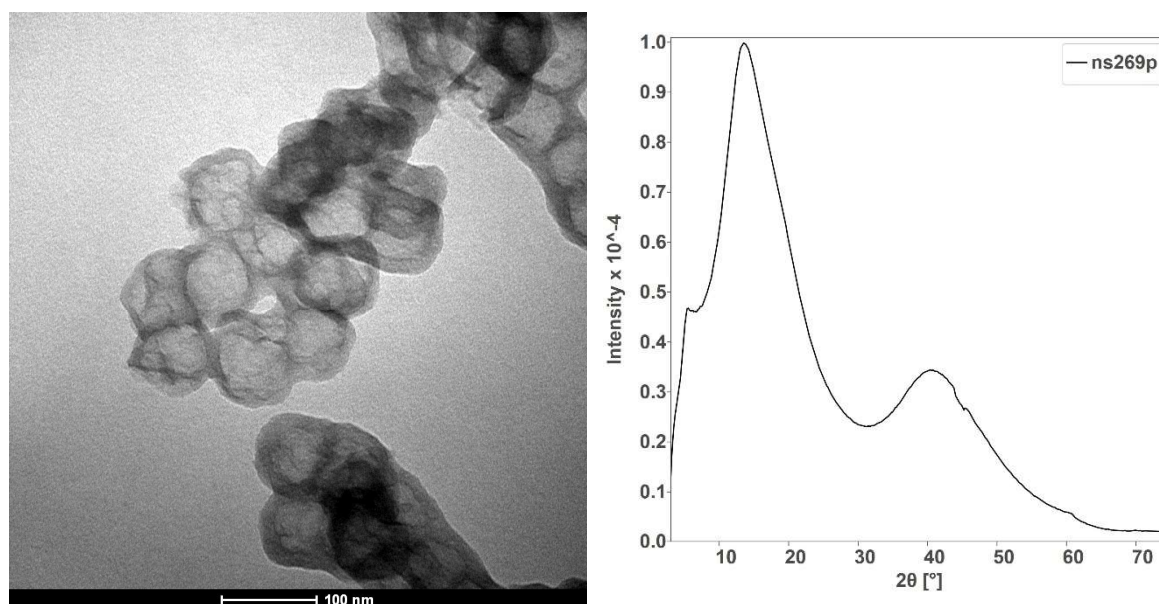


Figure 50 - TEM image(left) and PXRD pattern (right) of ns269p. Sample is shown to be completely amorphous.

Potassium Salt Formation

It is worth noting that the EDX spectrum obtained from ns266p contained strong potassium peaks, as shown below in Figure 51. This was initially thought to be due to mass transfer issues during pyrolysis, and therefore the sample was re-pyrolyzed under the same conditions (named ns266pp). As the EDX spectrum did not change after pyrolysis (again shown in Figure 51), it was realised that these peaks were due to potassium salts that had formed during pyrolysis[80]. The sample was washed by dialysis and renamed ns266pp_washed. The EDX spectrum of ns266pp_washed showed no potassium, as shown in Figure 52 below. This confirms that the potassium peaks were due to potassium salts that formed during pyrolysis, as these were soluble in the water used to wash ns266pp and were therefore removed by dialysis. Therefore the HPNC synthesis method was tweaked to include a washing procedure to remove these potassium salts after pyrolysis for all future samples.

PXRD patterns and TEM images of ns266pp_washed (see Figure S75 in the SI and Figure 52 below respectively) show that the Pd@HPNC seems unaffected by the second pyrolysis and washing it underwent when compared to other Pd@HPNC samples. This alludes to the stability of the produced Pd@HPNC.

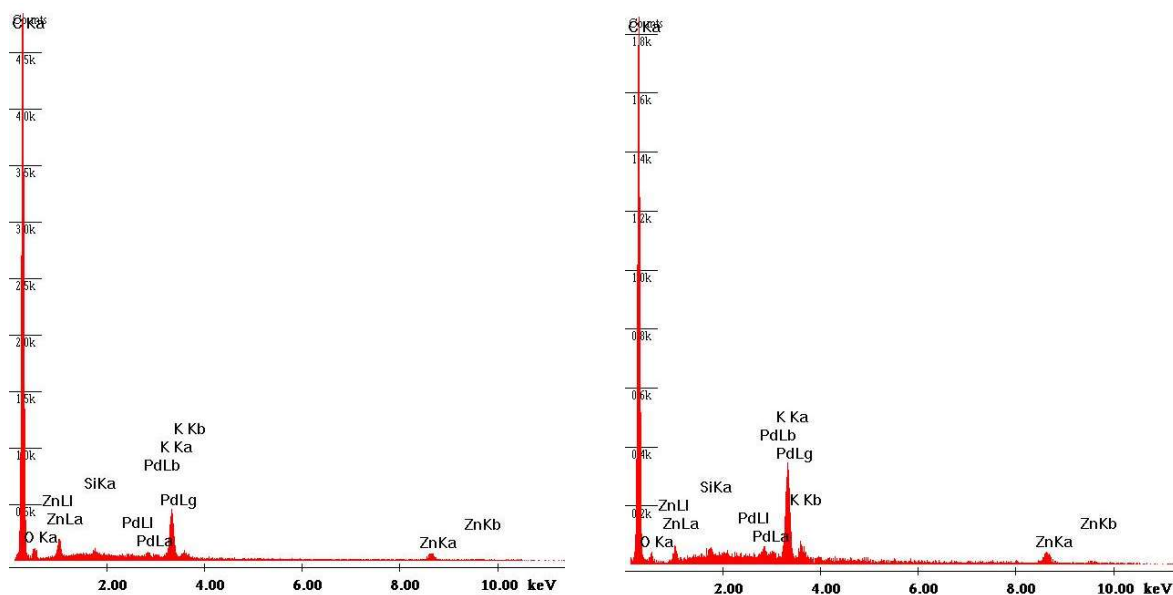


Figure 51 - EDX spectra of ns266p (left) and ns266pp (right). Both spectrum show significant potassium content, as well as trace palladium, silicon, oxygen and zinc.

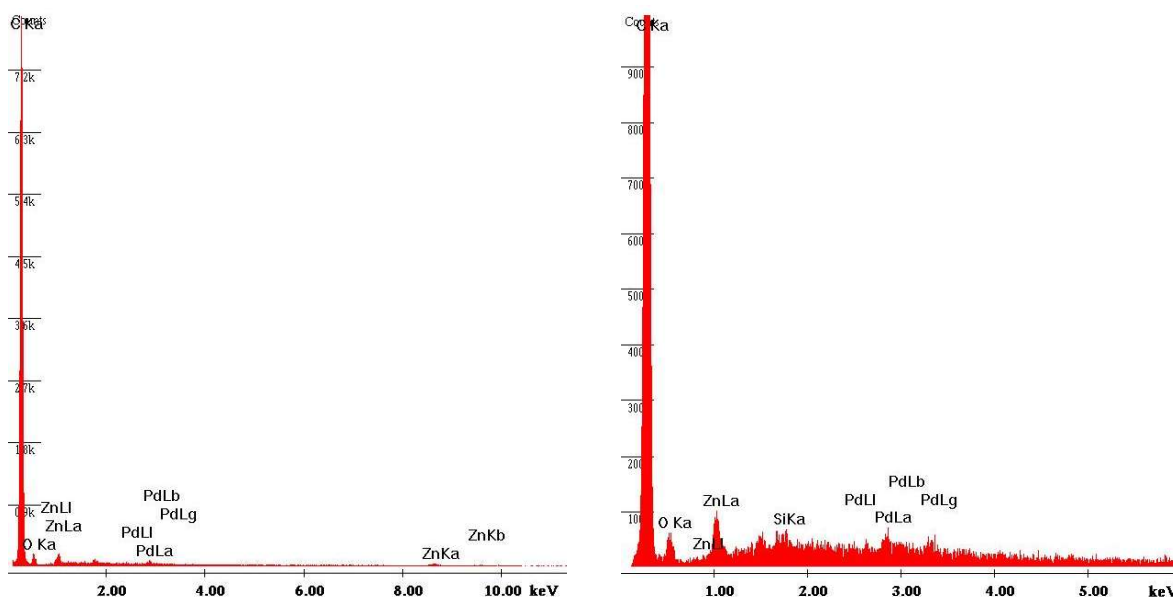


Figure 52 - EDX spectra of ns266pp_washed (left) and ns269p (right). Both spectrum show trace palladium, silicon, oxygen and zinc. No potassium peaks are observed.

As the method to produce Pd@HPNC without nanoparticles had been developed and confirmed, several samples were made at higher loadings to investigate the behaviour of the ion exchange process (discussed later) and to confirm that nanoparticles form from precursor ZIF-8@K-TA ns264 at the same conditions they did from ns243, the prior large-scale batch of ZIF-8@K-TA. Samples ns274pa, ns274pb and ns274pc were slightly scaled up samples at higher Pd²⁺ loadings, synthesized to show the presence of palladium nanoparticles under

TEM from samples made from precursor ZIF-8@K-TA ns264. Surprisingly, ns274pa and ns274pb were both found to be amorphous by both TEM and PXRD, despite ns265pb (a previous Pd@HPNC sample synthesized from the same ZIF-8@K-TA source under a lower palladium concentration during ion exchange) showing signs of nanoparticles by PXRD.

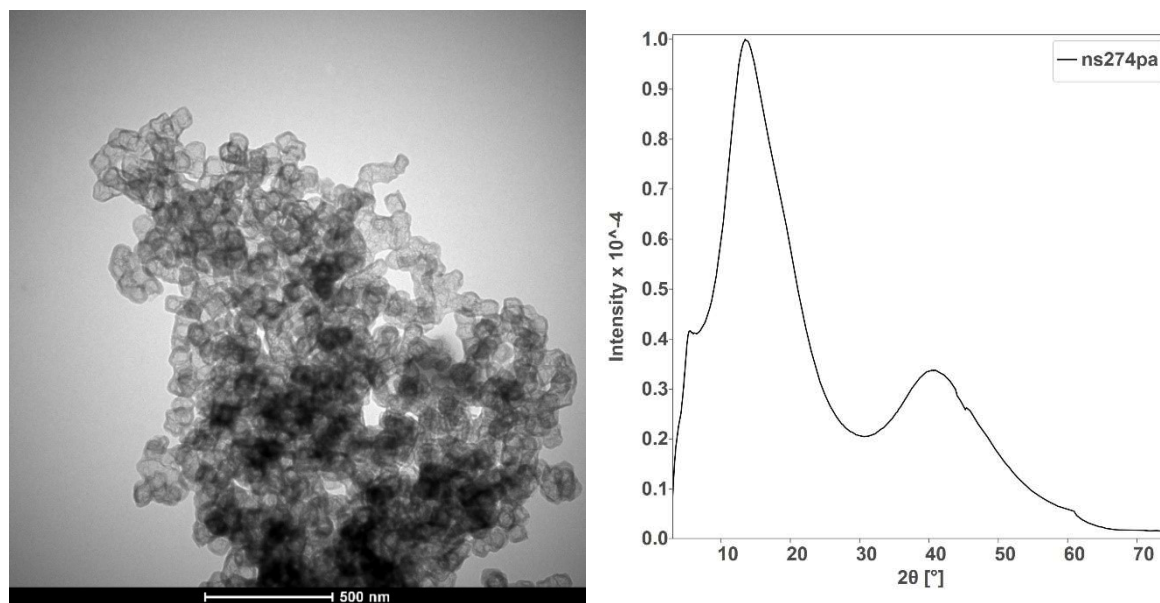


Figure 53 - TEM image (left) and PXRD pattern of ns274pa. Sample is shown to be completely amorphous.

Further, although sample ns274pc does show signs of nanoparticles, when compared to ns251pa above, a dramatic difference can be seen in both the TEM images and PXRD patterns, as shown below in Figure 55 and Figure 56. It is important to note that the small cluster of nanoparticles shown in the TEM image of ns274pc was found after hours of searching through amorphous HPNC. Even if all the palladium metal seen in this TEM image of ns274pc were to aggregate into a single nanoparticle it would still not even be 1/5th the size of a single nanoparticle seen in ns251pa, and these nanoparticles were found consistently throughout the sample. This is very surprising as these samples were synthesized under similar palladium loadings during ion exchange, although different ZIF-8@K-TA precursors and furnaces were used. It is expected that differences between ZIF-8@K-TA batches may cause slight differences in nanoparticle formation due to differences in the K-TA coating thickness, but the difference between ns274pc and ns251pa is too considerable to be accounted to this.

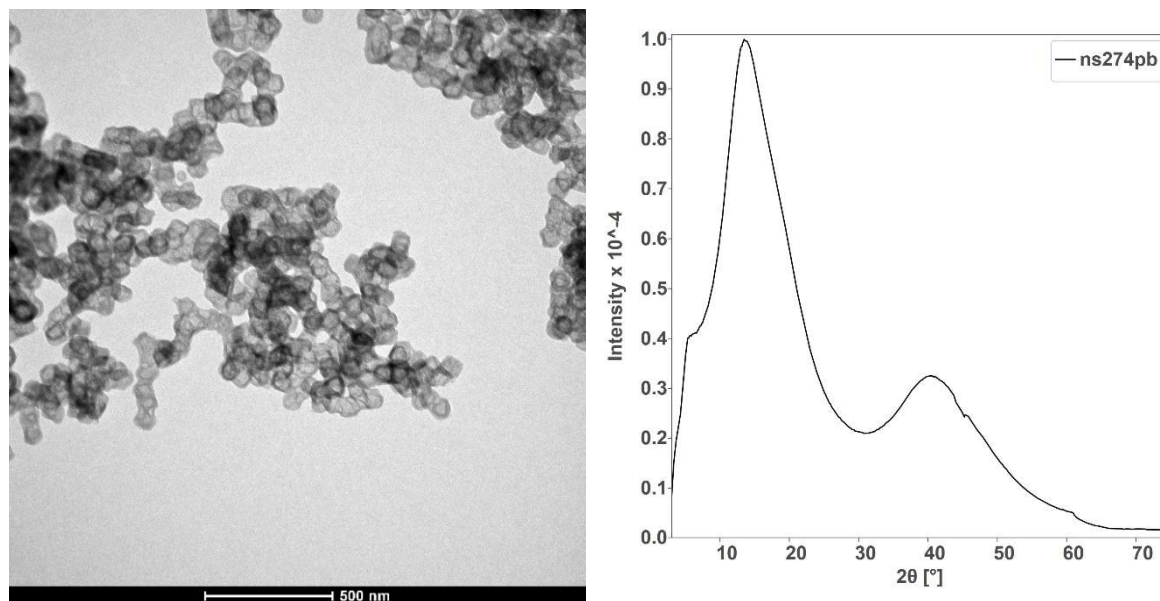


Figure 54 - TEM image (left) and PXRD pattern of ns274pb. Sample is shown to be completely amorphous.

The difference in furnace may have had some effect, as ns251pa was pyrolyzed in an older furnace that had less ideal conditions. Specifically, ns251pa was pyrolyzed in a furnace that ran four gas lines from their respective cylinders to a mixer, and then a single line to the furnace. This meant that gas contained in the three unused lines (one was used to supply argon) is slowly diffused into the feed gas to the tube furnace. Comparatively, ns274pc was pyrolyzed with a direct feed of argon directly from the cylinder, eliminating any potential contaminants. Also, more extensive purging procedures were used when pyrolysing ns274pc, as shown by the method descriptions in the SI.

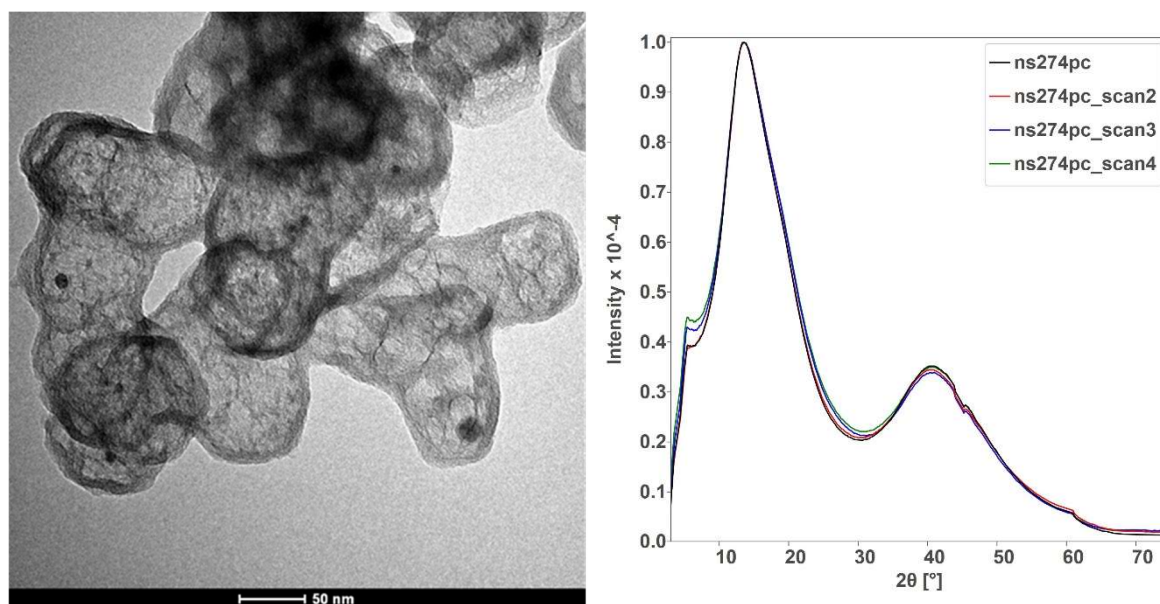


Figure 55 - TEM image (left) and multiple PXRD patterns of ns274pc. TEM image shows a many very small nanoparticles, however the PXRD patterns shows no obvious crystalline peaks.

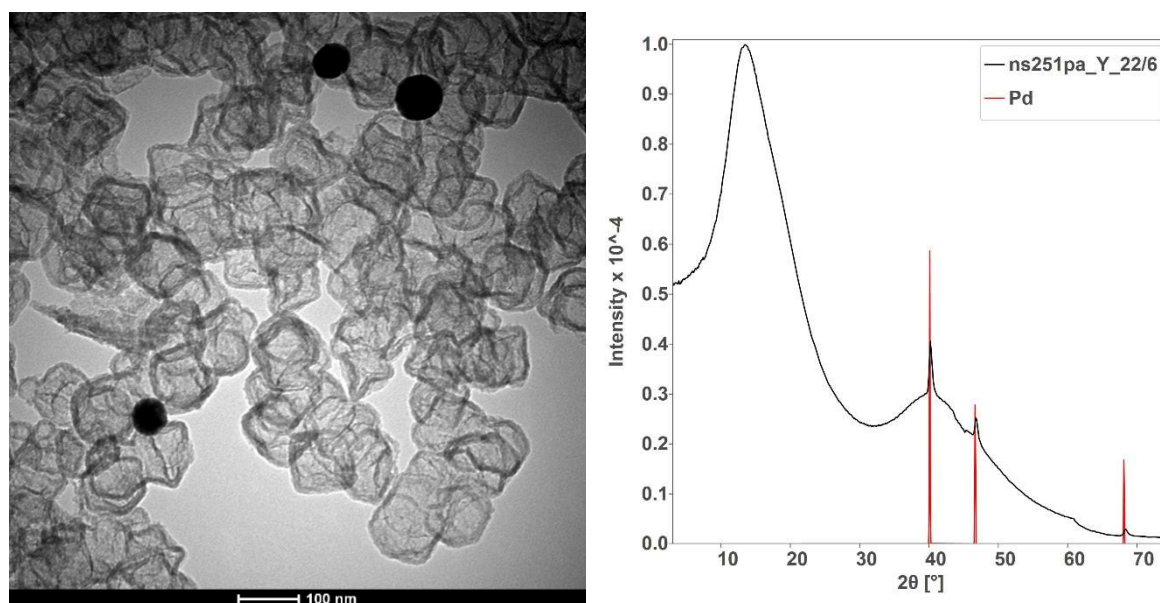


Figure 56 - TEM image (left) and PXRD pattern (right) of ns251pa_Y_22/6. TEM images show considerable nanoparticles and the PXRD pattern has crystalline peaks matching simulated palladium (Pd)^[77].

These differences between the process conditions of ns274pc and ns251pa suggest that the presence of oxygen may induce palladium nanoparticle formation. However, this is not conclusive evidence and a healthy amount of scepticism should be held. It should also be considered that the amount of palladium exchanged during the ion exchange process may vary more than expected. Although the ion exchange process is given two hours to minimise

kinetic effects, perhaps variation in temperature resulted in more palladium exchanging into ns251 than ns274c (ns251pa and ns274pc precursors, respectively). It is unlikely that factors such as synthesis scale would affect results as dramatically as shown. Therefore this work has developed a reliable method to avoid nanoparticle formation, but reliably forming nanoparticles simply by varying the palladium loading during ion exchange requires more work. This may entail using AAS systematically during the synthesis process to measure the amount of palladium actually exchanged into the K-TA layer, as this may be affected by external factors such as temperature.

Table 8 - Ion exchange conditions and corresponding pyrolysis results of a single ZIF-8@K-TA source (ns264) that were impregnated with varying amounts of palladium. Arranged in chronological order. Cells for PXRD and TEM results that were amorphous are omitted for clarity.

Sample	ns265pa	ns265pb	ns266p	ns269p	ns274pa	ns274pb	ns274pc
mol Pd²⁺ / mg ZIF-8@K-TA	1.58E-08	2.32E-08	1.50E-08	1.50E-08	3.03E-08	4.95E-08	6.88E-08
ZIF-8@K-TA (mg)	52.4	52.4	1048	1048	104.8	104.8	104.8
Volume THF (mL)	40	40	984	984	80	80	80
PXRD		Pd peaks					
TEM							NP present

Comparison to Cobalt and Nickel

As methods for the synthesis of Co@HPNC, Ni@HPNC and Pd@HPNC without nanoparticles have all been successfully developed in this work, it is of interest to compare them. For cobalt and nickel, nanoparticle formation was influenced by the presence of oxygen and therefore may have formed at lower concentrations than in an ideal scenario. However, samples impregnated with cobalt or nickel were able to avoid nanoparticle formation during pyrolysis after ion exchange at much higher metal concentrations than palladium, as shown below in Table 9.

Table 9 - Highest observed concentration of metal per ZIF-8@K-TA during ion exchange that reliably resulted in no nanoparticle formation after pyrolysis for cobalt, nickel and palladium.

	Co	Ni	Pd
mol M / mg ZIF-8@K-TA	14.3E-08	8.40E-08	1.50E-08
Sample	ns252p	ns245b	ns266p

This does not necessarily infer that cobalt and nickel are able to be loaded to much higher levels than palladium on a HPNC support before nanoparticles occur. This is because it is unknown how much cobalt or nickel is exchanged into the K-TA layer during ion exchange (see AAS results for palladium results). However, it is highly likely that palladium does not exchange as easily into the K-TA layer as cobalt or nickel as palladium is a noble metal. Therefore, it is likely that cobalt and nickel are able to achieve much higher loadings on HPNC before nanoparticles begin to form, although this must be confirmed by AAS.

Other Nanoparticle Formation Factors

This work has shown that the concentration of palladium introduced to ZIF-8@K-TA affects nanoparticles formation in the resulting Pd@HPNC. Other variables that can influence nanoparticle formation are the atmosphere during pyrolysis and the pyrolysis temperature. These variables are discussed below.

Reducing Atmosphere

During pyrolysis, a reducing atmosphere can be achieved by introducing hydrogen. This typically reduces metal cations to nanoparticles (NP) rather than single metal atoms (SMA)^[75]. Sample ns260 was, when pyrolyzed under a neutral 100% argon atmosphere, found to produce Pd@HPNC that gave a PXRD pattern with small palladium peaks. Conversely, no nanoparticles were found under TEM. Sample ns260 is therefore approximately at the point above which nanoparticles will consistently form and below which nanoparticles will not form at all. To investigate the effect of a reducing atmosphere, a small portion of ns260 was pyrolyzed under a slightly reducing atmosphere. This sample was named ns260p_Y_14/8.

Sample ns260p_Y_14/8 was pyrolyzed under a H₂/Ar (5/95) atmosphere. This sample was found to produce many, very small palladium nanoparticles (as shown in Figure 57 below). This evidence supports claims that a reducing atmosphere during pyrolysis promotes the aggregation of metal^[75]. It should be noted, however, that there are unknown peaks in the PXRD pattern at 42.2°. Further investigation into the cause of this peak is required, however the EDX spectra shown below suggests that this peak is likely caused by a palladium species of some sort (e.g. Pd-H), as there is little other material present that could form a crystalline structure at this angle.

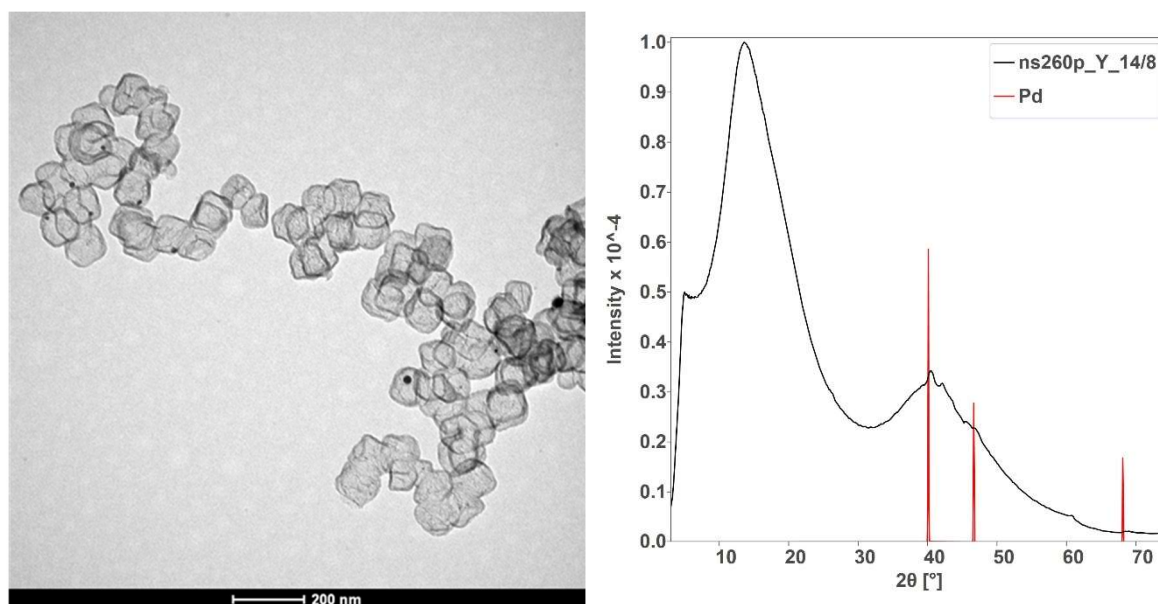


Figure 57 - TEM image (left) and PXRD pattern (right) of ns260p_Y_14/8. TEM image shows many small nanoparticles. PXRD shows crystallinity and is compared to simulated palladium (Pd)^[77]. Peaks at 40.5° and 47.0° can be attributed to palladium, but a peak at 42.2° cannot be attributed to any expected material.

This is important for future work, as, if palladium nanoparticles are found to be a more active catalytic site for a reaction, then it may be beneficial to produce many small, well-dispersed palladium nanoparticles rather than atomically disperse palladium atoms. Using a reducing atmosphere to achieve nanoparticles is beneficial for this purpose compared to simply increasing palladium loading. This is because nanoparticles achieved by increasing palladium loading are likely to still contain many atomically dispersed palladium sites present throughout the material. Comparatively, a reducing atmosphere allows palladium sites that would otherwise be atomically dispersed to aggregate into nanoparticles. This increases the ratio of nanoparticles to atomically dispersed palladium sites. This is also why a reducing atmosphere cannot be introduced to find the metal concentrations at which cobalt and nickel form nanoparticles. Although the reducing atmosphere will prevent the formation of oxides (which is why work on cobalt and nickel materials were stopped) the reducing atmosphere will also cause aggregation of otherwise atomically dispersed metal sites into nanoparticles, causing nanoparticles at lower metal concentrations.

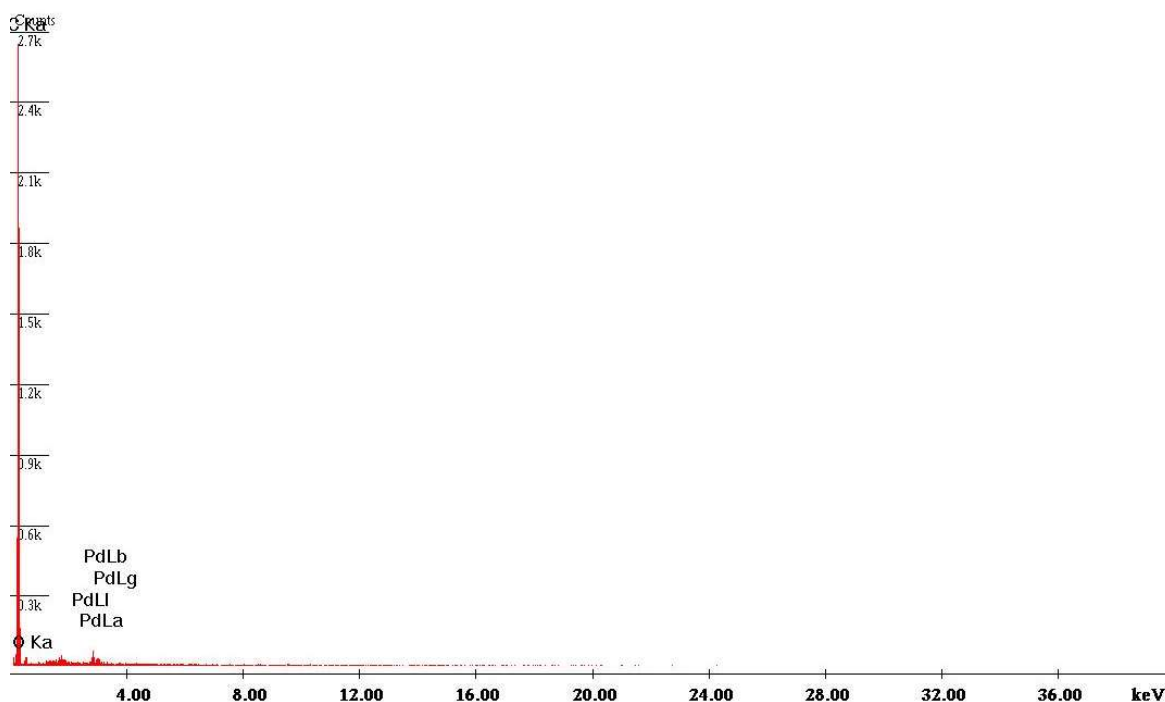


Figure 58 - EDX spectra of ns260p_Y_14/8. No zinc is present due to the prevention of zinc oxide formation during pyrolysis.

As explained earlier in ‘Zinc Contamination’ on page 37, zinc contamination of HPNC is caused by the formation of zinc oxide. A benefit of using a reducing atmosphere is that zinc oxide is not formed, meaning EDX spectrum is zinc free (as shown above in Figure 58). Unfortunately, it does not seem possible to both avoid zinc contamination and obtain purely single metal atoms with no nanoparticle formation.

Pyrolysis Temperature

Should doped single metal atom catalysts be formed by pyrolysis, the temperature at which they are pyrolyzed at is an important factor in producing atomically dispersed metal sites as opposed to nanoparticles^[96]. This has been replicated using Pd@HPNC in this work. Sample ns260p, as discussed above, was shown to have palladium nanoparticles by the presence of palladium peaks in the samples PXRD pattern. Sample ns260p_STA_3/8 was pyrolyzed from the same ZIF-8@Pd-TA source (ns260), but was pyrolyzed under 100% argon at 1000°C in the simultaneous thermal analysis (STA) instrument. This sample was scanned four times using PXRD but no palladium peaks were found (as shown in Figure 59 below). Therefore, sample ns260p_STA_3/8 has less palladium nanoparticles than ns260 samples pyrolyzed at 900°C, if any. This is a promising result, as it shows that the loading of

atomically dispersed palladium sites can be increased further by manipulating the pyrolysis temperature.

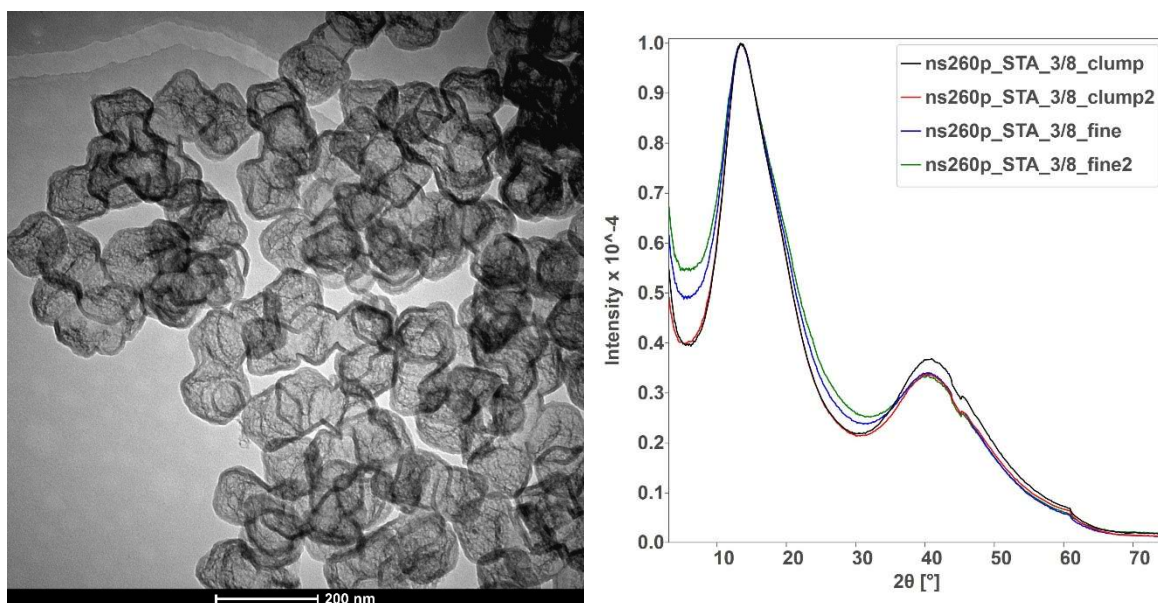


Figure 59 - TEM image (left) and PXRD patterns of ns260p_STA_3/8. Multiple PXRD patterns are shown, with the suffix ‘clump’ referring to aggregated material and ‘fine’ referring to fine powder. Sample is shown to be completely amorphous.

AAS Results

ZIF-8@Pd-TA

Atomic adsorption spectroscopy was used to determine the palladium content of various ZIF-8@Pd-TA precursor samples and their corresponding Pd@HPNC. These results shed light on the ion exchange process, during which palladium is exchanged into the K-TA coordination polymer of ZIF-8@K-TA. As this work aims to form catalysts with purely single metal atoms and no nanoparticles, the loading of palladium into the coordination polymer is extremely small. Also, during the pyrolysis process much of the mass of ZIF-8@Pd-TA is lost, as the majority of the zinc and potassium present is not retained in the product Pd@HPNC. This is because the zinc evaporates at the pyrolysis conditions and potassium does not integrate into the carbon lattice of HPNC. Therefore, while the loading of palladium in ZIF-8@Pd-TA is extremely low, once pyrolyzed into Pd@HPNC the loading is significantly higher.

As ZIF-8@Pd-TA has such a miniscule loading of palladium, it is more accurate to measure the drop in potassium loading, as these values sit within an appropriate range for AAS. The

amount of potassium should drop with correspondingly higher palladium loadings as palladium is exchanged for potassium in the K-TA layer during ion exchange. These results are tabulated below in Table 10, and shown compared to the palladium concentration during ion exchange below in Figure 60.

Table 10 - Results of AAS on various ZIF-8@Pd-TA samples.

Sample	Mass	Mean absorbance	%RSD	Potassium content			
	mg			$\mu\text{g/mL}$	μg	wt. %	+/-
ns264	2.4	0.1590	5.41%	1.648	16.48	0.69%	0.03%
ns269	6.3	0.3708	4.62%	4.359	43.59	0.69%	0.01%
ns274b	2.6	0.1560	6.30%	1.614	16.14	0.62%	0.02%
ns274c	3.7	0.2143	12.06%	2.293	22.93	0.62%	0.02%

The weight percentage of metal is calculated by determining the amount of metal in the solution by AAS and then dividing by the amount of material that was dissolved into the solution. Unfortunately, due to the use of a balance that was only accurate to 0.1 mg during weighing there is significant error in the final weight percentage of potassium. This error (only taking into account the error from the weighing process) is shown in column 8 of Table 10 above and as error bars below in Figure 60. Despite this, it is still evident that as the concentration of palladium present during ion exchange increases the amount of potassium present in the K-TA coordination polymer decreases.

As all samples tested for potassium by AAS (as shown in Table 10 above) were synthesized by ion exchange from ns264 (included as a control), it follows that they all originally had the same weight percent (wt.%) of potassium. Therefore, any drop in potassium can be attributed to palladium exchanging into the K-TA coordination polymer during ion exchange, as it is assumed that every palladium atom that is incorporated into the coordination polymer dislodges an equal amount of potassium out of the synthesized ZIF-8@Pd-TA. It can be seen that although only a small fraction of palladium is taken into the K-TA layer at very low loadings (ns269), with increased loading there is increased uptake of palladium (ns274b and ns274c). This is shown in Figure 60 by the corresponding loss of potassium. Further, as considerably more palladium was introduced in ns274c than ns274b during ion exchange and yet the incorporated palladium does not increase linearly, it can be concluded that at higher concentrations there is a lowered efficiency of palladium exchange into the K-TA layer. This is demonstrated in Table 11 below, as the 0.07 wt.% drop in potassium in ns274b and ns274c compared to ns264 must approximately correspond to a

0.07 wt.% increase in palladium. This shows that only 12.51 % of the palladium introduced during ion exchange was exchanged into the K-TA layer in ns274b, and further only 9.15 % was exchanged in ns274c.

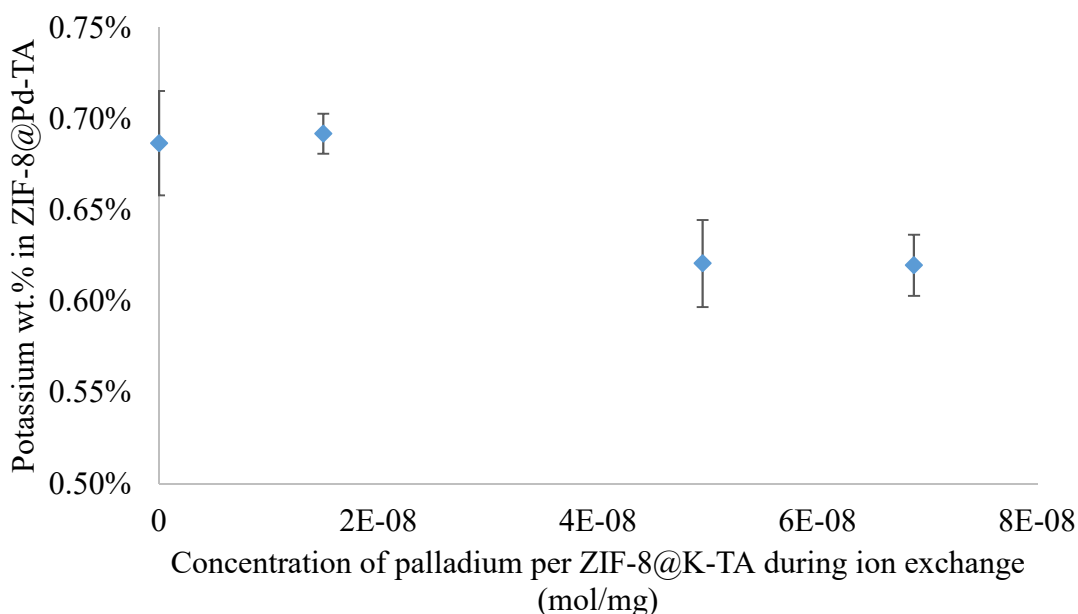


Figure 60 - Potassium wt.% of ZIF-8@Pd-TA as determined by AAS vs concentration of palladium per ZIF-8@K-TA during ion exchange.

Table 11 - Comparison of palladium approximated to be in ZIF-8@Pd-TA with the amount introduced during ion exchange and calculated uptake.

Sample	Pd content		During ion exchange	Uptake
	wt.%	mol Pd / mg ZIF-8@Pd-TA	mol Pd / mg ZIF-8@K-TA	
ns274b	0.07%	6.19E-09	4.95E-08	12.51%
ns274c	0.07%	6.29E-09	6.88E-08	9.15%

It is important to consider the fraction of palladium present during ion exchange that is exchanged into the K-TA layer as it was previously stated in this work that this method uses 100% of the metal involved and this is a benefit of this method over other single metal atom synthesis methods. While this method is shown to not utilise 100% of the metal introduced during ion exchange, it is still true that less metal is wasted using this method than using methods that simply form nanoparticles and then etch them away to achieve pure single metal site materials. This serves to highlight the benefit of implementing extremely low loadings of precious metals such as palladiums when utilizing synthesis methods such as this, as the lower the loading, the higher the efficiency of metal implementation into the final M@HPNC catalyst.

Pd@HPNC

AAS was then used to characterise the amount of palladium in the final Pd@HPNC material. The samples were weighed using a TGA balance, down to an accuracy of 0.01 mg. However, as the beam intensity of the palladium lamp was not very stable the relative standard deviation of the obtained results were too high to be measured. Despite this, the results are as expected, as shown below in Table 12 and Figure 62. Note that ns264p is a HPNC material synthesized directly from ZIF-8@K-TA (Route A of the synthesis method shown in Figure 16), and therefore will contain no palladium. This was included as a control, to confirm the results obtained were accurate.

Table 12 - Results of AAS on various Pd@HPNC samples.

Sample	Mass mg	Mean absorbance	%RSD	Palladium content		
				$\mu\text{g/mL}$	μg	wt. %
ns264p	3.72	-0.0006	HIGH	0.000	0	0.00%
ns266pp_washed	2.03	0.0125	HIGH	1.120	11.2	0.55%
ns269p	3.39	0.0203	10.25	1.805	18.05	0.53%
ns274pb	2.74	0.0272	HIGH	2.397	23.97	0.87%
ns274pc	3.30	0.0395	11.71	3.441	34.41	1.04%

It was found that the samples that featured purely single palladium sites had 0.55 wt.% and 0.53 wt.% palladium content (ns266pp and ns269p respectively). This demonstrates that the results are repeatable. This also allows us to calculate some values of interest. For instance, sample ns266pp (and ns269p) contain approximately one palladium atom for every 1606 carbon atoms (based on the molecular weight of the two materials and assuming the material consists of purely carbon and palladium). This can be investigated further when we investigate the distance between palladium atoms embedded into a graphene lattice. A schematic of how this might look is shown below in Figure 61. The relationship between the amount of carbon atoms present and the number of hexagons wide a square of graphene is, is shown in Equation S1 and Equation S2 in the SI, for an even and odd number of hexagons wide respectively.

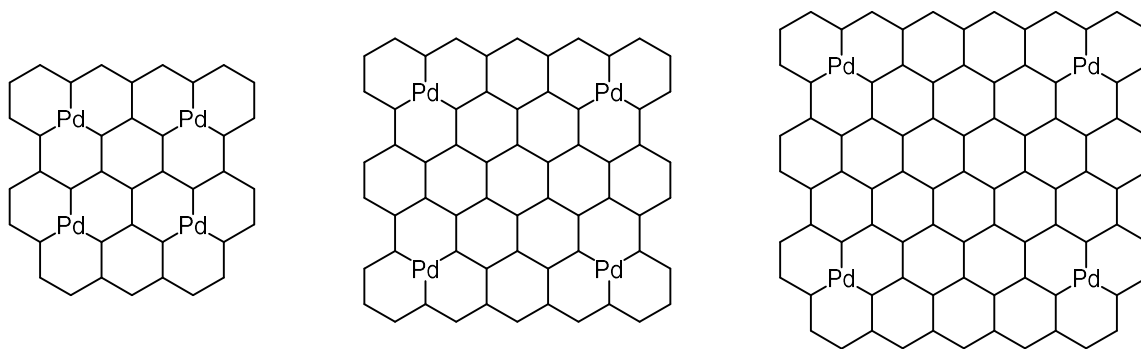


Figure 61 – Schematic illustrating how palladium atoms embedded into a graphene lattice are oriented to give equal distance between each atom, and how the number of carbon atoms present grows as the distance between palladium atoms increases.

If we assume that palladium is evenly dispersed and that bonds lengths are not significantly affected by the presence of palladium, the distance between palladium atoms can be determined as a function of the palladium to carbon ratio. It can be found that at 56 hexagons wide there are 1608.75 carbon atoms for every palladium atom, with a distance of 13.28 nm between palladium atoms. As the HPNC synthesized in this work were determined to have approximately 1606 carbon atoms per palladium atom, it can be assumed that the distance between palladium atoms in these Pd@HPNC has a similar distance between palladium atoms.

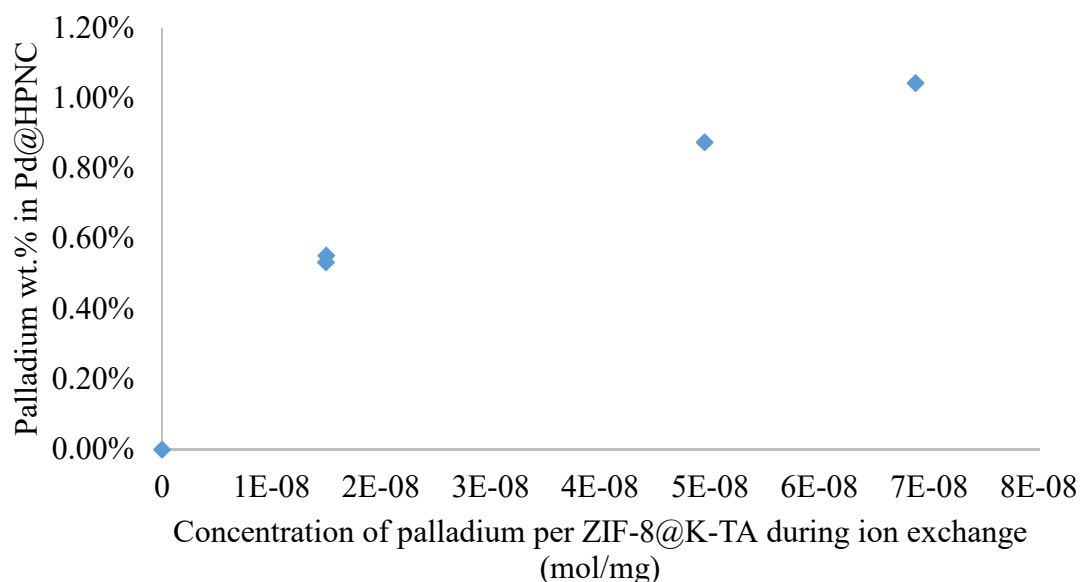


Figure 62 - Palladium wt.% in Pd@HPNC vs concentration of palladium per ZIF-8@K-TA during ion exchange.

Samples that had higher loadings (which resulted in nanoparticle formation), had correspondingly higher palladium content at 0.87 w.t% and 1.04 wt.%. When compared to the concentration of palladium introduced per ZIF-8@K-TA precursor, it can be seen that the percentage of palladium that is exchanged into the precursor decreases as the amount of palladium present increases. This is shown above in Figure 62. This confirms that there is a fundamental limit to the amount of metal that can be introduced to the ZIF@K-TA precursor. This is expected as the K-TA coordination polymer can only have a certain amount of binding sites. It also alludes to the driving mechanism of the ion exchange process. This data suggests that the ion exchange process is driven by a concentration gradient. This means that initially there is little resistance to metal exchanging into the K-TA layer, but as the concentration of the metal in the layer increases there is more resistance to further metal exchanging into the layer. This data agrees with earlier AAS data on ZIF-8@Pd-TA samples and shows increased detail due to the minimized errors. A control sample of HPNC was also measured to palladium content via AAS and was confirmed to have no palladium (as shown by the 0,0 plot point in Figure 62).

Gas Adsorption Results

Sample ns266pp_washed was the first large scale batch of Pd@HPNC synthesized with no indications of nanoparticles (by either TEM or PXRD). The pore size, pore volume, and surface area of ns266pp_washed was tested by gas adsorption. To activate the sample for gas adsorption measurements, the sample was heated to 100°C for 5 hours while under a dynamic vacuum with a turbomolecular pump. The N₂ isotherm of ns266pp_washed was then measured at 77 K, as shown below in Figure 63. From these measurements the BET surface area was calculated as 226.61 m²/g. This is significantly below the values expected, as previous results have been in the range 380 to 930 m²/g^[80].

Density functional theory was then used to calculate the pore size and pore volume of ns266pp_washed from the N₂ isotherm results. The mode pore size was measured to be 10.07 Å. The surface area per pore size is shown in Figure 64 below. These values match the expected pore size and pore size distribution from previous studies. However, the pore volume was calculated to be 0.11 cm³/g, far below the expected values of 0.75 to 1.28 cm³/g^[80].

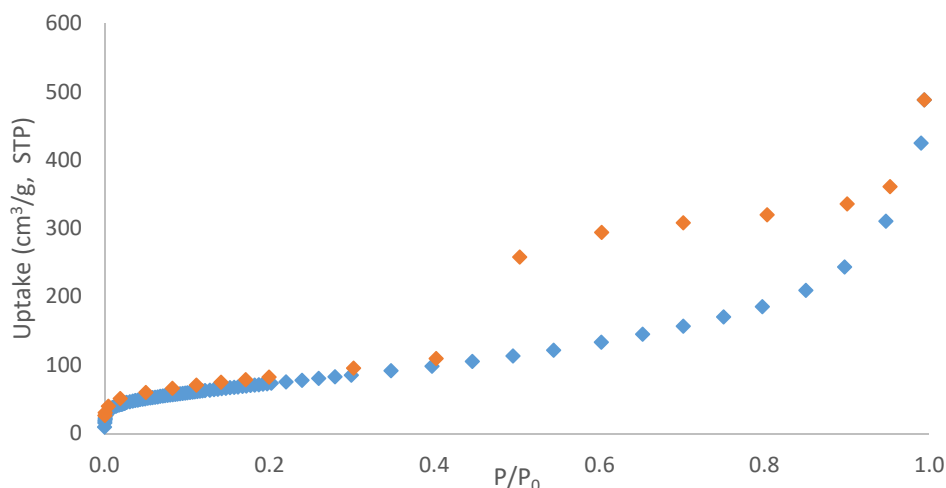


Figure 63 - N₂ adsorption (blue) and desorption (orange) isotherms measured at 77 K of ns266pp_washed.

As previous studies have found that K-TA pyrolyzed in the absence of a ZIF-8 template lacks porosity^[80], it is likely that the porosity of the material is directly related to the thickness of the K-TA before pyrolysis, as thinner carbon structures are less densely packed and are therefore more porous. This work used more K-TA per ZIF-8 during the K-TA coating process than previous studies^[80], resulting in a thicker K-TA layer and therefore a thicker carbon wall of the Pd@HPNC after pyrolysis. This would therefore directly explain the significantly lowered porosity of ns266pp_washed synthesized in this work. It is likely that the inner layers of the walls of the Pd@HPNC synthesized in this work are densely packed like graphite, and only the outer layers feature significant porosity.

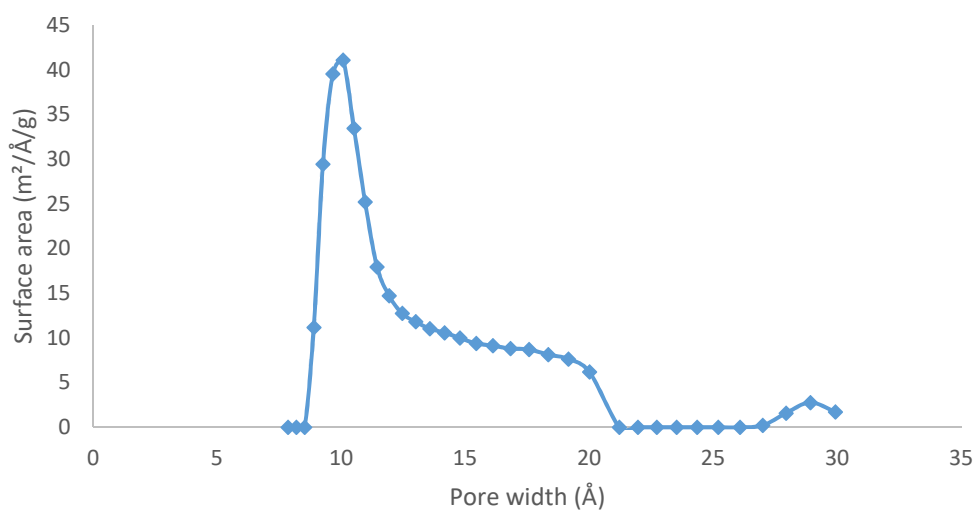


Figure 64 - Surface area per pore size of ns266pp_washed as calculated by density functional theory from gas adsorption results.

These results are concerning in regard to the catalytic performance of the Pd@HPNC synthesized in this work. This is because the palladium that is embedded in the carbon walls are likely distributed evenly throughout the wall. The thickness of the walls is estimated by TEM to be ~10 nm thick, which corresponds to ~30 layers of carbon, assuming the distance between layers is similar to that of bulk graphite^[72]. If, for example, the inner 15 layers are densely packed, the palladium sites present in these layers will be inaccessible to reactants during catalysis, even if the reactant is below 10 Å in size and is able to penetrate the pores of the material. In this example, this would result in half the catalytic sites of the material becoming completely inactive as catalytic sites. This is worthy of note and should be investigated further in the future.

Chapter 4 Catalysis

Introduction

Catalysis is a phenomenon by which a material, named a catalyst, lowers the energy required for a reaction. As discussed earlier, catalysts can vary widely. This work focuses on the catalytic performance of the single site palladium catalyst supported on carbon capsules (Pd@HPNC) that was synthesized as described in earlier chapters. The performance of a catalyst is measured by the consumption and selectivity of the catalysed reaction. The consumption of a reactant is an indicator of the overall reactivity of a catalyst, while the selectivity measures how well the catalyst increases the reactivity of one reaction over another. Both are equally important metrics.

The reactions chosen to screen the catalytic performance of the synthesized Pd@HPNC catalyst are the conversion of furfural to cyclopentanone, the hydrogenation of quinoline and the Suzuki coupling reaction. These reactions were chosen for their historical successes with supported palladium catalysts and their significance.

Selectivity

Catalysts are often selective towards one product over another, as they catalyse some reactions better than others. For example, the hydroformylation of styrene can be catalysed by supported rhodium complexed dendrons with high selectivity as shown in Figure 65^[97]. The solvent and support used dramatically affect the ratio of products A:B, ranging from 1:2.2 to 100:0. Selectivity is extremely important in catalysis as it dramatically simplifies the process of obtaining desired products. Without selective catalysts, separation of the products is required, which is often a time and energy extensive process. Also, any reactants that could otherwise have formed the desired product has now been converted into an undesirable by-product, which may be useless. Therefore, selectivity is a key performance indicator for catalysts.

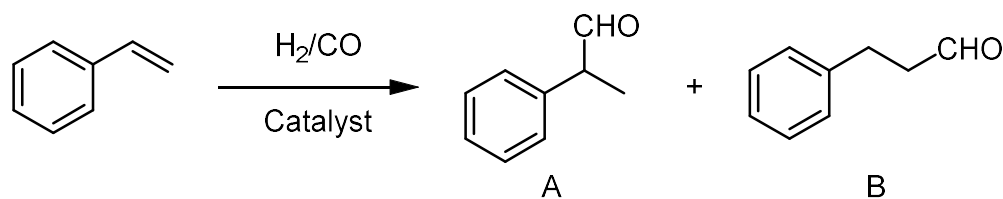


Figure 65 - Reaction scheme for the catalysed hydroformylation of styrene^[97].

Consumption

Often confused with conversion, consumption is the measure of the amount of reactant converted into any product during a reaction. Conversely, conversion is the amount of reactant converted into the desired product. Consumption is a better measure of the catalysts overall catalytic ability, but this is not to say that a higher consumption makes a better catalyst. Conversion takes into account the selectivity of the catalyst, and therefore a higher conversion would indicate a better catalyst. However, when using the selectivity metric it is superfluous to also use the conversion metric and it is therefore better to use consumption as this provides a better overview of the catalytic performance.

Catalyst Properties

Dispersion

Although the Pd@HPNC catalyst produced in this work is extremely light and disperses well in most solvents, there is a limit to how much catalyst can be dispersed into a set amount of solvent. While catalyst can be added to the solvent past this dispersion limit, and be present as solid aggregated material, this material often cakes on the wall of the flask and does not have enough contact with the reaction mixture. Therefore, it is not participating as a catalytic site as it otherwise would. This creates an issue, as adding more catalyst past this point lowers the efficiency of the catalyst. This could be solved by adding solvent, but this lowers the concentration of the reactants and therefore this also lowers reaction kinetics. This is why the ratio of reactant to palladium is extremely small in the following reactions. The Pd@HPNC catalyst ns266p_washed has an extremely low palladium loading of 0.55 wt.%, and it is impossible to load enough of the catalyst into the reaction mixture to achieve a high palladium to reactant ratio without heavily diluting the reactants. In literature, other catalysis reactions load 0.015 mmol of the catalytic species per 5 mL of solvent^[98]. Comparatively, if this is attempted with the catalyst synthesized in this work it is necessary to load 290 mg of

ns266pp_washed into 5 mL of solvent. This is impractical as this amount of solvent will only hold ~10 mg of ns266pp_washed before caking on the walls becomes prominent.

Access to Active Sites

As discussed earlier, reactants ability to access the catalytic palladium sites of Pd@HPNC is likely not high. This is due to the significant thickness of the carbon walls of the Pd@HPNC, as well as the lack of porosity compared to previous work. This means that many of the palladium sites contained in Pd@HPNC may be unavailable to reactants and therefore catalytically inactive. However, although the Pd@HPNC synthesized in this work is less porous than expected, the material still contains a significant number of micro pores sized at 10 Å, and reactants below this size will still be able to access these pores. It is worth noting that reaction rates around these pores will be affected by mass transfer of reactants and products in and out of the pores. These reaction rates will therefore be significantly lower than reaction rates of catalytic sites on the outer layer of the Pd@HPNC.

Conversion of Furfural to Cyclopentanone

Conversion of biomass-derived materials into useful fine chemicals is an important aspect of creating a sustainable future. This is becoming increasingly important due to the decline of available fossil fuels and the abundance of biomass^[99]. Catalysts for these reactions will be paramount to the economic feasibility of using these reactions in an industrial setting. The conversion of furfural to cyclopentanone was chosen as a screening reaction of the catalytic activity of the catalyst synthesized in this work. This is because furfural is one of the major biomass platform chemicals and catalysts that perform well in this reaction may be useful in creating a sustainable economy in the future.

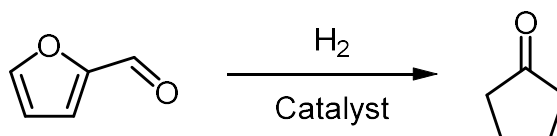


Figure 66 - Reaction scheme of the conversion of furfural to cyclopentanone.

The reaction was first tested using a commercial platinum catalyst on carbon (10 wt.%) (see “ns198” in the SI for full experimental details). The commercial catalyst used was, as a noble metal supported on carbon, expected to have similar properties to the Pd@HPNC catalyst synthesized in this work. Although cyclopentanone was not formed, some consumption of

furfural did take place. This means that the commercial catalyst was catalytically active but was not selective for this reaction. The reaction was then tested with the Pd@HPNC synthesized in this work (see “ns275” in the SI for full experimental details). No furfural was consumed. This shows that the Pd@HPNC catalyst developed in this work is not catalytically active for this reaction in this solvent. Due to time constraints, no further work was done on the conversion of furfural to cyclopentanone.

Hydrogenation of Quinoline

Hydrogenation is a reaction in which a substance is chemically converted by treating with hydrogen. This is done with H₂ gas (or formic acid^[100-101]) in the presence of a cobalt^[21, 100-103], nickel^[32, 104], palladium^[13, 105-106] or platinum^[24] catalyst. This generally results in reducing or saturating organic compounds. The hydrogenation of quinoline was chosen as a screening reaction as it has been successful with previous palladium catalysts supported on carbon^[105].

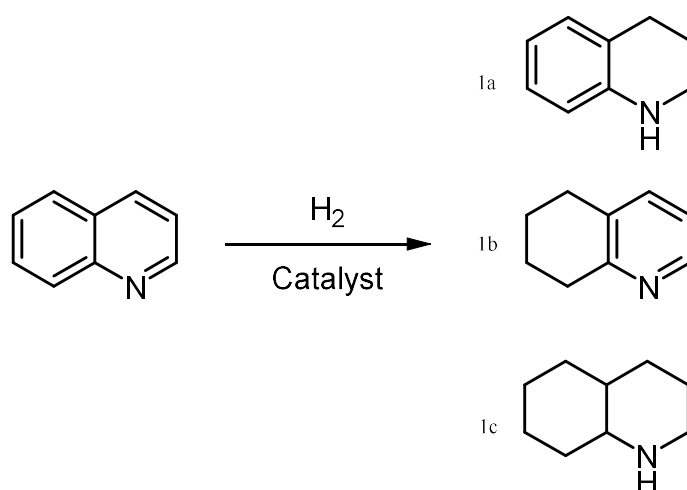


Figure 67 - Reaction scheme of the hydrogenation of quinoline.

The hydrogenation of quinoline was trialled using a commercial palladium on carbon (10 wt.%) catalyst and showed complete conversion by thin-layer chromatography (see Figure S92 in the SI). At 20°C higher the Pd@HPNC catalyst synthesized in this work showed no catalytic activity as no products were formed (measured by GC, see Figure S93 in the SI). Therefore, due to time constraints, no more work was done on this reaction.

Suzuki-Miyaura Coupling

Suzuki-Miyaura coupling (or Suzuki coupling) is a reaction first published in 1979 by Akira Suzuki^[107-108] that typically requires a zerovalent palladium catalyst. This is often produced in-situ from a Pd^{2+} precursor. The reaction has become a staple of organic chemistry due to its ability to create conjugates with C-C bonds between complex organic molecules. Suzuki coupling was chosen as a test reaction for the synthesized single palladium atom (Pd@HPNC) catalyst due to the reactions importance^[109] and the previous success of similar catalysts in this reaction^[93]. A similar catalyst to the synthesized material in this work has proven to outperform even homogeneous palladium catalysts in the Suzuki coupling reaction^[8].

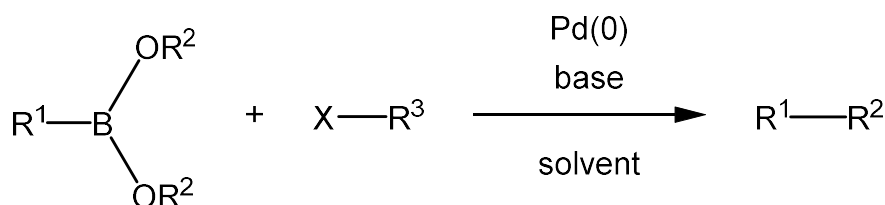


Figure 68 - General reaction scheme for the Suzuki coupling reaction, where R^1 = aryl, alkene (vinyl), alkyne), R^2 = H (boronic acid), alkyl (boronic ester), R^3 = aryl, alkene (vinyl), alkyne, X = halide (I, Br, Cl^*). *Cl requires special conditions for activation.

The mechanism by which palladium bound to a support catalyses cross-coupling reactions is also a topic for consideration. Some palladium systems have shown that the palladium is pulled into solution for the reaction cycle and deposited back on the support in a form that will make it active again for another catalytic cycle^[91, 110]. However, Chen et al. have shown that their catalyst with single palladium atoms supported on carbon cannot catalyse reactions in this way using a continuous flow reaction setup^[8]. This means that no leaching of the palladium should occur, and therefore the product should be contaminant free and the catalyst should have high recyclability. However, in this case palladium was bound to a heptazine-based vacancy (see Figure 9 on page 8). It is unlikely that the HPNC synthesized in this work will feature such large vacancies for palladium to integrate into the graphene layer, and this may affect the mechanism by which the palladium sites interact with reactants.

The Pd@HPNC catalyst synthesized in this work was found to catalyse the Suzuki coupling reaction. Iodobenzene and 4-boronobenzoic acid were coupled to form [1,1'-biphenyl]-4-carboxylic acid (referred to from now on as BPC) in Figure 69.

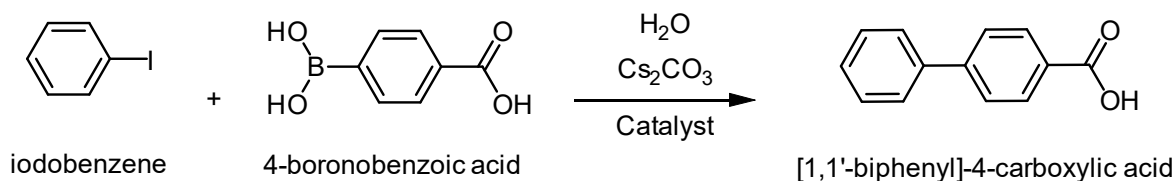


Figure 69 - Reaction scheme of the Suzuki coupling of iodobenzene and 4-boronobenzoic acid.

The initial screening experiment of the coupling of iodobenzene and 4-boronobenzoic acid in the presence of Cs_2CO_3 in a 10:1 distilled water to dioxane mixture was successful, as a significant amount of BPC crystallised out of the solution after heating to 90°C for 24 hours in a microwave and subsequent cooling. These conditions were accidental (due to a misunderstanding of the solubility of 4-boronobenzoic acid) and have no literature to support them, but were pursued further due to the success of the reaction. The NMR of the solid formed is shown below in Figure 70. Further details of this reaction can be found under “ns279” in the SI.

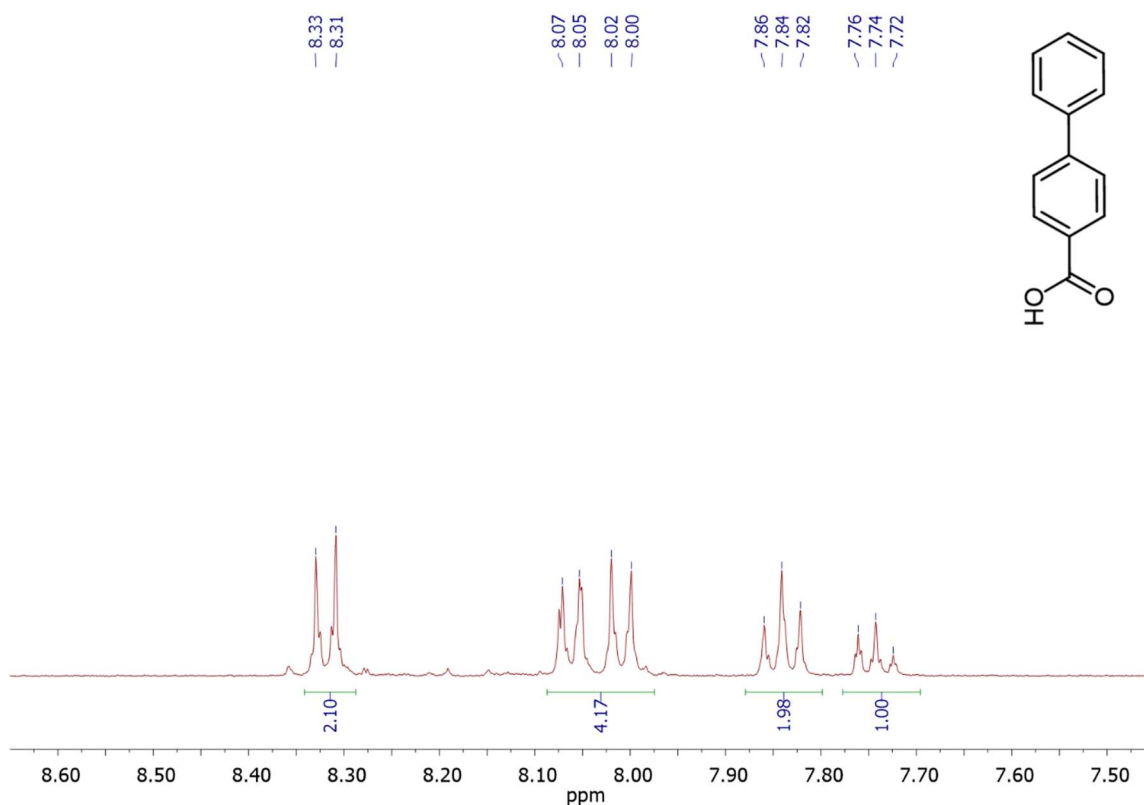


Figure 70 - ^1H NMR spectrum of white precipitate formed in the coupling of iodobenzene and 4-boronobenzoic acid (ns279) dissolved in DMSO-d_6 .

There are two ways that this catalysis can occur. The reactant can either be catalysed by palladium on the surface of the HPNC support or it can be catalysed by palladium that has

been drawn into the solution. The migration of palladium from the HPNC support material is referred to as leaching. If the palladium leaches into the solvent this will cause a significant drop in the recyclability of the catalyst as well as cause high palladium contamination in the reaction product. These are both extremely undesirable, and therefore this mechanism must be determined.

This was initially tested by mixing the Pd@HPNC catalyst, solvents and Cs_2CO_3 and exposing this solution to the reaction conditions (microwaved to 90°C in a microwave for 24 hours). After this, the solution was centrifuged and subsequently filtered to remove the Pd@HPNC catalyst. The solution was allocated to a fresh reaction vessel and the reactants were added. This reaction mixture was then again exposed to the reaction conditions. Surprisingly, a similar amount of precipitate formed as in this initial screening. This was confirmed to be BPC by HNMR. Further details of this reaction can be found under “ns281” in the SI.

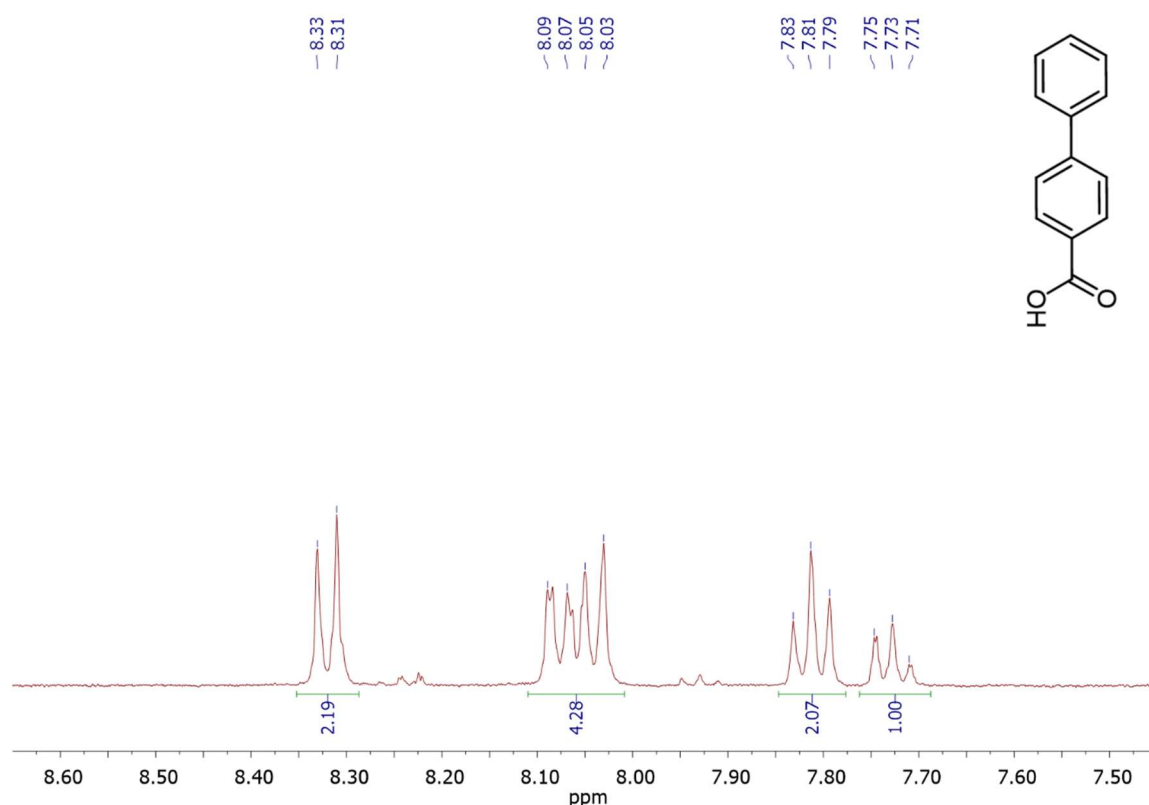


Figure 71 - HNMR spectrum of white precipitate formed in the control reaction of the coupling of iodobenzene and 4-boronobenzoic acid (ns281) dissolved in DMSO-d_6 .

This is an unfortunate result and is concerning, but may not be due to the leaching of palladium into the solution. Other potential causes include palladium contamination in the glassware and that the Pd@HPNC catalyst may not have been entirely filtered out. As palladium is known to contaminate glassware, it was attempted to avoid this issue by using a new vessel during control reactions. However, as this glassware had been used by other lab members before it is not impossible that palladium had been used in the vessel previously. However, the other issue mentioned is far more concerning. The diameter of the Pd@HPNC synthesized in this work was measured roughly by TEM to be ~70 nm. Most filters cannot filter out particulates this small, and the ones that can, may also trap any free palladium in solution and render the experiment meaningless. Therefore, an experiment was designed that would allow for these variables and still test for leaching of palladium.

Instead of simply determining whether the reaction occurs or not, the reaction rate over time is useful as it allows the detection of leaching of palladium into solution while avoiding the issues described earlier. This is because, if a reaction rate over time is determined, the experimental conditions can be replicated while removing the catalyst part way through the reaction. If the reaction continues at the rate it did when the catalyst was still present then leaching must have occurred, but if the reaction rate drops significantly then palladium is not leaching into the solution. This allows for a small portion of the Pd@HPNC catalyst to break through the filter as the reaction rate is proportional to the amount of catalytic sites present.

A reaction rate over time was therefore desired. To do this an initial sample was taken, and further additional samples were taken after 2, 5, 11, 21, 25 and 31 hours at 90°C. The resulting HNMRs of this process are shown below in Figure 72. Unfortunately, as the reactants formed some undesired by-products over time under the reaction conditions it was impossible to simply determine the conversion over time by the relative integrals of the reactant and product HNMR peaks. It also highlighted the issue of solubility in this reaction. As iodobenzene is not soluble in water, no samples taken from the bulk mixture contain iodobenzene and therefore its consumption cannot be measured. This is extremely important here as iodobenzene is the limiting reagent and consumption cannot be measured without measuring the presence of iodobenzene. This would not be an issue if by-products did not form, as the consumption of iodobenzene could simply be determined using a standard and measuring the relative consumption of 4-boronobenzoic acid. Further details

of this reaction and individual HNMR spectra of each sample can be found under “ns289” in the SI.

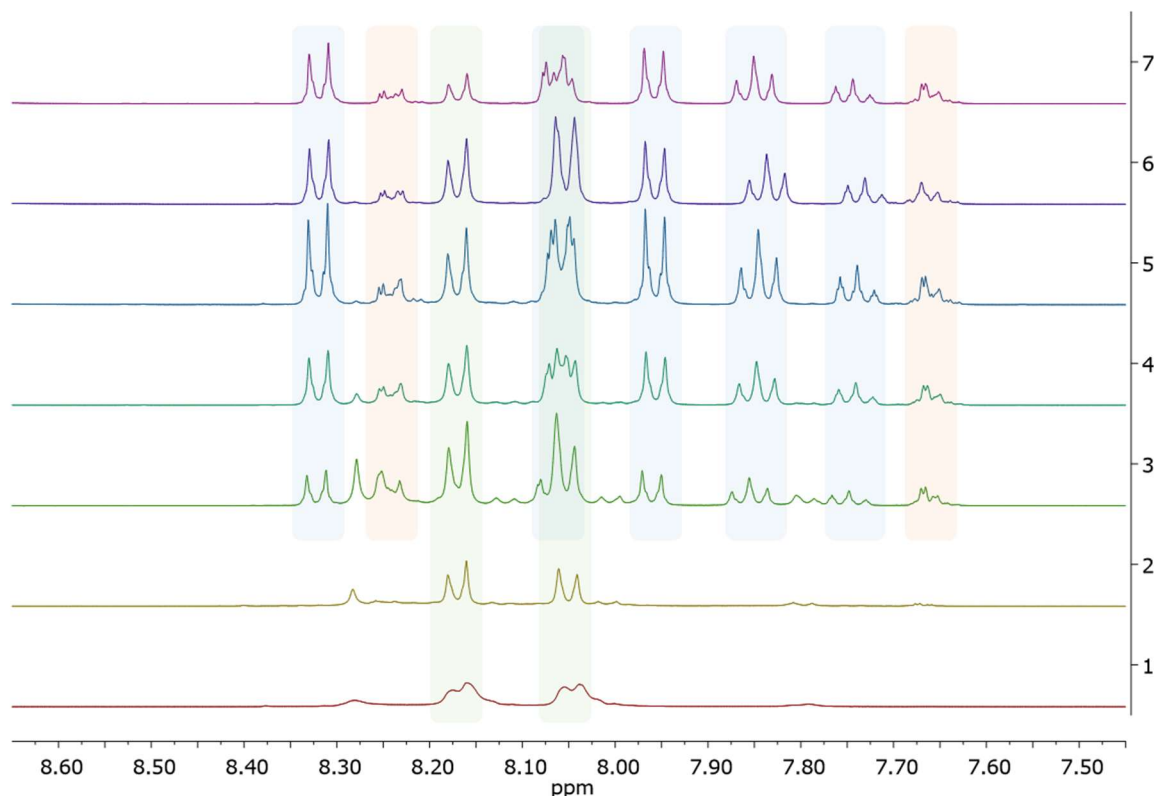


Figure 72 - HNMR spectra of the Suzuki coupling of iodobenzene and 4-boronobenzoic acid to form BPC over time (ns289). Samples 1 to 7 were taken after 0, 2, 5, 11, 21, 25 and 31 hours at 90°C respectively (displayed in ascending order). 4-boronobenzoic acid peaks are shaded green, BPC peaks blue and by-product peaks red.

Further, the product of the Suzuki coupling of iodobenzene and 4-boronobenzoic acid to form BPC over time (ns289) was isolated by hot filtration and subsequent crystallisation in the reaction mixture. The product was washed two times with deionised water and dried under vacuum. The yield was measured at 31 mg from 18 mL of solution. The reaction was started with 33 mL but as samples had been taken over time the volume had dropped significantly. The true yield can therefore be estimated to be 56.8 mg. The product was confirmed to be BPC by HNMR, as shown below in Figure 73. This allows us to calculate a yield of 19.57% after 31 hours. Therefore the TON of the reaction, defined here as the amount of product formed per catalytic site, was calculated as 189.3. Metrics such as turn over frequency (TOF, equal to TON/time), which incorporate time, are not useful here as it can be seen from Figure 72 above that, after an initial delay, the majority of the reaction

happens within a few hours before tapering off. This is because the concentration of reactants in the solution drops, although, the mass transfer of product species out of the Pd@HPNC catalyst pores may also play a role. The initial delay seen in the reaction is found throughout all experiments performed with this reaction, and is likely due to the mass transfer of iodobenzene to the catalytic site due to its poor solubility in water.

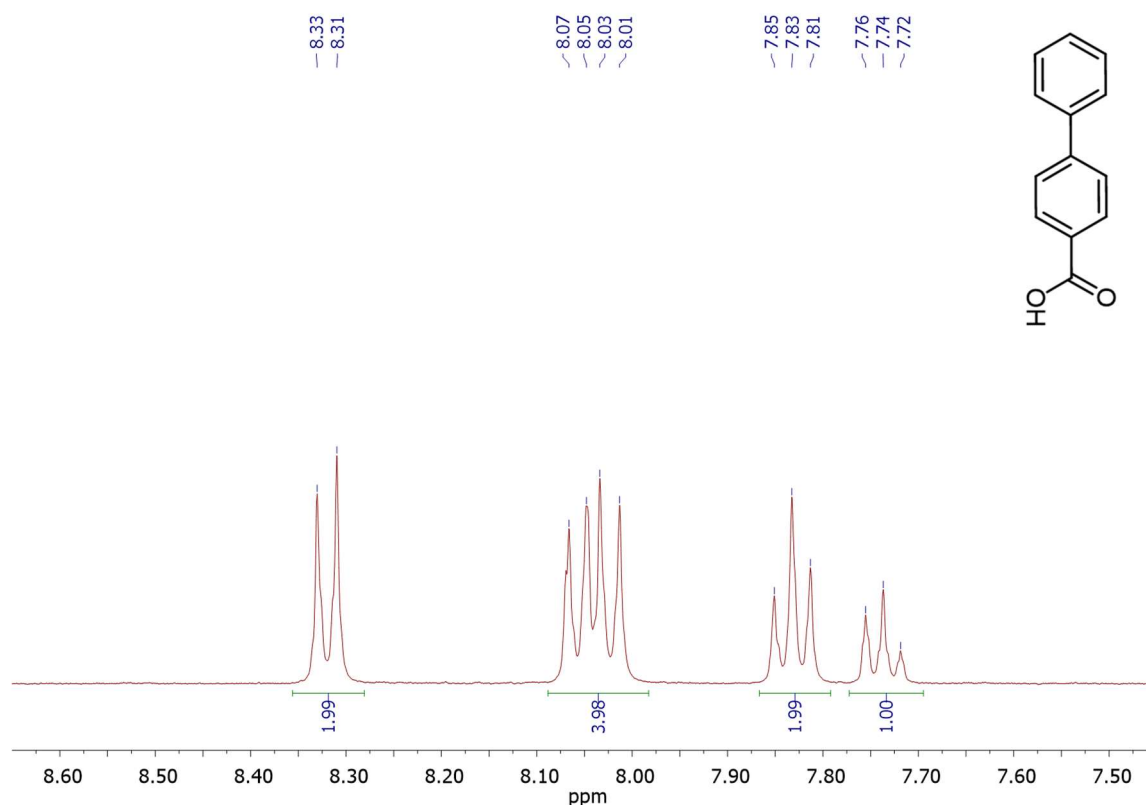


Figure 73 - HNMR spectrum of the isolated white precipitate formed after 31 hours in the coupling of iodobenzene and 4-boronobenzoic acid (ns281) dissolved in DMSO- d_6 .

Control reactions were performed to confirm that by-product formation occurred without the presence of the Pd@HPNC catalyst (i.e. the palladium was not catalysing some unknown reaction). The resulting HNMR spectra of samples taken from this reaction over time are shown below in Figure 74. It can be seen that the 4-boronobenzoic acid is consumed, no desired product forms and only the by-product HNMR peaks seen earlier in Figure 72 are formed. Further details of this reaction and individual HNMR spectra of each sample can be found under “ns290” in the SI.

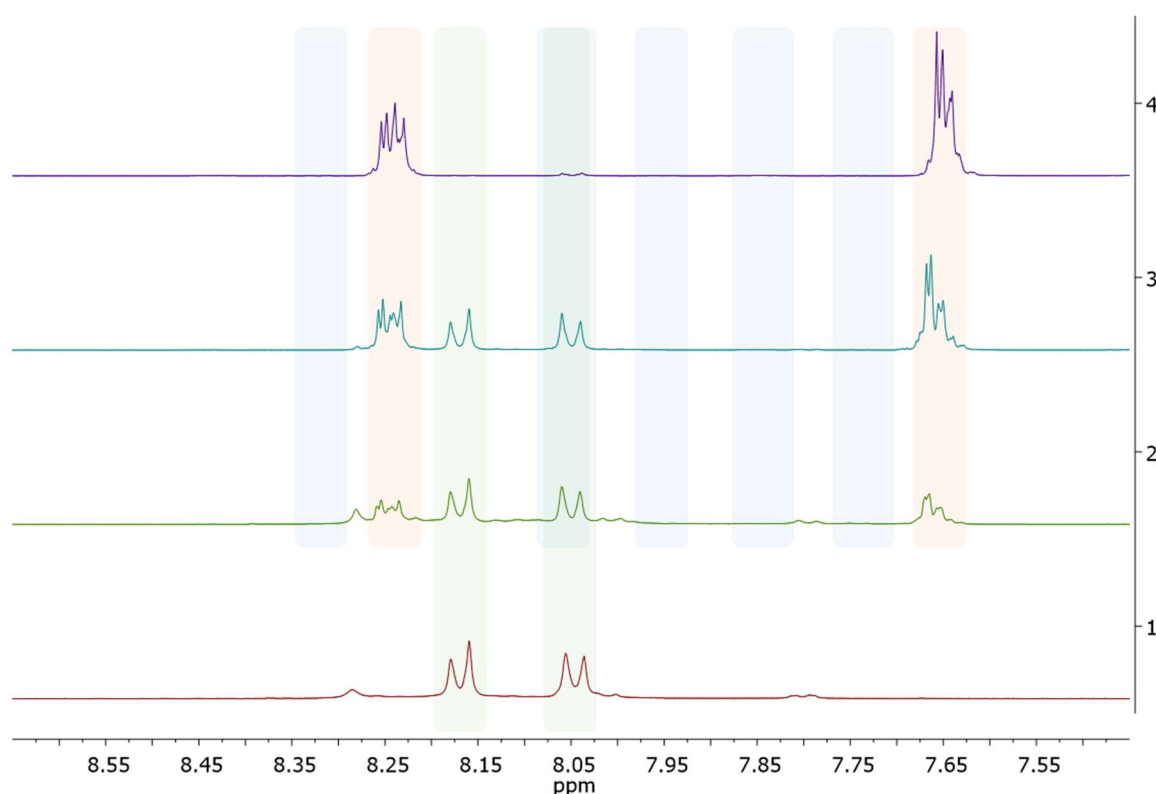


Figure 74 - ^1H NMR spectra of samples taken from a control reaction with no catalyst (ns290), initially and after 2, 5 and 11 hours at 90°C (displayed in ascending order). 4-boronobenzoic acid peaks are shaded green, BPC peaks blue and by-product peaks red.

A control reaction was also performed to ensure that palladium was the active site on the Pd@HPNC. This was performed by substituting the Pd@HPNC used previously for HPNC containing no palladium (as confirmed by AAS in Chapter 3). The resulting ^1H NMR spectra of samples taken from this reaction over time is shown in Figure 75. It can be seen that the 4-boronobenzoic acid is consumed, no desired product forms, and only the by-product ^1H NMR peaks seen earlier in Figure 72 are formed. Further details of this reaction and individual ^1H NMR spectra of each sample can be found under “ns292” in the SI.

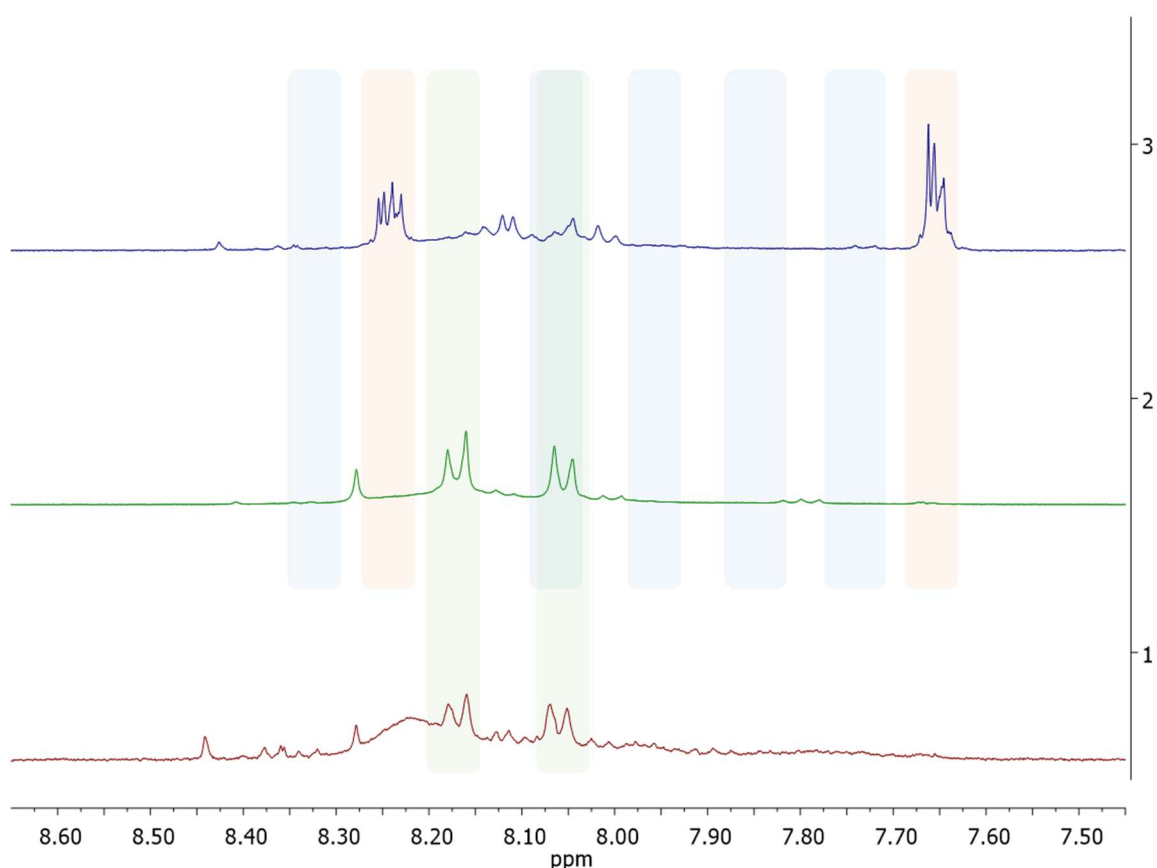


Figure 75 - ^1H NMR spectra of samples taken from a control reaction with HPNC used in place of Pd@HPNC (ns292), initially and after 3 and 9 hours at 90°C (displayed in ascending order). 4-boronobenzoic acid peaks are shaded green, BPC peaks blue and by-product peaks red.

As a reasonable understanding of the reaction rate of this reaction had been roughly determined (as shown above in Figure 72) a control experiment to test for the leaching of palladium into the solvent by measuring the reaction rate over time was attempted. The reaction was performed as usual with the Pd@HPNC catalyst for 5 hours until product formed, and then the catalyst was filtered off. The reaction was then continued for 7 hours at 90°C , taking samples immediately after filtration, and at 2, 5 and 7 hours. A nitromethane standard was used to allow quantitative measurements. The relaxation time of the ^1H NMR was also extended to allow for the longer time that aromatic species need to relax to their normal state after each scan. This allows for more accurate quantitative comparisons between aromatic species and non-aromatic species. It was found that after filtration the concentration of BPC did not increase. This is shown below in Figure 76. It was also found that the ^1H NMR peaks corresponding to 4-boronobenzoic acid decreased over time and this resulted in increasing by-product ^1H NMR peaks, as identified by the control reactions. This

suggests that after filtration and removal of the Pd@HPNC catalyst, the Suzuki coupling reaction does stop. This would mean that the Pd@HPNC catalyst synthesized in this work does not leach palladium into the solvent during the reaction. Further details of this reaction and individual HNMR spectra of each sample can be found under “ns295” in the SI.

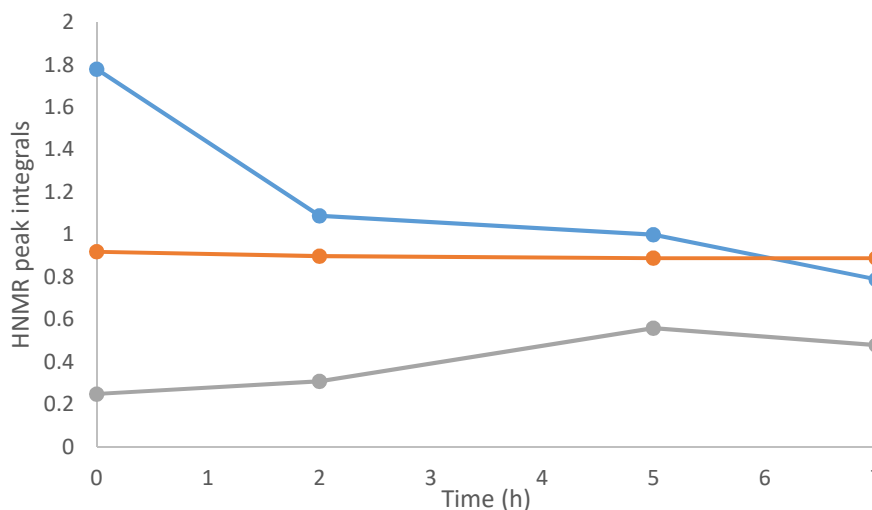


Figure 76 - Integral values of the HNMR peaks of 4-boronobenzoic acid (blue), BPC (orange) and a by-product peak at 7.67 ppm (grey) over time after filtration of the catalyst, in a control reaction of the coupling of iodobenzene and 4-boronobenzoic acid (ns295). Integral values were set to one on the standard peak that each sample was spiked with.

Ideally, testing the catalytic activity of the Pd@HPNC synthesized in this work for the Suzuki reaction would be performed by catalysing a reaction in which both reactants and the product were very soluble in the solvent used in the reaction, and neither the reactants or products would degrade or undergo side-reactions. However, due to time constraints and the availability of chemicals, the coupling of iodobenzene and 4-boronobenzoic acid in a 10:1 distilled water to dioxane mixture was the only reaction found to show increased reactivity when exposed to the Pd@HPNC synthesized in this work.

Unfortunately, although much effort was devoted to scaling up the synthesis process and producing large scale batches of Pd@HPNC catalyst, eventually the catalyst was completely consumed. The Pd@HPNC catalyst was not recycled and re-tested for catalytic activity because the performance of the catalyst may change over time. This an important experiment for the future but during initial testing of a catalyst it is important to ensure that the catalyst is as consistent as possible between reactions so that metrics such as TON can be calculated first.

Chapter 5 Conclusions and Future work

This work has investigated the implications of the original method on scalability and reproducibility and had modified the method to better address these issues. This work then moved to investigate the loading of palladium required during ion exchange to produce a Pd@HPNC catalyst that does not contain palladium nanoparticles and therefore features only single palladium sites. Finally, the catalytic activity of the produced catalyst was investigated and was found to be active for the Suzuki-Miyaura Coupling reaction. Although this work is very promising and has shown excellent results, due to time constraints many key experiments will be left for future work. This includes further characterization and investigation of the catalytic performance of the synthesized Pd@HPNC catalyst. There are also a plethora of variables in the synthesis method that have not been fully investigated. These could be tuned to control the properties of the produced Pd@HPNC catalyst.

Method Variables Worth Investigation

Coordination Polymer

This work focused on coating K-TA on ZIF-8 to create a precursor for pyrolysis that would result in a hollow carbon capsule. Metals are introduced to the precursor before pyrolysis and are impregnated in the coordination polymer. The K-TA coordination polymer therefore provides a site for the metal to be impregnated as well as forming the outer layer of carbon in the final M@HPNC catalyst. Other coordination polymers could achieve similar results. K-TA was used due to previous success with the polymer^[63, 68, 80, 111-112] and its low price. A potential disadvantage in using K-TA is the oxygen present in tannic acid that is released during pyrolysis. This may have been the cause of oxides forming during trials for impregnating cobalt and nickel. A coordination polymer that is free of oxygen would therefore provide an advantage. Other coordination polymers that utilise potassium are a promising alternative, as K-TA has shown to be able to exchange a diverse array of metals into the formed polymer (although this may be due to the many potential binding sites of tannic acid). Although not many coordination polymers are entirely oxygen-free, there are promising alternatives in the literature^[113].

MOF Scaffold

ZIF-8 was used as a scaffold for the coordination polymer as it is cheap to synthesize, well researched, easily size-controlled, has zinc centres that will evaporate at 900°C and is a good nitrogen source during pyrolysis. Many other zinc based MOFs could also be used that may provide better results. This work has shown that the size of the carbon capsules is directly related to the size of the ZIF-8 crystals used as a scaffold. It would therefore be of interest to see the size limits that the M@HPNC catalyst can be synthesized, as upon reaching a large enough size the capsule is likely to contort and eventually collapse.

Coating Process

Coordination layer thickness is also likely directly related to the thickness of the walls of the carbon capsule and this may affect the availability of metal atoms to act as catalytic sites. This is because the thicker the carbon layer, the more likely that an embedded metal is not exposed to solvent (and therefore reactants) but is instead covered by surrounding carbon layers. This effect can be mitigated somewhat by the porosity of the carbon material, however it has been concluded that increasing thickness of the carbon layer also results in decreasing porosity of the carbon material. Ideally, the carbon capsule would consist of a single graphene layer, as this would allow all metal atoms to act as catalytic sites. This would likely increase catalytic activity significantly, allowing for substantial increases in metrics such as consumption, turnover number (TON) and turnover frequency (TOF).

It is worth noting that all of Yang's published work^[68, 80, 111-112] using this synthesis method has used a slightly different method as only use 3 mL of K-TA solution is used per 200 mg of ZIF-8 rather than 5 mL. This was not known when the project was started as an unpublished manuscript^[63] was used as a starting method. This change in ratio between the ZIF-8 surface area and the amount of K-TA available likely results in a thinner K-TA coating, and therefore a thinner carbon layer after pyrolysis. This is likely also a much simpler method of solving many of the issues found with the K-TA coating process. This is because if the K-TA to ZIF-8 ratio is controlled, the green by-product that occurs as K-TA forms larger structures will not occur as the amount of K-TA is limited. Therefore the time that ZIF-8 and K-TA are left mixing no longer needs to be measured carefully, as once a thin layer of K-TA has formed on the ZIF-8 surface (this should take no longer than a minute^[69]) there is no more K-TA precursor left in the solution. At this point, the only warrantable

concerns are the self-nucleation of K-TA and the etching of ZIF-8. It has been shown that pH levels higher than 8.0 actually decreases the rate of K-TA formation, although this does promote the formation of the green by-product (shown in Figure 25 and Figure 26 of the SI). Therefore, it makes sense for future work to investigate the use of K-TA synthesized at pH 8.2-8.4 on ZIF-8@K-TA formation under varying ZIF-8 to K-TA ratios. Ideally, this process will become both facile and reactant-limited.

Ion Exchange

To confirm the relationship between metal concentration per ZIF-8@K-TA introduced during the ion exchange process and the resulting concentration of palladium contained in the product ZIF-8@M-TA, it would be beneficial to perform a systematic study on this process alone. It would be of interest to control, and perhaps vary, temperature during this study, as it is unknown if this plays a role in the uptake of metal into the coordination polymer layer.

Metals

One of the major benefits of the method used in this work is the ability to introduce seemingly any metal into the coordination layer, and therefore into the produced M@HPNC catalyst. There are many other metals to screen to confirm this, but future work using this method will likely investigate further into this and test the catalytic abilities of each metal in the environment provided by the hollow carbon capsule support. This may take some time however, as the method used in this work requires a metal salt that is stable in a solvent in which the precursor is also stable. Metals such as platinum do not have many salts available as of yet but these may become available in the future.

Pyrolysis

The formation of nanoparticles during pyrolysis has been investigated by varying concentration of metal per ZIF-8@K-TA. Other factors that influence nanoparticle formation is nitrogen availability and pyrolysis temperature. Pyrolysis temperature has already been shown (both in this work and in the literature^[96]) to influence nanoparticle formation (and lack thereof). It would therefore be beneficial to understand how high the pyrolysis temperature can reach before the carbon capsule M@HPNC catalyst is affected,

and then find the concentration of metal below which only single metal atoms form at this temperature. It is likely that the concentration of single metal atom sites in the final M@HPNC catalyst can be increased significantly.

The amounts of graphitic nitrogen, pyridinic nitrogen, and pyrrolic nitrogen present in nitrogen doped carbon resulting from pyrolysis changes significantly with pyrolysis temperature^[114]. This may allow more binding sites for metals to bind to, allowing for atomically dispersed metal sites at higher loadings. The change in nitrogen states will also significantly alter the chemical and electronic properties of the material accordingly, which may affect the catalytic properties of the material^[33, 41]. This is worth investigation. Firstly, the influence of additional nitrogen added during pyrolysis to nanoparticle formation and the catalytic performance of the product would be of interest. Further, a comprehensive study varying the nitrogen availability and temperature during pyrolysis would allow optimisation of both the metal loading and catalytic performance of the produced material.

Aggregation

As materials are made smaller and smaller, it becomes exponentially more difficult to keep their surface energy low and prevent them from aggregating. This is a large part of why this work is necessary, as nanoparticles form to lower the surface energy of the metal atoms. An unexpected occurrence of this is that the aggregation of ZIF-8 crystals during K-TA coating means that these aggregates are carried through until the final M@HPNC catalyst, as the K-TA coating holds the aggregate in place (or worse, the aggregate breaks and broken capsules are formed). It therefore would be best if the ZIF-8 did not aggregate like this during the coating step. Future work could consider how to better disperse ZIF-8 in solution (perhaps diluting the solution would be enough, though this may promote free-floating K-TA formation) during the coating process.

Characterization

High-Resolution Transmission Electron Microscopy

Samples have already been sent away for high-resolution transmission spectroscopy. These images will provide valuable insight into the quality of the carbon capsules and may provide a more accurate visual estimation of the carbon wall thickness than was possible on the TEM available during this work.

High-Angle Annular Dark-Field Scanning Transmission Electron Microscopy

High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) of the M@HPNC catalyst synthesized in this project was not possible during this project due to time constraints. However, this may be pursued in the future, as it is an invaluable tool in catalyst characterisation – especially in identifying single metal atom sites. Equipped with an EDXS unit, HAADF-STEM is able to generate images that identify individual metal atom sites and can show their dispersion throughout a material. This would be extremely beneficial to understanding the nature of the M@HPNC catalyst synthesized in this work.

X-ray Photoelectron Spectroscopy

Samples have also been sent away for X-ray photoelectron spectroscopy (XPS), as this will allow confirmation that there are no palladium nanoparticles in the synthesized M@HPNC catalyst (as well as the confirmation of nanoparticles in samples with higher metal concentration). This is because XPS will show the valence state of the palladium present in the sample. If there is palladium present in the zerovalent state, this will provide evidence that nanoparticles are present (and *vice versa*).

Extended X-ray Absorption Fine Structure

Extended X-ray absorption fine structure (EXAFS) is another important characterisation technique that will ideally be used to characterise the synthesized M@HPNC catalysts in the future. EXAFS allows the identification of the bond types present in the material, such as Pd-Pd, Pd-N and Pd-C. This would be extremely beneficial, as not only does the existence of Pd-Pd bonds give undeniable evidence for the existence of nanoparticles (or lack thereof), the amount of Pd-N and Pd-C bonds present provides great insight into the need for nitrogen as a binding mechanism. A study could even be done by varying the nitrogen present during pyrolysis, confirming the change in binding sites with EXAFS and then experimenting to see if the metal is better bound to the support and less likely to leech or be poisoned.

In-Situ TEM During Pyrolysis

Interestingly, Yang found that the K-TA layer begins carbonisation at 250°C, while the inner ZIF-8 does not begin decomposing until 550°C^[80]. This matches thermogravimetric analysis data obtained during the STA of ZIF-8@Pd-TA (shown in Figure S68 of SI). This is

interesting to consider as the state of the palladium is unknown during the pyrolysis process. The palladium must no longer be bound to the coordination layer after it begins carbonisation at 250°C, and yet by the end of the process the palladium is stable and dispersed throughout the material. From literature, it is likely that the palladium forms nanoparticles during this process and then disperses as the temperature increases^[96]. This also makes sense as more nitrogen will be released from the ZIF-8 as the temperature increases, increasing the available binding sites. However, this is an interesting phenomenon and is worth investigation if *in-situ* TEM is available during future work.

Catalysis

Nanoparticles

Although this work has focused on avoiding nanoparticle formation and working with pure single palladium site Pd@HPNC catalysts, palladium nanoparticles may provide a new mechanism for catalysis. This was avoided in this work in order to understand the properties of the single metal atom site (as well as to investigate the feasibility of 100% atom efficiency). However, testing the catalytic performance of Pd@HPNC catalysts with palladium nanoparticles may show that the catalytic sites of the nanoparticles provide some advantage over the single palladium catalytic sites. If this work is pursued it would be beneficial to produce the palladium nanoparticles under a 5% hydrogen atmosphere, as this work has shown this produces smaller, better dispersed nanoparticles.

Mixed Metals

This work focused simply on palladium (after cobalt and nickel were found to have oxidation issues), but there is great potential for mixed-metal catalysts^[115-116], and producing these has been proven possible using this method^[80]. Further investigation into introducing multiple metals, such as palladium and platinum or palladium and ruthenium, would be an extremely interesting and exciting prospect.

Biomass Conversion and Hydrogenation of Quinoline

Although the Pd@HPNC catalyst synthesized in this work was not shown to be catalytically active for the conversion of furfural to cyclopentanone and the hydrogenation of quinoline, these reactions were not investigated fully due to time constraints. This is especially true

because the solvent used can play a large role in dictating the catalytic performance of a catalyst for a given reaction, and this was not varied at all for these reactions in this work. Future work could investigate this further to confirm that the Pd@HPNC catalyst synthesized in this work is truly not catalytically active for this reaction. Literature indicates that the hydrogenation of quinoline could perform better using solvents such as THF or hexane^[117].

Suzuki Coupling

The Suzuki coupling reaction was successful when using the Pd@HPNC catalyst synthesized in this work, and was found to not leach palladium into the reaction solvent. Future work will investigate the Suzuki coupling by first coupling more species to find a suitable combination of reactants and solvents for optimisation. A library of combinations of reactants will then be explored to provide depth to the evidence of the Pd@HPNC catalysts ability as a Suzuki coupling catalyst.

Heck Reaction

Literature shows that catalysts that are active for Suzuki coupling also have promise for the Heck reaction^[16]. The Heck reaction is a similar reaction to Suzuki coupling as it is also a C-C coupling reaction^[83]. Therefore, as the Pd@HPNC catalyst synthesized in this work shows catalytic activity for the Suzuki reaction, the Heck reaction should also be screened for catalytic activity in future work.

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Supporting Information

for

**Single palladium sites supported on carbon capsules: Synthesis,
structure, and catalysis**

By Nicholas Symon, Shane Telfer

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Instrumentation

Gas chromatography

Gas chromatography (GC) was done using a Shimadzu-2010 instrument with a Restek Rtx-5Sil MS column (Length: 30 m, Internal diameter: 0.25 mm) for non-chiral GC.

X-ray crystallography

A Rigaku Spider diffractometer equipped with a MicroMax MM007 rotating anode generator ($\text{Cu}\alpha$ radiation, 1.54180 Å), high-flux Osmic multilayer mirror optics, and a curved image plate detector was used to collect PXRD data.

Crystallography open database

The website “<http://www.crystallography.net/cod/index.php>” was used to search for crystallographic information files that could be used as reference PXRD patterns^[1-5].

Nuclear magnetic resonance (NMR) spectroscopy

A Bruker Avance 400 MHz equipped with a 5 mm BBI probe and a Bruker Avance 500 MHz spectrometer equipped with a 5 mm QXI probe (Bruker BioSpin GmbH, Rheinstetten Germany) were used to collect NMR data.

Tube furnaces

Furnace Y

The tube furnace that was used for the first half of the project was a Carbolite HST 12/400. This furnace was fed gas through a mixer that was connected to 4 gas cylinders and originally used a steel tube with Teflon seals. The temperature probe in this furnace is imbedded in the heating coils. Along with the new furnace, a quartz tube for furnace Y came in the middle of the project.

Furnace X

The tube furnace that was used for the last half of the project was a SIOMM SKGL-1200C with a tube size of 60 mm outer diameter and 1000 mm length. This furnace was directly fed from an argon cylinder, used a quartz tube and utilized insulation blocks to increase the uniformity of the temperature profile within the furnace. The temperature probe in this furnace is suspended beside the tube to ensure that the temperature of the tube is being accurately controlled.

The new furnace purchased during the project had a variety of benefits. Most notably for the experimental method were the valves at either end of the tube. By closing the inlet valve and opening the outlet it is possible to vacuum the tube using a vacuum pump attached to the exhaust. It is also possible to pressurize the tube by closing the outlet valve and opening the inlet. This allows the tube to be purged to a high quality atmosphere very quickly by vacuuming the tube to below -0.09 MPag and then re-pressurizing the tube back to above 0.5 MPag with argon zero. The more the tube is cycled through this process the better quality the atmosphere in the tube will become. This is referred to as purge/vac cycling for simplicity.

Transmission electron Microscope

A FEI Tecnai G² Spirit BioTWIN transmission electron microscope (Czech Republic) was used to obtain all TEM images.

Scanning electron microscope

A FEI Quanta 200 Environmental scanning electron microscope (Hillsboro) was used to obtain all SEM images.

Electron-dispersive x-ray spectroscopy

Spectral data was collected with a silicon EDAX unit (NJ, USA) running Genesis Spectrum software (version 5.21). This was run on a FEI Quanta 200 Environmental scanning electron microscope (Hillsboro).

Gas sorption

Gas sorption data was collected using a Quantachrome-Autosorb-iQ2.

Simultaneous thermal analysis

A Netzsch 449 F1 Jupiter was used to obtain simultaneous thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) data.

Atomic adsorption spectroscopy

A GBC XplorAA was used to obtain atomic adsorption spectroscopy data.

Experimental

ZIF-8 synthesis

Yang's method^[6] states "4 g of 2-methylimidazole was dissolved in 60 mL of methanol (MeOH) to form a clear solution. 1.68 g of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in 20 mL MeOH was added into above solution followed by vigorous stirring for 1 hour. The mixture was then incubated at room temperature without stirring. After 24 hours, the product was isolated as a white powder by centrifugation and washed several times with MeOH, and finally dried under vacuum.

ns000 – ZIF-8 synthesis following method given by Yang^[6]

ns000 was made at $\frac{1}{4}$ scale of the method given by Yang^[6].

1 g of 2-methylimidazole was dissolved in 15 mL of methanol by stirring to form a clear solution. Separately, 0.42 g of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was dissolved in 5 mL of methanol by stirring to form a clear solution. The $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ solution was added to the 2-methylimidazole solution followed by vigorous stirring for 1 hour. The stirrer bar was then removed and the solution left to incubate for 24 hours. The top layer was then poured off and the bottom layer of white solution was centrifuged to separate the white ZIF-8 solid. This was washed 3 times with methanol and dried overnight. TEM image and PXRD pattern shown in main text.

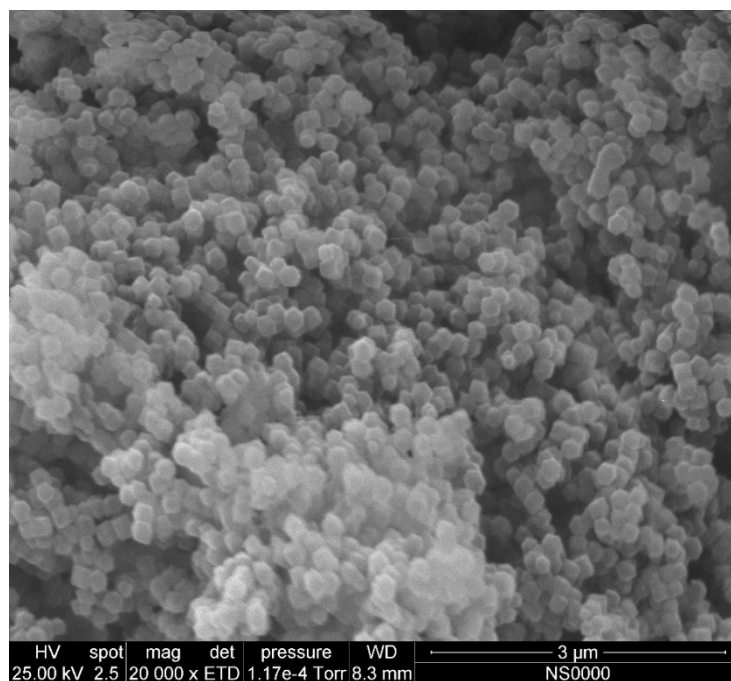


Figure S1 - SEM image of ZIF-8 made using Yang's method^[6] (ns000).

ns127 – ZIF-8 synthesis at double scale

8 g of 2-methylimidazole was dissolved in 120 mL of methanol by stirring to form a clear solution. Separately, 3.36 g of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was dissolved in 40 mL of methanol by stirring to form a clear solution. The $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ solution was added to the 2-methylimidazole solution followed by vigorous stirring for 1 hour. The stirrer bar was then removed and the solution left to incubate for 24 hours. The top layer was then poured off and the bottom layer of white solution was centrifuged at 5k rpm for 20 minutes in a swinging bucket rotor to separate the white ZIF-8 solid. This was washed 3 times with methanol and dried overnight.

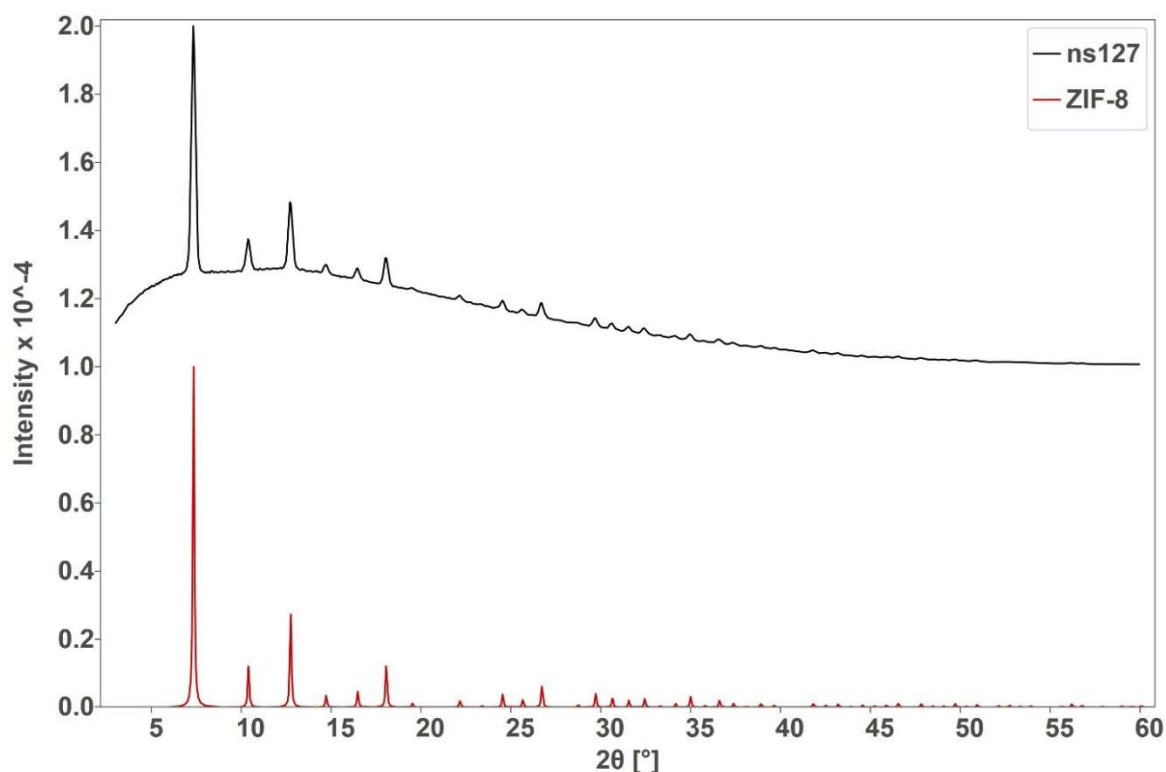


Figure S2 - PXRD of ns127 compared to simulated PXRD pattern of ZIF-8.

ns262

60.04 g of 2-methylimidazole was dissolved in 0.9 L of methanol by stirring to form a clear solution. Separately, 22.17 g of $\text{Zn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ was dissolved in 0.3 L of methanol by stirring to form a clear solution. The $\text{Zn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ solution was added to the 2-methylimidazole solution followed by vigorous stirring for 1 hour. The stirrer bar was then removed and the solution left to incubate for 24 hours. The top layer was then decanted and the bottom layer of white solution was centrifuged at 5k rpm for 10 minutes on a swinging bucket rotor to separate the white ZIF-8 solid. This was washed 2 times with an equal parts methanol and distilled water mixture and 2 further times with pure methanol and then dried overnight. Aliquots were taken before washing and after each wash for TEM. The product was then dispersed in deionised water ready for K-TA coating. Product density in water was measured by extracting 1 mL of dispersed solution, centrifuging to remove bulk water, drying overnight and weighing mass of dried product. Additional deionised water was added to dilute the solution to the correct ZIF-8 : water ratio for K-TA coating. TEM images shown in main text.

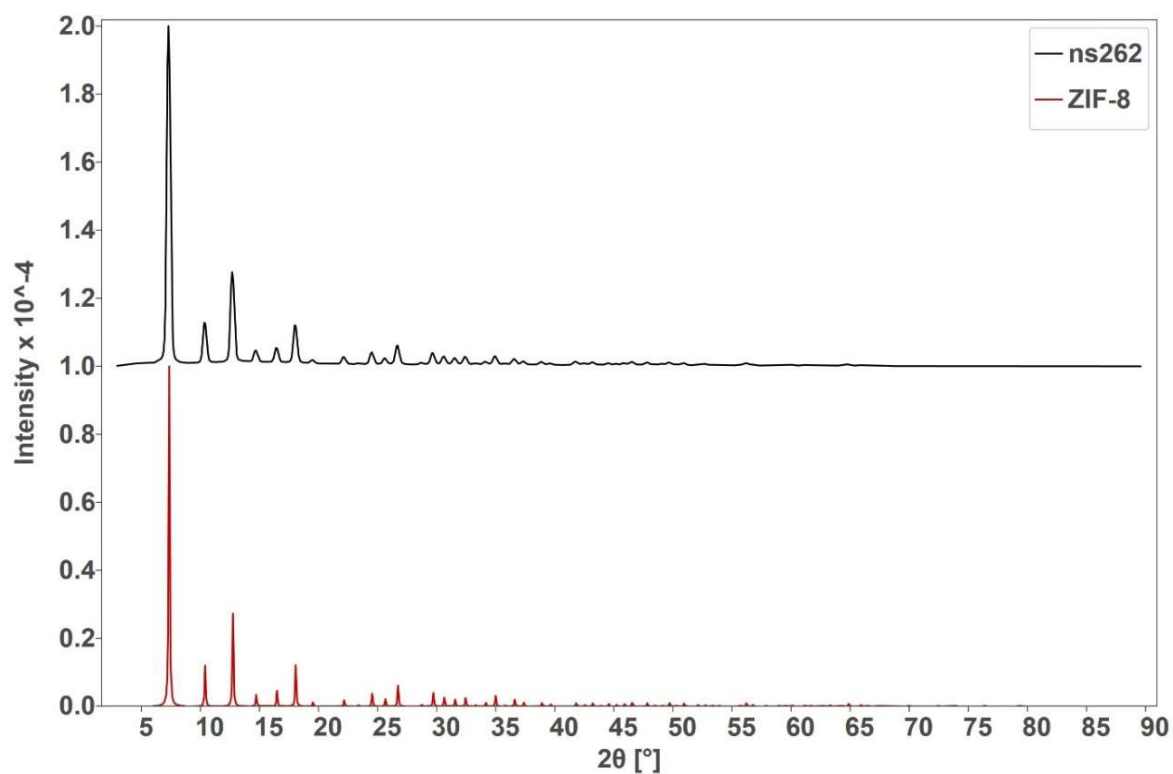


Figure S3 - PXRD pattern of ns262, ZIF-8 synthesized at 15x the scale given by Yang, compared to a predicted ZIF-8 pattern.

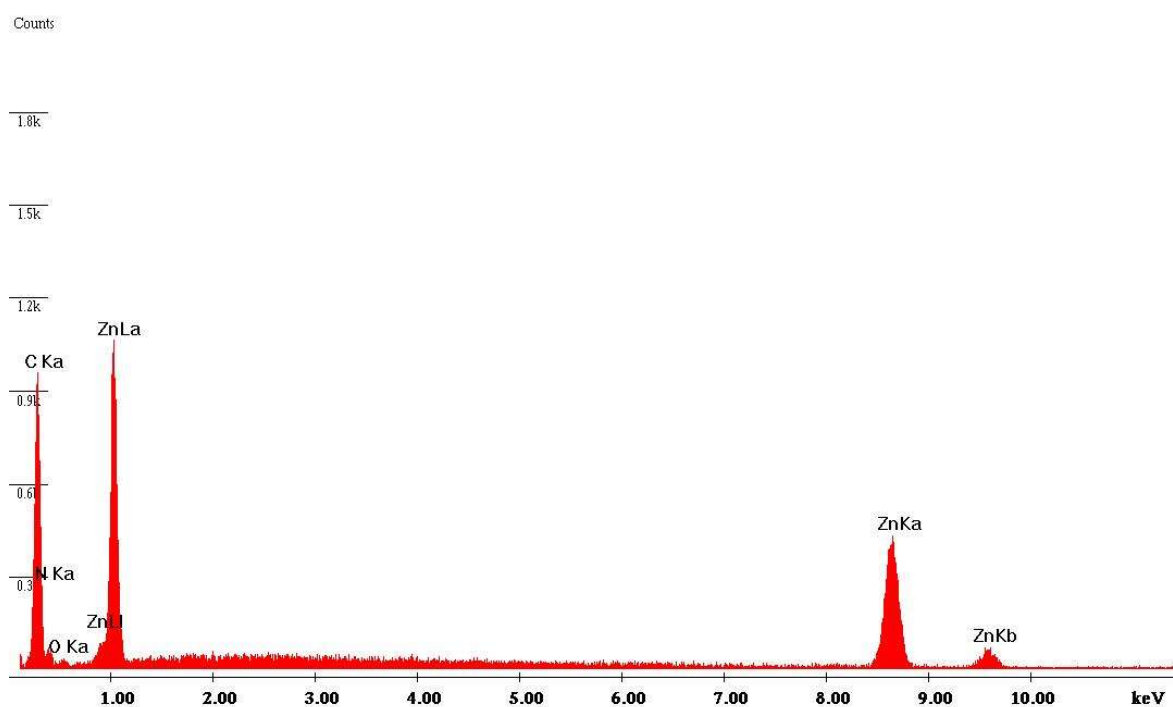


Figure S4 - EDX spectrum of ns262.

Effect of mechanical stress

ns143 – Effect of mechanical stress on TEM images of ZIF-8

ZIF-8 was ground dry overnight by a magnetic stirrer bar. This experiment was done to understand what observations under TEM can be attributed to mechanical stress. TEM images of ZIF-8 affected by the mechanical stress are shown below.

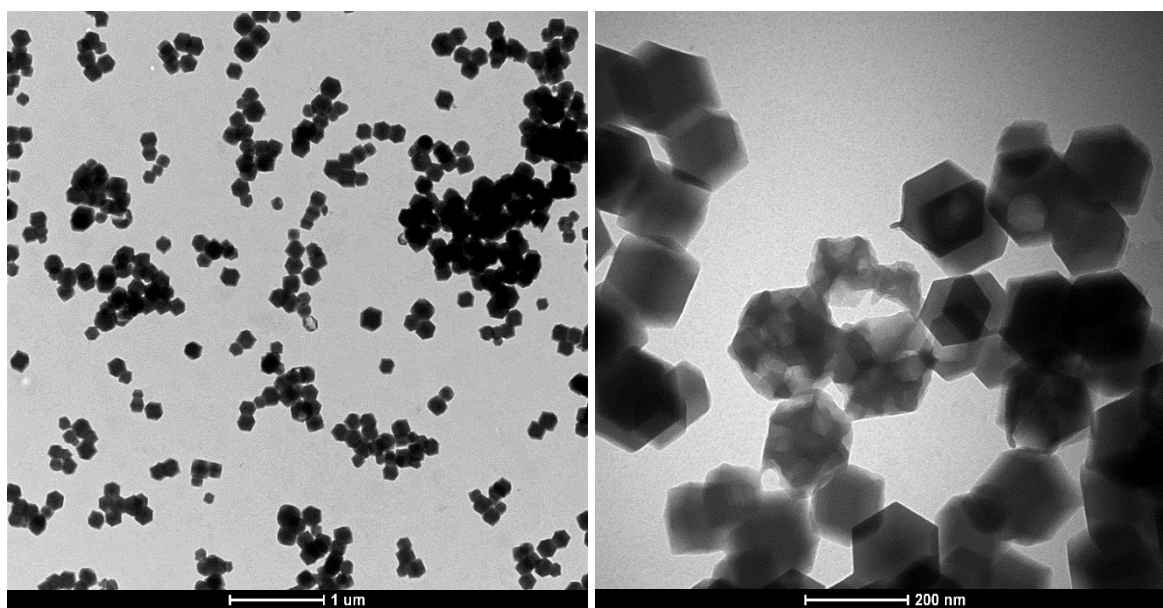


Figure S5 - TEM images taken of ZIF-8 ground dry overnight by a magnetic stirrer bar.

Effect of washing

ns239

60.01 g of 2-methylimidazole was dissolved in 0.9 L of methanol by stirring to form a clear solution. Separately, 25.23 g of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was dissolved in 0.3 L of methanol by stirring to form a clear solution. The $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ solution was added to the 2-methylimidazole solution followed by vigorous stirring for 1 hour. The stirrer bar was then removed and the solution left to incubate for 24 hours. The top layer was then decanted and the bottom layer of white solution was centrifuged at 8k rpm for 10 minutes on a fixed angle rotor to separate the white ZIF-8 solid. This was washed 2 times with an equal parts methanol and distilled water mixture and 2 further times with pure methanol and then dried overnight. Aliquots were taken before washing and after each wash for TEM. The product was then dispersed in methanol for storage. Product density in methanol was measured by extracting

1 mL of dispersed solution, centrifuging to remove bulk methanol, drying overnight and weighing mass of dried product.

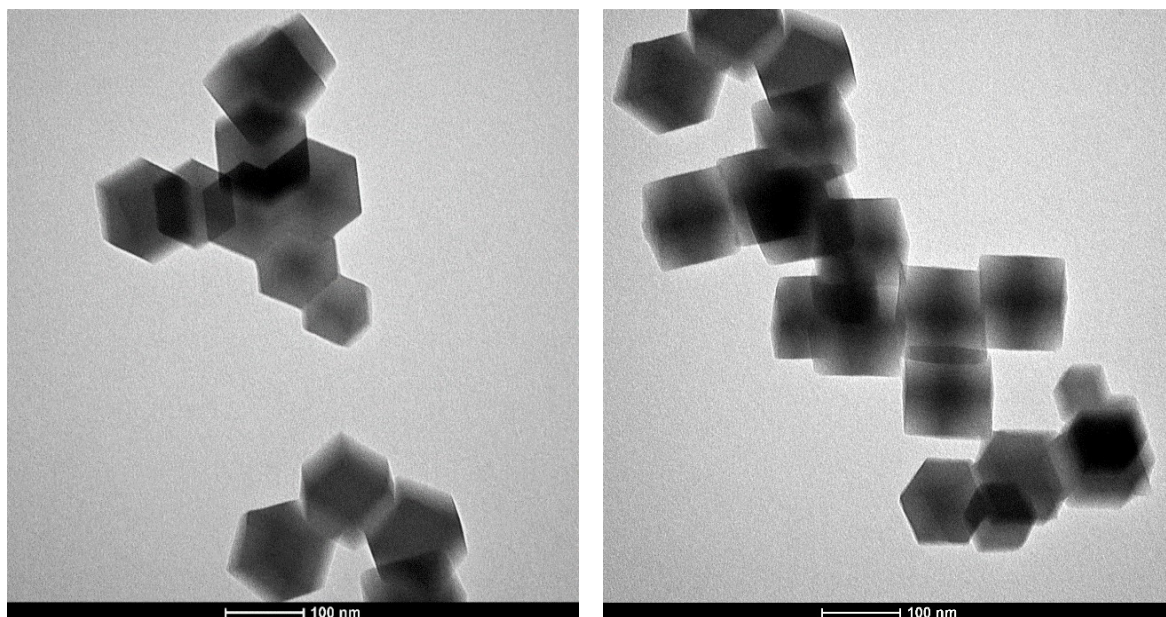


Figure S6 - TEM image of ns239 before washing.

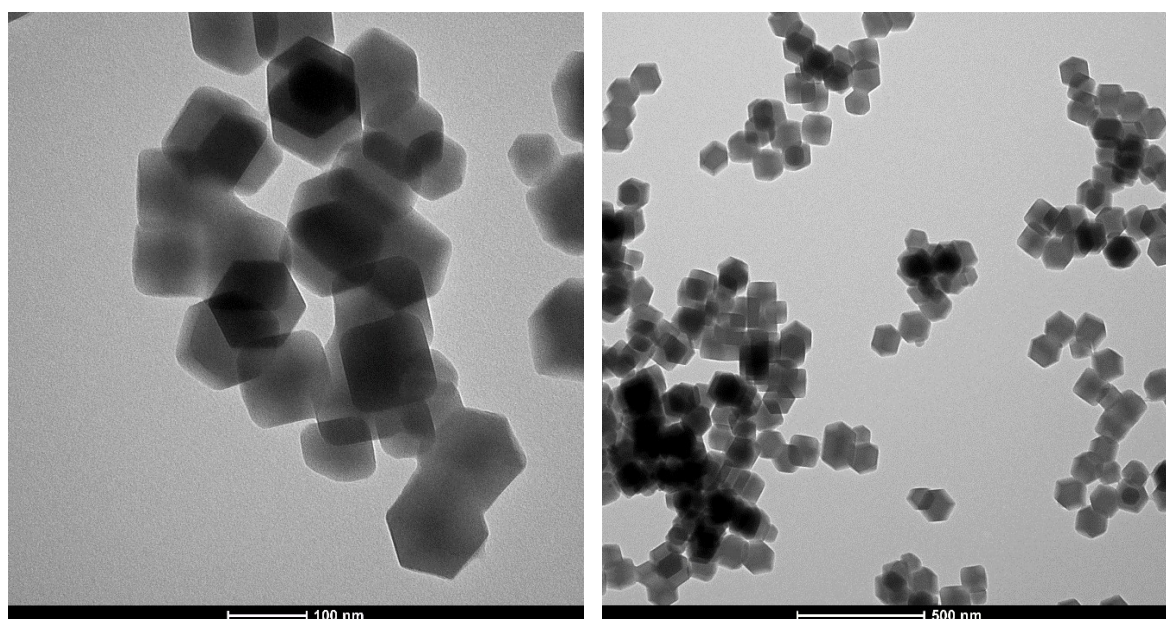


Figure S7 - TEM image of ns239 after washing once with an equal parts methanol and distilled water mixture.

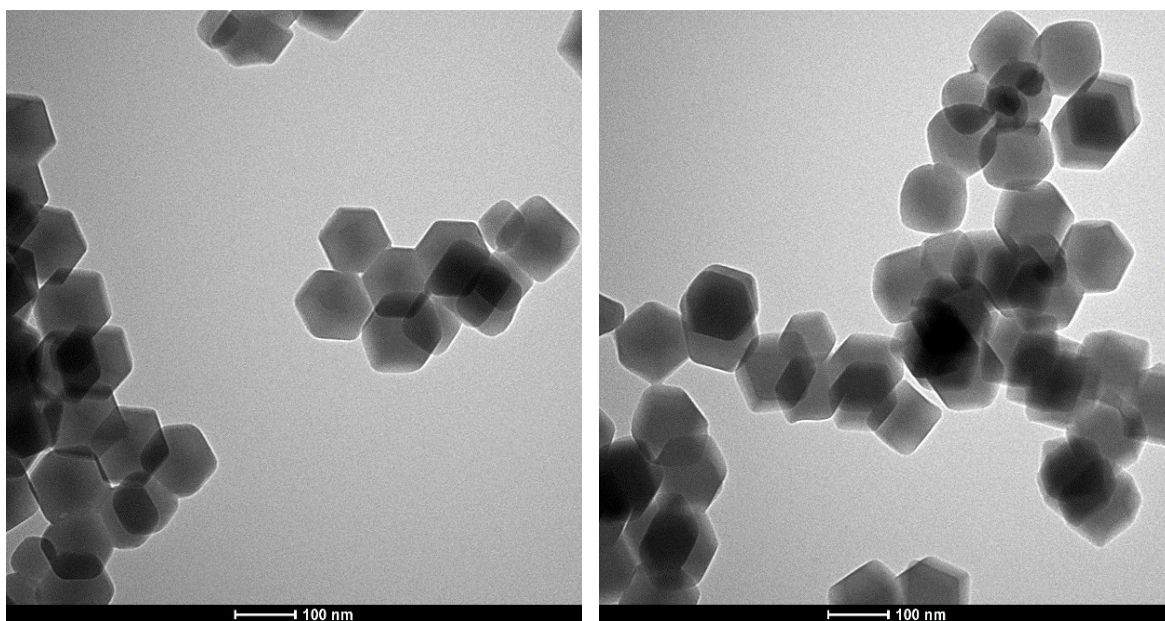


Figure S8 - TEM image of ns239 after washing twice with an equal parts methanol and distilled water mixture.

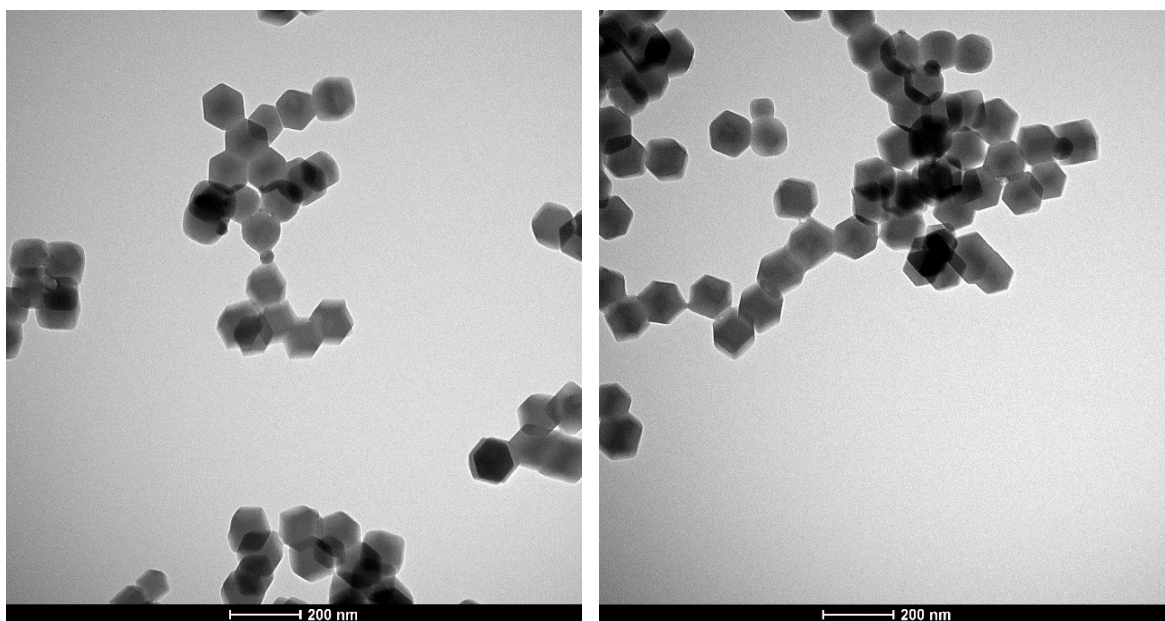


Figure S9 - TEM image of ns239 after washing twice with an equal parts methanol and distilled water mixture and once with pure methanol. Contamination (smaller growth can be seen on left image connecting two aggregates of ZIF-8 crystals) became apparent but not significant.

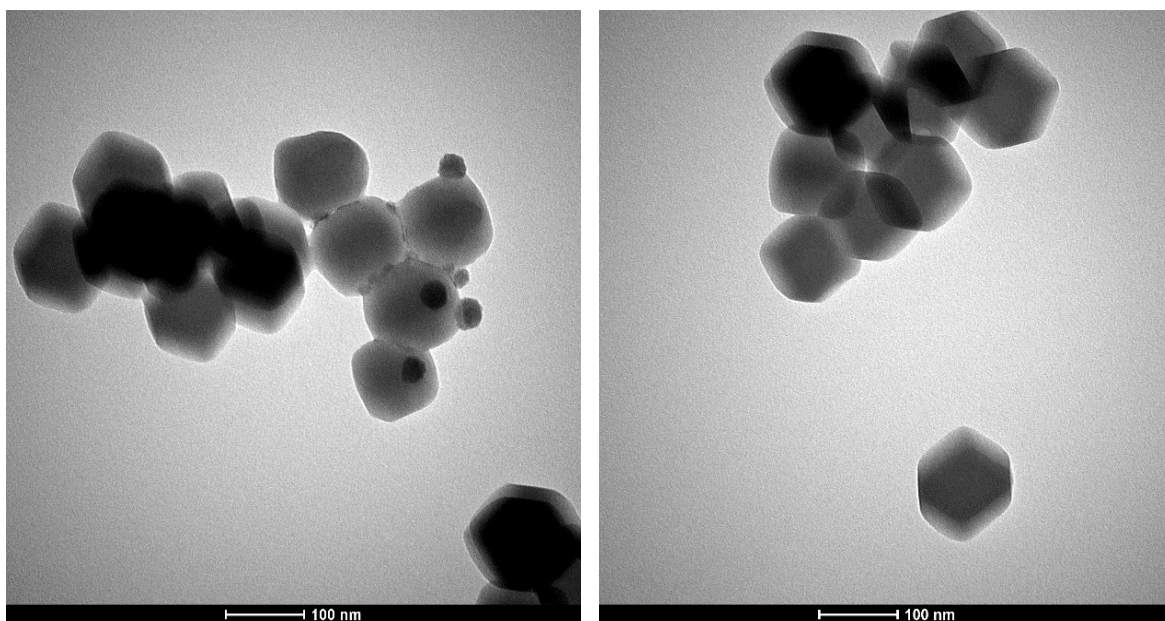


Figure S10 - TEM image of ns239 after washing twice with an equal parts methanol and distilled water mixture and twice with pure methanol. Contamination (smaller growths seen on left image) became apparent but not significant.

K-TA Coating

K-TA Synthesis

ns241 – KOH (6.011 M) vs TA (24 mM) pH curve

26.98 g of KOH added to 80 mL of water to make a 6.011 M aqueous KOH solution. 5.72 g of tannic acid added to 140 mL of water to make a 24 mM aqueous TA solution. 5 mL aliquots of the TA solution were distributed into 20 mL scintillation vials. Varying amounts of the KOH solution were added and the pH of the resulting solution was measured using a pH meter. The pH was measured immediately, and then occasionally after 5 minutes and 10 minutes it was measured again.

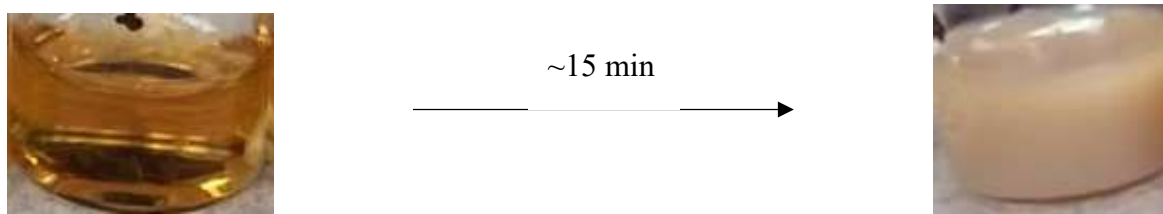


Figure S11 - K-TA formation colour change over 15 minutes after addition of 6.011 M KOH to 24 mM tannic acid aqueous solution. The product formed on the right was able to be separated by centrifugation (this isn't possible until K-TA has formed).

Table S1 - Amount of KOH (6.011 M) added to 5 mL of TA (24 mM) solution vs resulting pH.

<i>KOH</i> (μ L)	pH	pH after ~5 min	pH after ~10 min
0	3.00	3	3
10	4.32	4.35	4.32
50	7.15	7.1	7.08
57	7.48		
58	7.55		
60	7.59		
70	7.85		
75	7.92		
76	8.01		
77	8.00		
78	8.02		
79	8.04		
80	8.06		
90	8.28		
100	8.48	8.35	8.35
300	11.65		
500	13.07	12.89	12.54

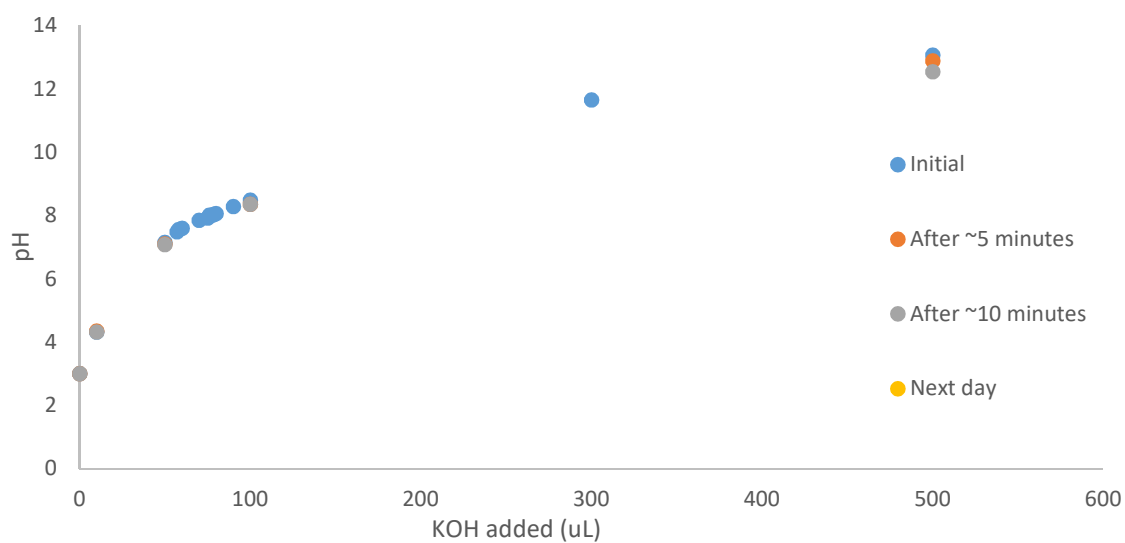


Figure S12 - Graph of amount of KOH (6.011 M) added to 5 mL of tannic acid solution (24 mM) vs resulting pH.



Figure S14 - Picture taken of the solutions shown in Figure 26 and Figure 27 in the main text after leaving them overnight. This shows that K-TA solutions form the green by-product (the dark green top layer of solution) eventually, regardless of pH, as the pH just affects the rate of formation. Note that the desired K-TA that has formed has sunk to the bottom to form a thin layer of solid.

K-TA Coating

Yang's method^[6] states "200 mg of ZIF-8 nanocrystals were dispersed in 10 mL of deionized water. Separately, a freshly prepared tannic acid solution (24 mM, 5 mL) was adjusted to pH 8 by the addition of aqueous KOH solution (6 M). Subsequently, the suspension of ZIF-8 nanocrystals was added to the tannic acid solution. After stirring for 5 min, ZIF-8@K-TA was collected by centrifugation, washed several times with methanol, and dried overnight under vacuum".

Communication with Hui Yang via email has resulted in extra detail, including: 5 mL of methanol can be added before centrifugation to aid separation, the centrifuge is best run at 8k rpm for 5 minutes (roughly 13,000 xg) with a deceleration speed of 8 and the ZIF-8 can be dispersed in water by shaking the solution while it is sonicated (leaving/not shaking in the sonicator will not aid dispersion according to Hui).

ns000c – K-TA coating following method given by Yang^[6]

ns000c was made at ¼ scale of the method given by Yang^[6], using the ZIF-8 product from ns000 (described above on page 3) as the ZIF-8 source.

It was noted that despite communication with Yang (see above text under K-TA Coating heading) to disperse the ZIF-8 in water by shaking the solution while sonicating, it was

extremely difficult to completely disperse the ZIF-8 in solution. Clumps of ZIF-8 still floated on top of the solution.

The pH was measured by pH strip to be between 7 and 8. The solution went a green colour during the 5 minutes that the ZIF-8 and K-TA were stirred, resulting in a green powder upon drying. This is an indication that some by-product formed, according to K-TA formation observations (see Figure 14 above). TEM image and PXRD pattern shown in main text.

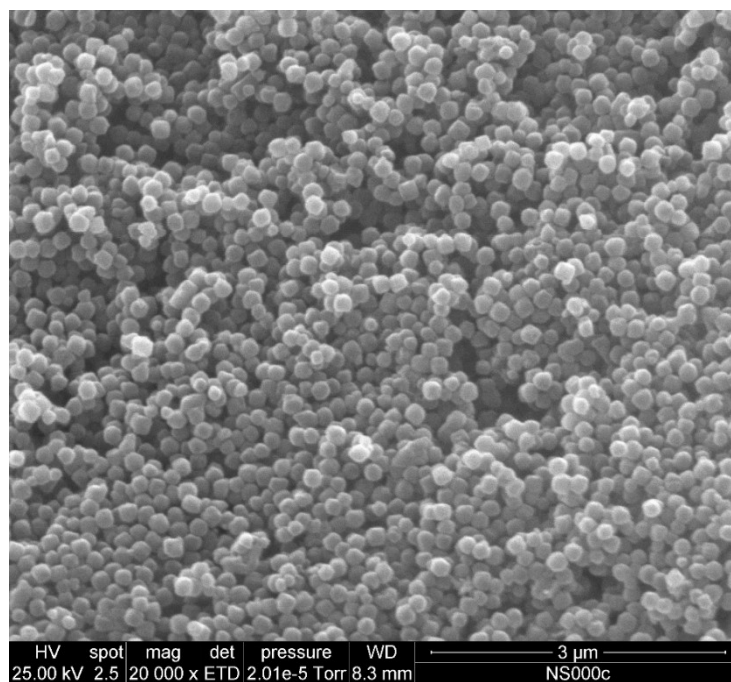


Figure S15 - SEM image of ZIF-8@K-TA made using Yang's method^[6] (ns000c) compared to simulated PXRD pattern of ZIF-8.

ns133 – K-TA coating of ns133

803.5 mg of ZIF-8 nanocrystals were dispersed in 40 mL of deionized water. Separately, a freshly prepared tannic acid solution (24 mM, 20 mL) was adjusted to pH 8 by the addition of aqueous KOH solution (6 M). Subsequently, the suspension of ZIF-8 nanocrystals was added to the tannic acid solution. After stirring for 5 min, 60 mL of methanol was added to stall the K-TA formation process. ZIF-8@K-TA was collected by centrifugation, washed several times with methanol, and dried overnight under vacuum.

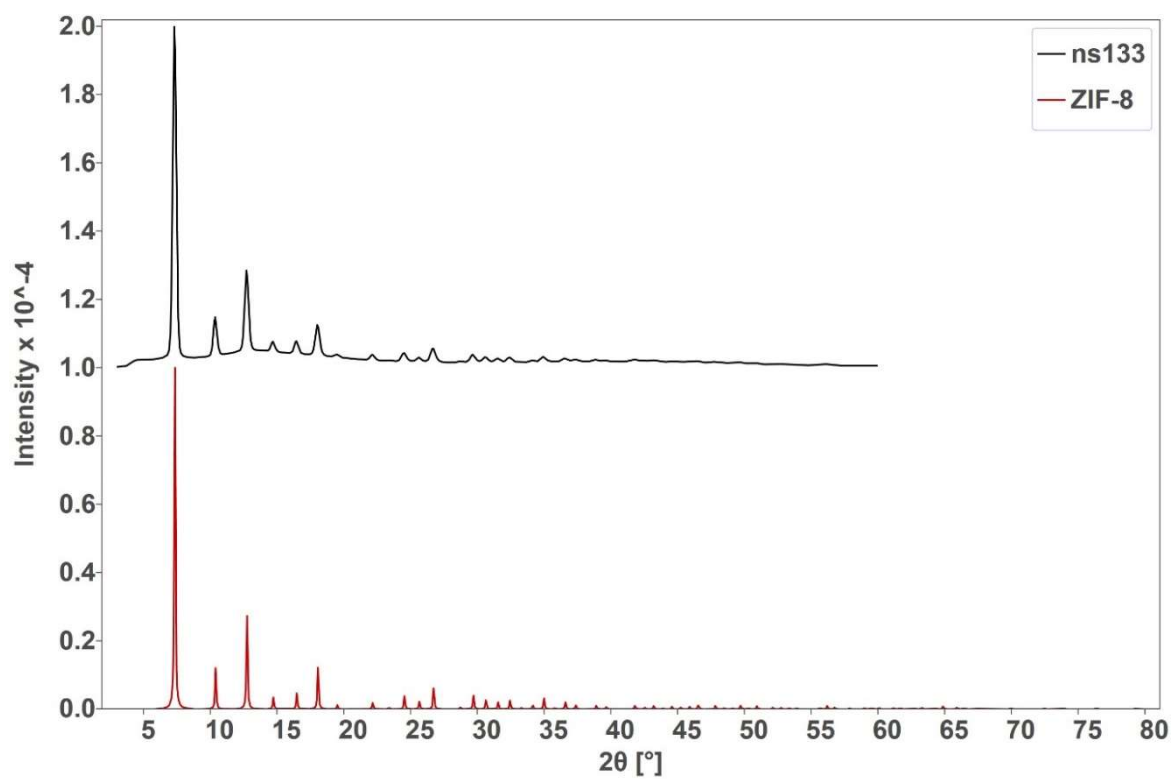


Figure S16 - PXRD pattern of ns133 compared to simulated PXRD pattern of ZIF-8.

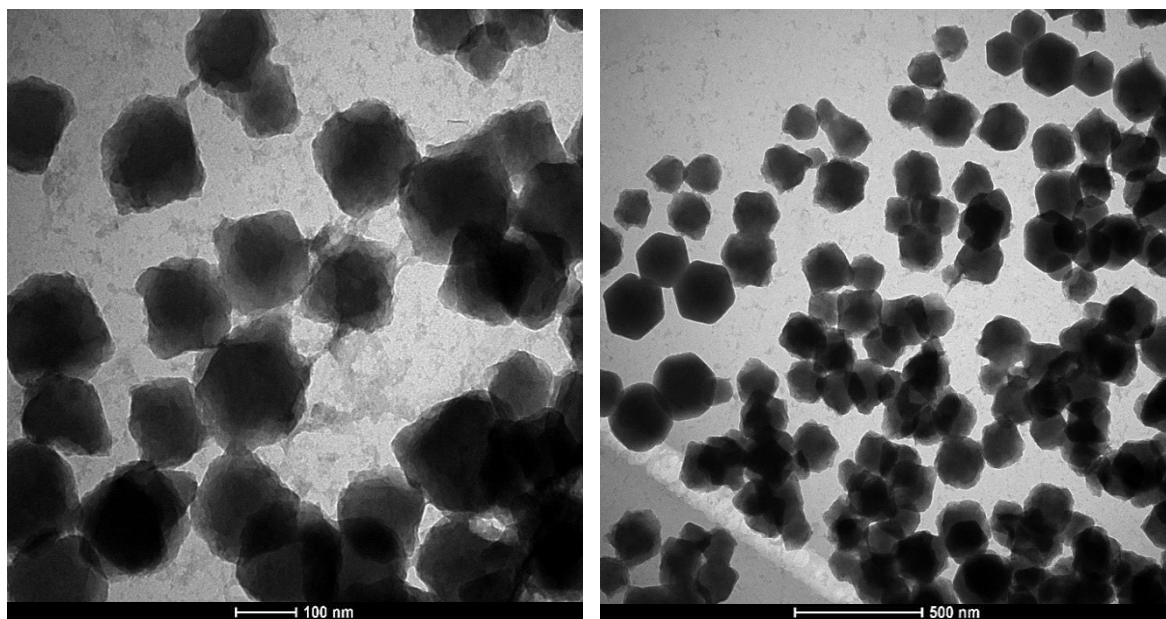


Figure S17 - TEM images of ZIF-8@K-TA formed in ns133.

ns242 - Effect of time that ZIF-8 is held in K-TA solution on coating

7 mL of ns239 (see page 7 above) centrifuged. Remaining solid dispersed in 8 mL water. 5 mL of this solution (100 mg ZIF-8) stirred in a 20 mL scintillation vial. 10 mL aqueous tannic acid solution added to separate vial. 155 μ L KOH (6.01M) added to tannic acid solution to form a K-TA solution at pH 7.99. 2.5 mL of this solution added to the ZIF-8 solution in a 20 mL scintillation vial while stirring. After 1, 5, 30 and 60 minutes (ns242 0, ns242 5, ns242 30 and ns242 60 respectively) 1 mL aliquots of the ZIF-8@K-TA solution were taken, centrifuged (14.5k rpm for 60 seconds) and washed 2 times with methanol.

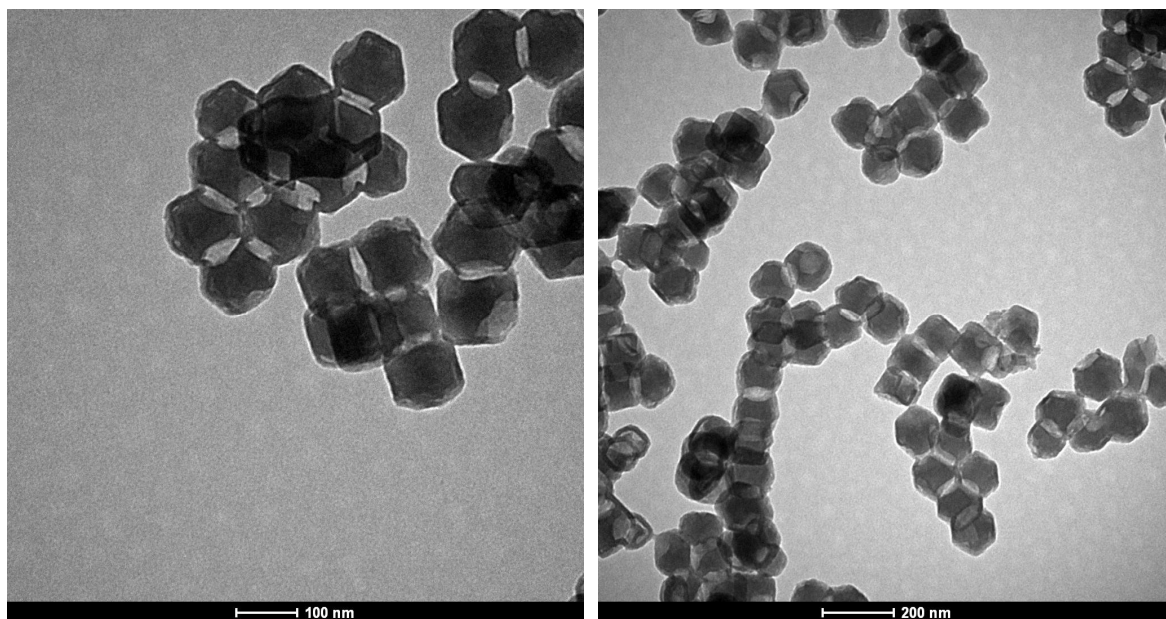


Figure S18 - TEM images of ZIF-8@K-TA that was only stirred in K-TA for ~1 minute before removing (ns242 0). The interface between each ZIF-8 crystal that is in contact with another crystal looks to be etched.

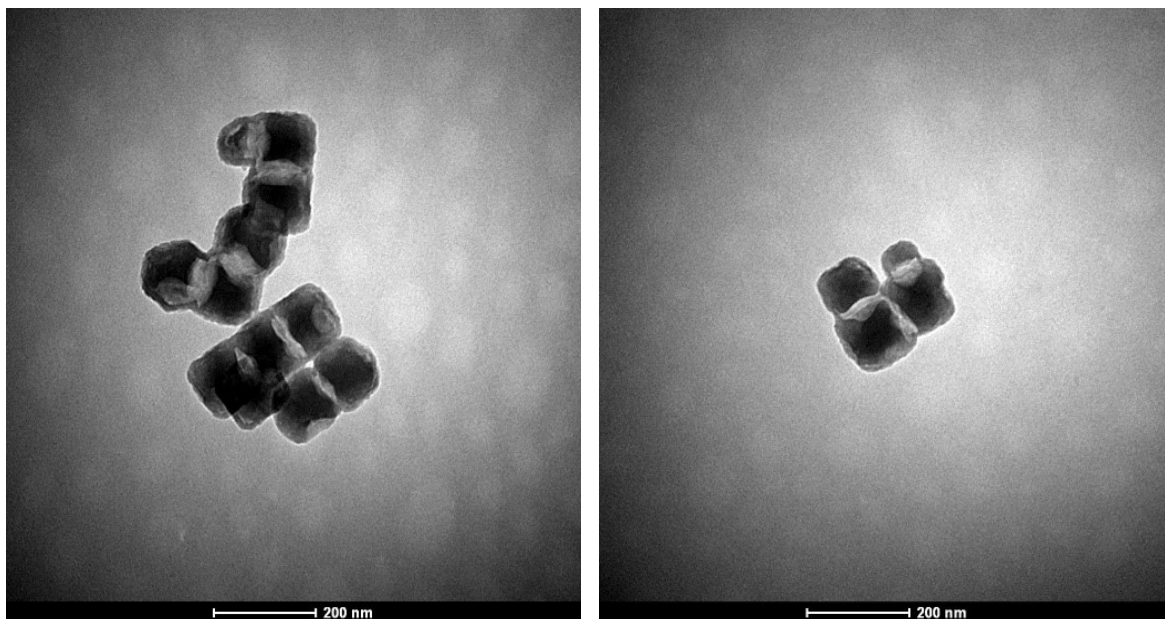


Figure S19 - TEM images of ZIF-8@K-TA that was only stirred in K-TA for ~5 minutes before removing (ns242 5). The interface between each ZIF-8 crystal that is in contact with another crystal looks to be etched.

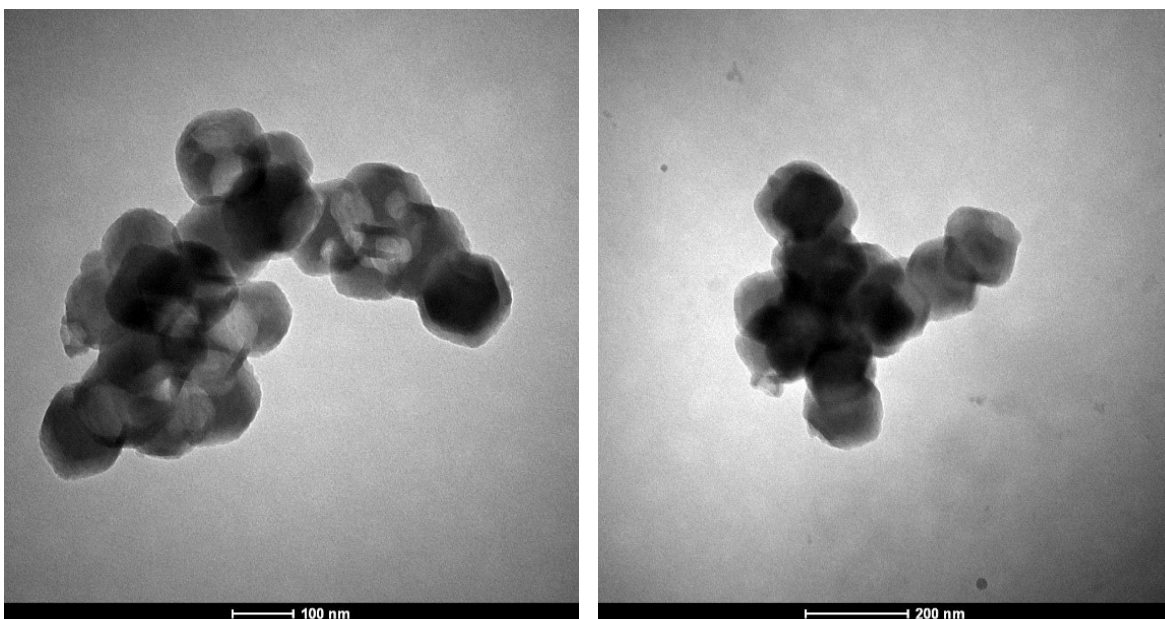


Figure S20 - TEM images of ZIF-8@K-TA that was only stirred in K-TA for ~30 minutes before removing (ns242 30).

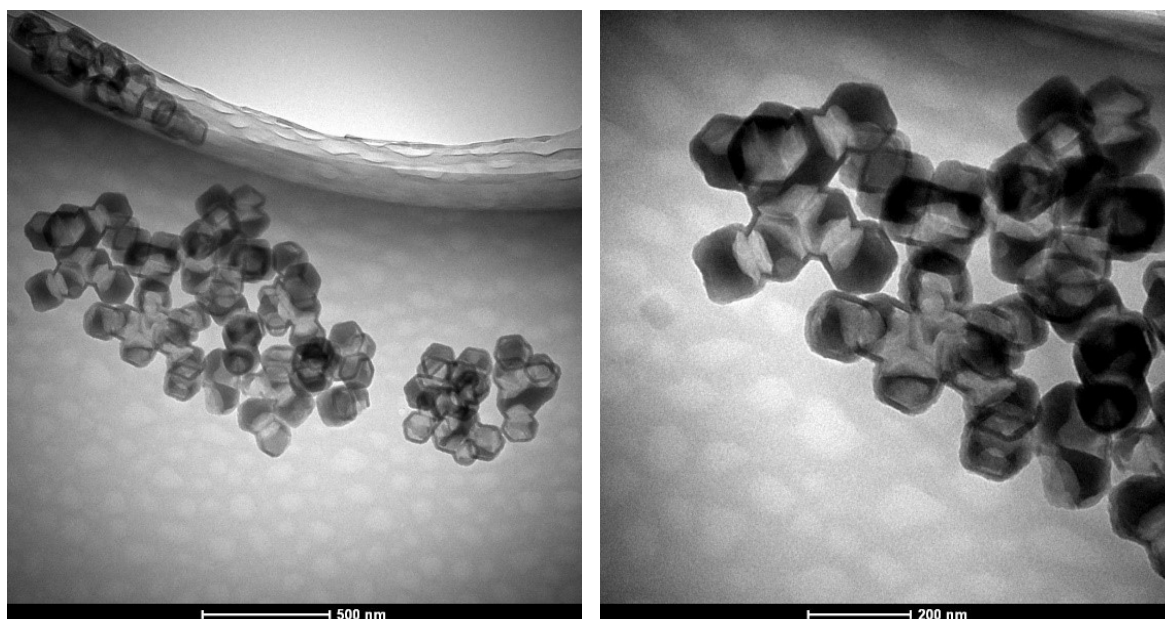


Figure S21 - TEM images of ZIF-8@K-TA that was only stirred in K-TA for ~60 minutes before removing (ns242 60). There is noticeably more etching than in samples that were not left in K-TA for as long.

ns243 – K-TA coating of ns239

The product ZIF-8 from ns239 described above on page 7 was used as the ZIF-8 source for this coating. After 5 days of storage in methanol, 175 mL of ns239 was centrifuged to give approximately 4025 mg of ZIF-8 (according to product density calculations done during ns239). This ZIF-8 was then dispersed in 200 mL of deionised water by sonication.

4.11 g of tannic acid was dissolved in 100 mL deionised water by stirring. 1.55 mL KOH (6.01 M) added to the tannic acid solution but the pH had not reached a sufficient level, so 6 additional drops of KOH were added to reach a pH of 8.02. The K-TA solution was added to the ZIF-8 solution while stirring. After 5 minutes of stirring, the stirrer bar was removed and the solution was centrifuged at 8k rpm for 5 minutes on a fixed angle rotor to separate out the product ZIF-8@K-TA. The product was washed with methanol 2 times and then stored in methanol. Product density in methanol was measured by extracting 1 mL of dispersed solution, centrifuging to remove bulk methanol, drying overnight and weighing mass of dried product. TEM and PXRD shown in the main text.

Solvent exchange to tetrahydrofuran

24 days later, 60 mL of the product solution was centrifuged down, washed with tetrahydrofuran 2 times and then stored in tetrahydrofuran. This is to be used for palladium ion-exchange.

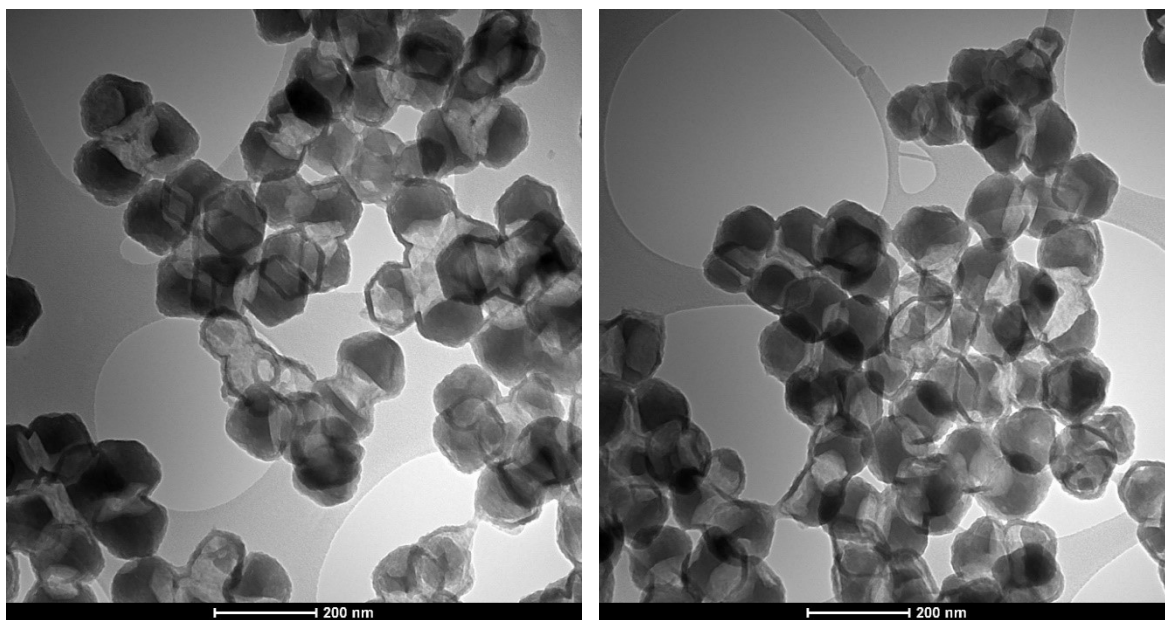


Figure S22 - TEM images of ZIF-8@K-TA (ns243) stored in tetrahydrofuran. The holes on the TEM grid are thought to be caused by the tetrahydrofuran as this may dissolve the material used in the grid.

ns263 – Effect of time spent adjusting pH of K-TA solution before adding to ZIF-8

0.6921 g of tannic acid added to 17 mL of distilled water and stirred to dissolve. 10 mL ZIF-8 (ZIF-8 source is ns262) added to 3 50 mL centrifuge tubes. 230 μ L of KOH (6.01 M) was added to reach pH 7.7, followed by 1.5 further drops to reach a pH of 8.0. This process took 7 minutes and 35 seconds. Immediately, after 5 minutes and then again after a further 5 minutes, 5 mL of the K-TA solution was added to one of the previously prepared ZIF-8 solutions in centrifuge tubes while stirring (ns263 0, ns263 5 and ns263 10 respectively). Each of the 3 solutions was given 5 minutes of stirring before the stirrer bar was removed, the solution was centrifuged at 8k rpm for 4 minutes and then washed with methanol. Dried overnight. Dispersed in a water/ethanol mixture for TEM.

Note that adjusting the pH to 8.0 took significantly longer than usual (hence the 7 minutes and 35 seconds) and this resulted in the K-TA forming (i.e. the solution went cloudy) before it was added to the ZIF-8 solutions.

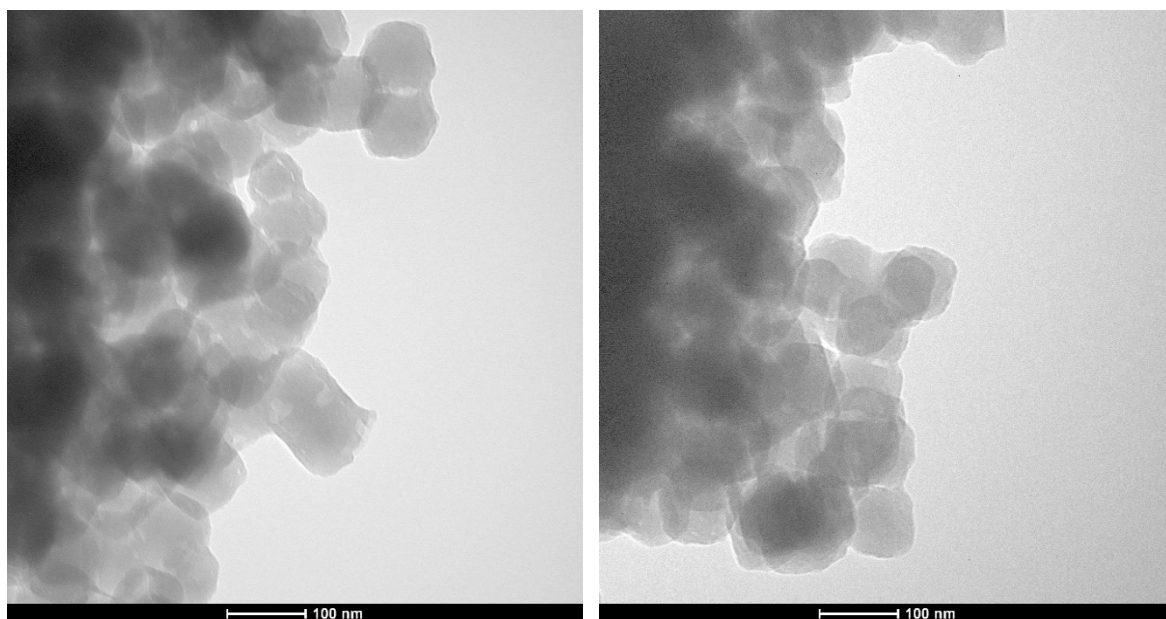


Figure S23 - TEM images of ZIF-8@K-TA synthesized by the addition of K-TA that was adjusted to pH 8.0 over ~7 minutes (ns263 0).

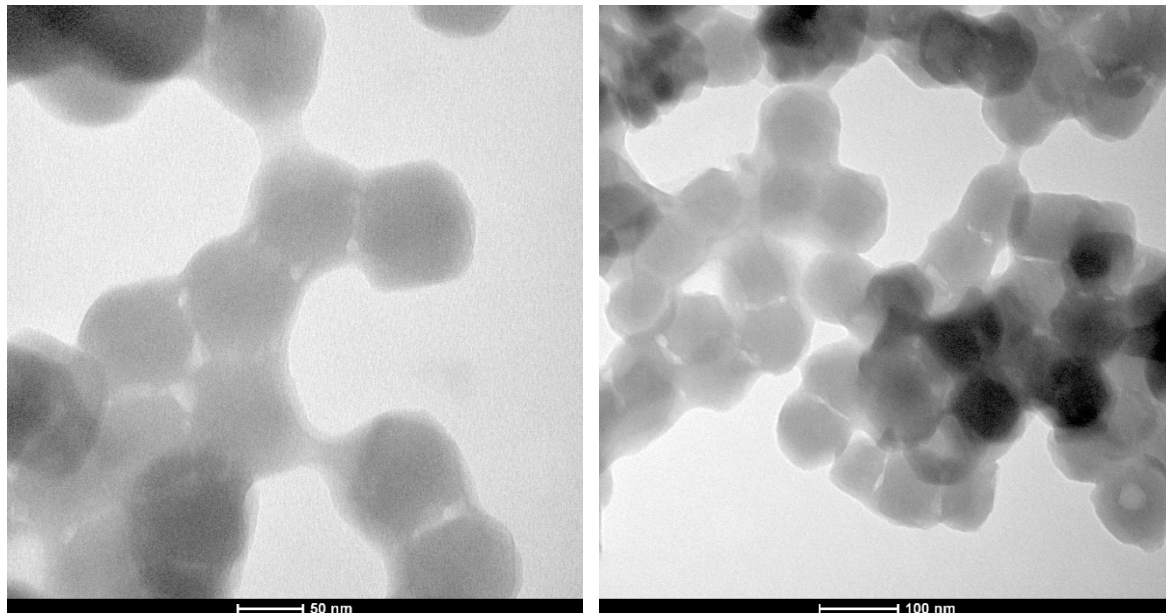


Figure S24 - TEM images of ZIF-8@K-TA synthesized by the addition of K-TA that was adjusted to pH 8.0 over ~12 minutes (ns263 5).

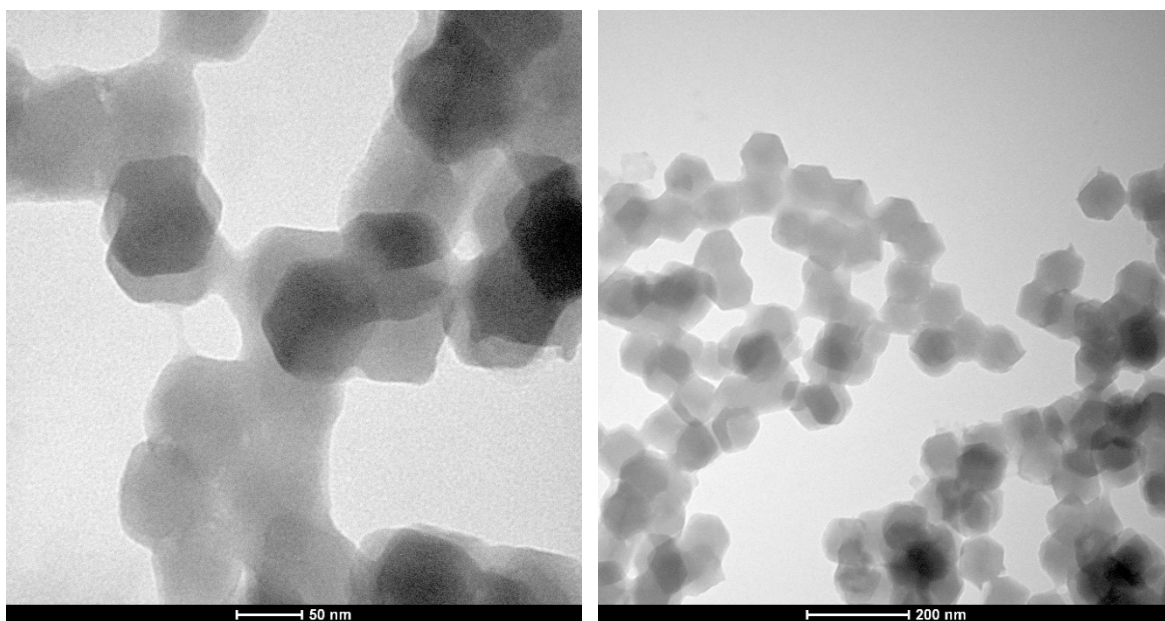


Figure S25 - TEM images of ZIF-8@K-TA synthesized by the addition of K-TA that was adjusted to pH 8.0 over ~17 minutes (ns263 10).

ns264

6.31 g of tannic acid was added to 155 mL deionised water. This was stirred and sonicated to dissolve. 2.38 mL of KOH (6.01 M) was added, adjusting the pH to 7.9. 5 additional drops of KOH were added to reach a pH of 8.0. Adjusting the pH took 8 minutes (during which the K-TA began to form, as the solution became visibly cloudy). This K-TA solution was added to 310 mL of ZIF-8 stored in water (ns262) while stirring. After 5 minutes of stirring the stirrer bar was removed and the solution was centrifuged at 8k rpm for 10 minutes with a fixed angle rotor. The product was washed with methanol once before washing in tetrahydrofuran 2 times. The product was then dispersed in tetrahydrofuran for storage. Product density in tetrahydrofuran was measured by extracting 1 mL of dispersed solution, centrifuging to remove bulk tetrahydrofuran, drying overnight and weighing mass of dried product. TEM image and PXRD pattern shown in the main text.

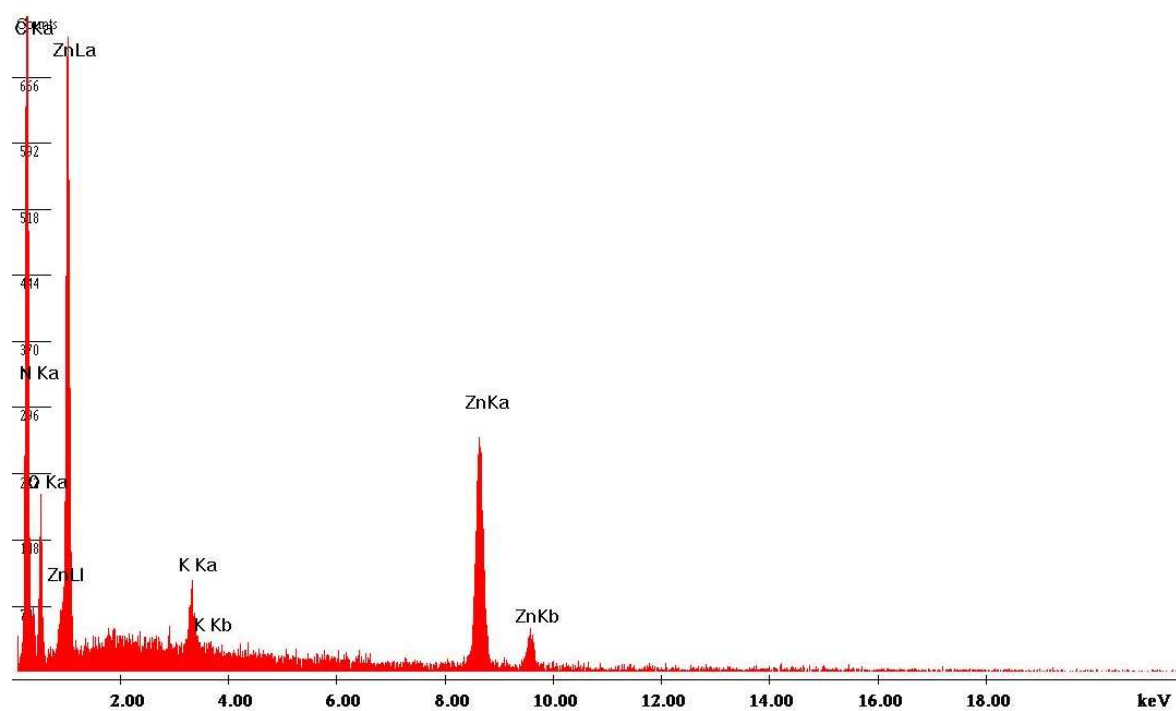


Figure S26 - EDX spectrum of ns264.

Ion exchange

Yang's method^[6] states "ZIF-8@K-TA was soaked in a methanolic solution (100 mL) of iron(III) nitrate nonahydrate $[\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}]$, 50 mg]. After stirring for 2 hours, the ZIF-8@Fe-TA solid was collected by centrifugation, washed several times with methanol, and dried overnight under vacuum."

This method was modified for this work in that the ZIF-8@K-TA was not dried out in the prior ZIF-8@K-TA synthesis, and therefore was not 'soaked' but instead the metal ion-containing solution was added to a stirring ZIF-8@K-TA solution. Yang also does not state the quantity of ZIF-8@K-TA used. In this work, approximately 60 to 80 mg of ZIF-8@K-TA is added per 80 mL of solvent. The amount of metal salt is varied throughout the work to finding a loading at which no nanoparticles form during pyrolysis, and therefore only single metal atoms are present.

Iron

ns134

51.7 mg of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was dissolved in 100 mL of methanol. 150 mg of ns133 was added. The solution was stirred for 2 hours before removing the stirrer bar and centrifuging at 5k rpm for 15 minutes with a swinging bucket rotor to remove the product. This was washed with methanol and dried under vacuum. TEM image and PXRD pattern shown in main text.

Cobalt

ns244

37.4 mg of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was dissolved in 37.5 mL of methanol, labelled ns244X. 1 mL of ns244X taken and diluted with 75 mL of methanol, labelled ns244Xa. 1.5 mL of ns244X taken and diluted with 75 mL of methanol, labelled ns244Xb. 4 mL of ns243 (60 mg ZIF-8@K-TA) added to 2 fresh 100 mL round bottom flasks (labelled ns244a and ns244b) and set to stir. Solution ns244Xa was added to ns244a and ns244Xb was added to ns244b. After 2 hours of stirring, the stirrer bar was removed and the solutions were centrifuged at 8k rpm

for 10 minutes in a fixed angle rotor to separate out the product. The product was then washed 2 times with methanol and dried overnight under vacuum.

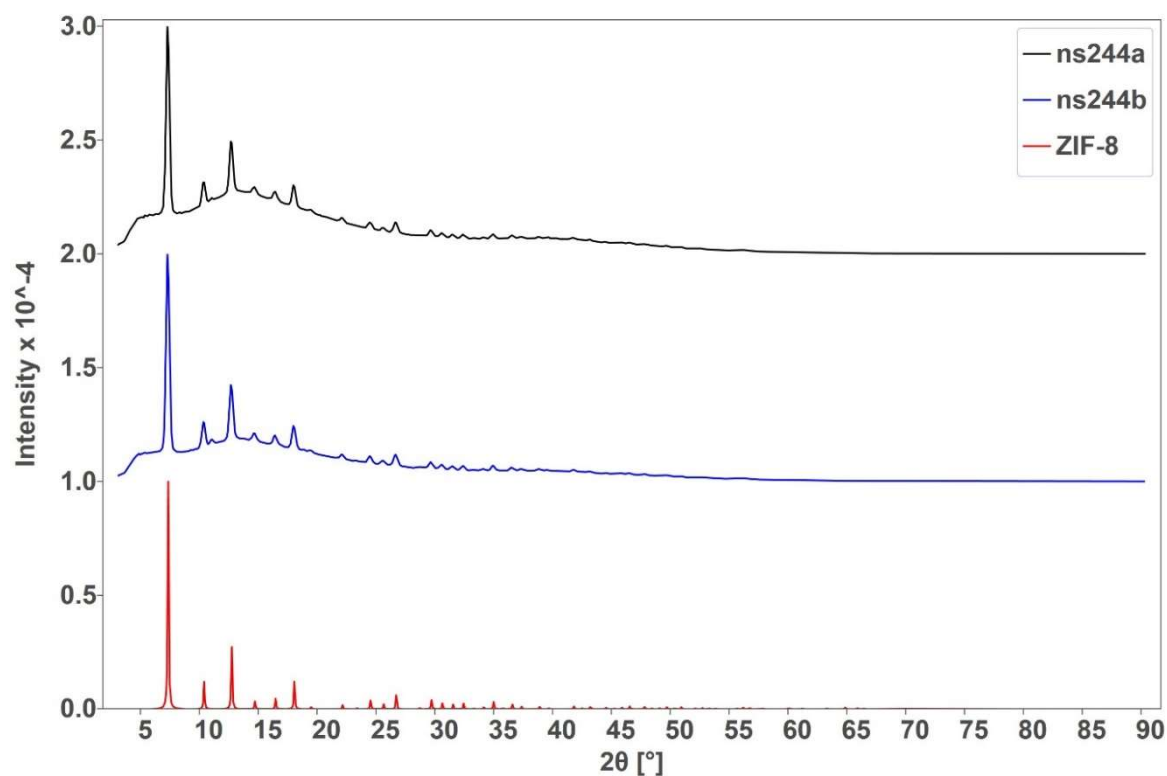


Figure S27 - PXRD patterns of ns244a and ns244b compared to simulated ZIF-8.

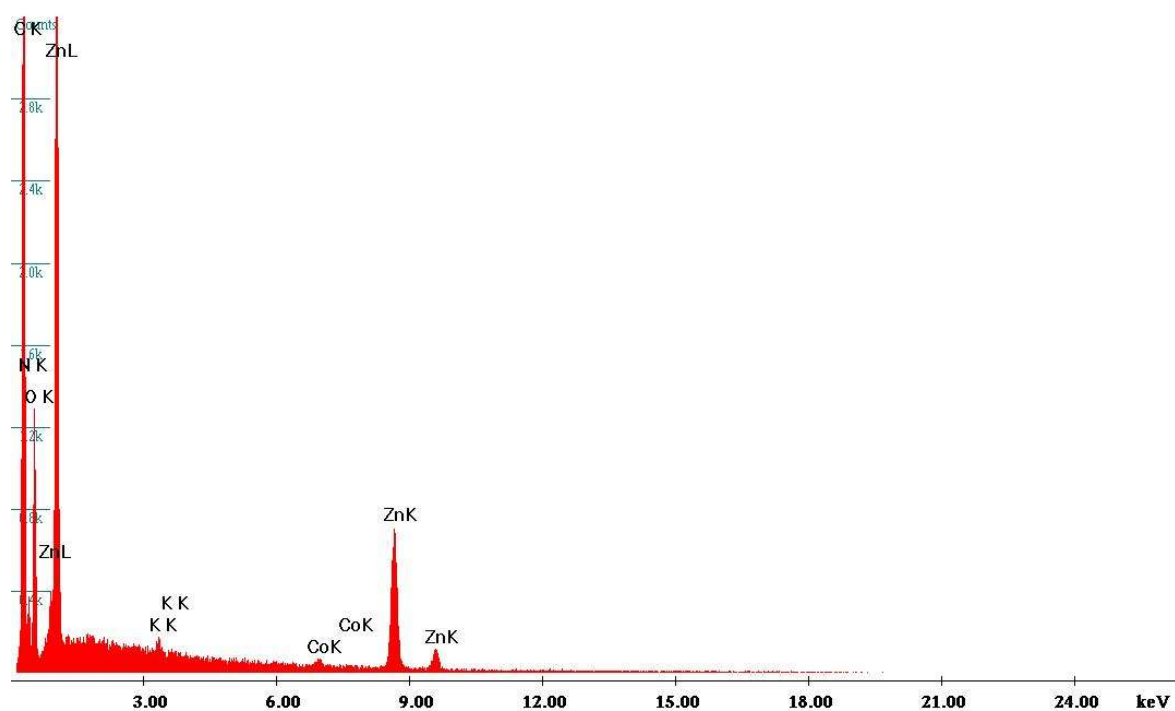


Figure S28 - EDX spectrum of ns244b.

ns252

7.1 mg of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was dissolved in 7 mL of methanol. 2.5 mL of this solution was taken and diluted with 76 mL of methanol and the rest was discarded. 4 mL of ns243 (60 mg ZIF-8@K-TA) was added to a separate vessel. The diluted $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ solution was added to the ZIF-8@K-TA solution while stirring. After 2 hours of stirring, the stirrer bar was removed and the solutions were centrifuged at 5k rpm for 20 minutes in a swinging bucket rotor to separate out the product. The product was then washed 2 times with methanol and dried overnight under vacuum.

ns255

81.4 mg of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was dissolved in 81 mL of methanol. 3, 3.5, 4, 4.5 and 5 mL of this solution was taken and diluted with 35 mL of methanol in separate vessels labelled a, b, c, d and e respectively. The rest of the solution was discarded. 2 mL of ns243 (30 mg ZIF-8@K-TA) was added to 5 separate vessels. Solutions a, b, c, d and e were added to ns243 solutions while stirring and labelled ns255a, ns255b, ns255c, ns255d and ns255e respectively. After 2 hours of stirring, the stirrer bar was removed and the solutions were centrifuged at 5k rpm for 20 minutes in a swinging bucket rotor to separate out the product.

The product was then washed 2 times with methanol and dried overnight under vacuum. The product was ground lightly with a spatula to create a powder.

Nickel

ns245

75.6 mg of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was dissolved in 75.5 mL of methanol, labelled ns245X. 1 mL of ns245X taken and diluted with 75 mL of methanol, labelled ns245Xa. 1.5 mL of ns245X taken and diluted with 75 mL of methanol, labelled ns245Xb. 4 mL of ns243 (60 mg ZIF-8@K-TA) added to 2 fresh 100 mL round bottom flasks (labelled ns245a and ns245b) and set to stir. Solution ns245Xa was added to ns245a and ns245Xb was added to ns245b. After 2 hours of stirring, the stirrer bar was removed and the solutions were centrifuged at 8k rpm for 10 minutes in a fixed angle rotor to separate out the product. The product was then washed 2 times with methanol and dried overnight under vacuum.

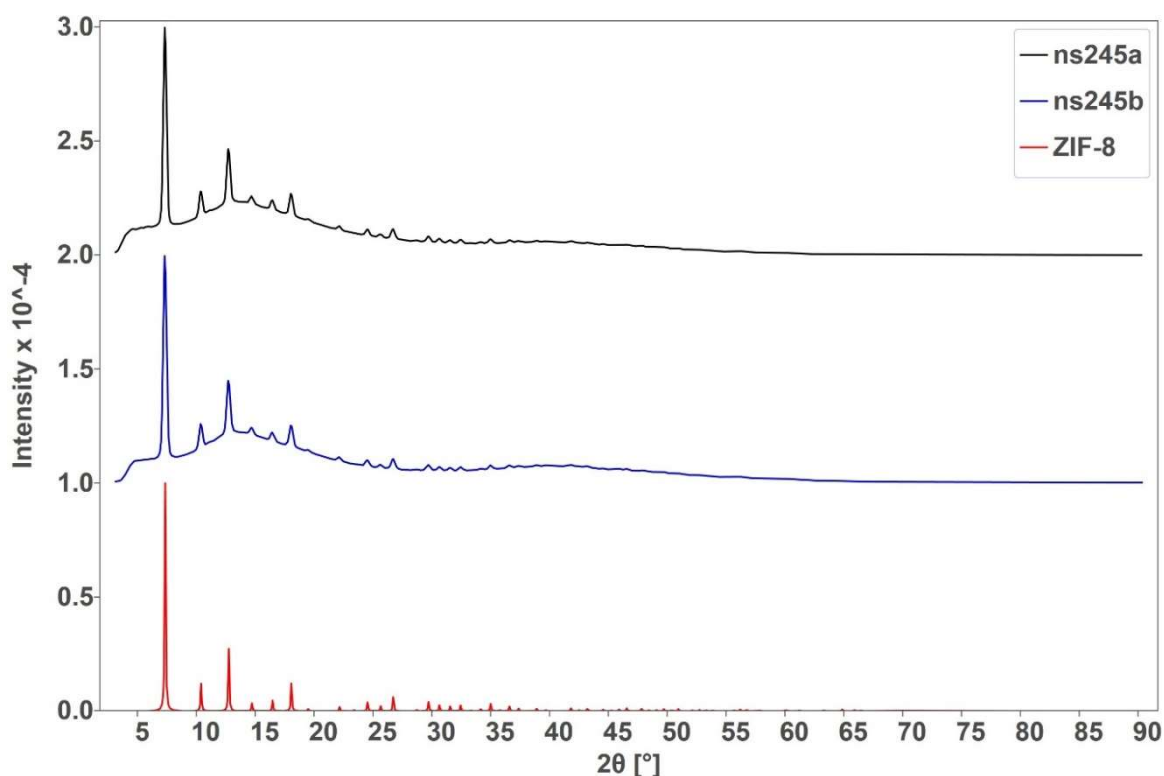


Figure S29 - PXRD patterns of ns245a and ns245b compared to simulated ZIF-8.

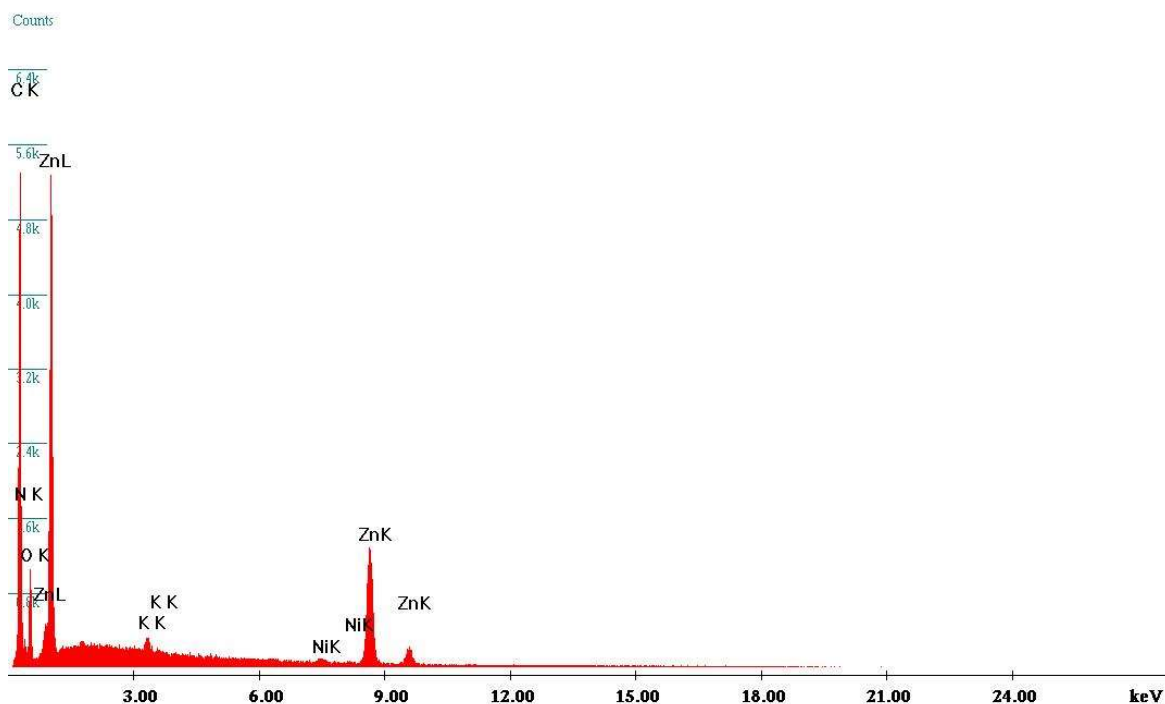


Figure S30 - EDX spectrum of ns245a.

ns253

42.3 mg of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was dissolved in 10 mL of methanol. 590 μL of this solution was taken and diluted with 76 mL of methanol and the rest was discarded. 4 mL of ns243 (60 mg ZIF-8@K-TA) was added to a separate vessel. The diluted $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ solution was added to the ZIF-8@K-TA solution while stirring. After 2 hours of stirring, the stirrer bar was removed and the solutions were centrifuged at 5k rpm for 20 minutes in a swinging bucket rotor to separate out the product. The product was then washed 2 times with methanol and dried overnight under vacuum.

ns256

98.6 mg of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was dissolved in 99 mL of methanol. 3, 3.5, 4, 4.5 and 5 mL of this solution was taken and diluted with 35 mL of methanol in separate vessels labelled a, b, c, d and e respectively. The rest of the solution was discarded. 2 mL of ns243 (30 mg ZIF-8@K-TA) was added to 5 separate vessels. Solutions a, b, c, d and e were added to ns243 solutions while stirring and labelled ns256a, ns256b, ns256c, ns256d and ns256e respectively. After 2 hours of stirring, the stirrer bar was removed and the solutions were centrifuged at 5k rpm for 20 minutes in a swinging bucket rotor to separate out the product.

The product was then washed 2 times with methanol and dried overnight under vacuum. The product was ground lightly with a spatula to create a powder.

Palladium

ns251

2 portions of 4 mL of ns243 (60 mg ZIF-8@K-TA) were washed with tetrahydrofuran 2 times before dispersing in 4 mL of tetrahydrofuran. 6.8 mg of palladium acetate was dissolved in 6.8 mL of tetrahydrofuran by sonication. 900 μ L and 1.4 mL of this solution were distributed into 2 fresh round bottom flasks, labelled a and b respectively. 74 mL of tetrahydrofuran was added to each. Solutions a and b were added to the ZIF-8@K-TA solutions while stirring and were labelled ns251a and ns251b respectively. After 2 hours of stirring, the stirrer bar was removed and the solutions were centrifuged at 5k rpm for 20 minutes in a swinging bucket rotor to separate out the product. The product was then washed 2 times with tetrahydrofuran and dried overnight under vacuum. The product was ground lightly with a spatula to create a powder.

ns254

0.9 mg of palladium acetate was dissolved in 3.6 mL of tetrahydrofuran by sonication. 0.8 mL and 1.6 mL of this solution were distributed into 2 fresh round bottom flasks, labelled a and b respectively. 75 mL of tetrahydrofuran was added to each. 4 mL of ns243 stored in THF (85.2 mg ZIF-8@K-TA) was added to 2 separate vessels. Solutions a and b were added to the ZIF-8@K-TA solutions while stirring and were labelled ns254a and ns254b respectively. After 2 hours of stirring, the stirrer bar was removed and the solutions were centrifuged at 5k rpm for 20 minutes in a swinging bucket rotor to separate out the product. The product was then washed 2 times with tetrahydrofuran and dried overnight under vacuum. The product was ground lightly with a spatula to create a powder.

ns258

7.0 mg of palladium acetate was dissolved in 35 mL of tetrahydrofuran by sonication. 740 μ L and 810 μ L of this solution were distributed into 2 fresh round bottom flasks, labelled a and b respectively. 38 mL of tetrahydrofuran was added to each. 2 mL of ns243 stored in THF (42.6 mg ZIF-8@K-TA) was added to 2 separate vessels. Solutions a and b were added

to the ZIF-8@K-TA solutions while stirring and were labelled ns254a and ns254b respectively. After 2 hours of stirring, the stirrer bar was removed and the solutions were centrifuged at 8k rpm for 5 minutes in a fixed angle rotor to separate out the product. The product was then washed 2 times with tetrahydrofuran and dried overnight under vacuum. The product was ground lightly with a spatula to create a powder.

ns260

14.8 mg of palladium acetate was dissolved in 50 mL of tetrahydrofuran by sonication. 10.92 mL of this solution was taken into a fresh vessel and the rest discarded. 750 mL of tetrahydrofuran was added. 40 mL of ns243 stored in THF (852 mg ZIF-8@K-TA) was added to a fresh vessel. The palladium acetate solution was added to the ZIF-8@K-TA solution while stirring. After 2 hours of stirring, the stirrer bar was removed and the solutions were centrifuged at 5k rpm for 10 minutes in a swinging bucket rotor to separate out the product. The product was then washed 2 times with tetrahydrofuran and dried overnight under vacuum. The product was ground lightly with a mortar and pestle to create a powder.

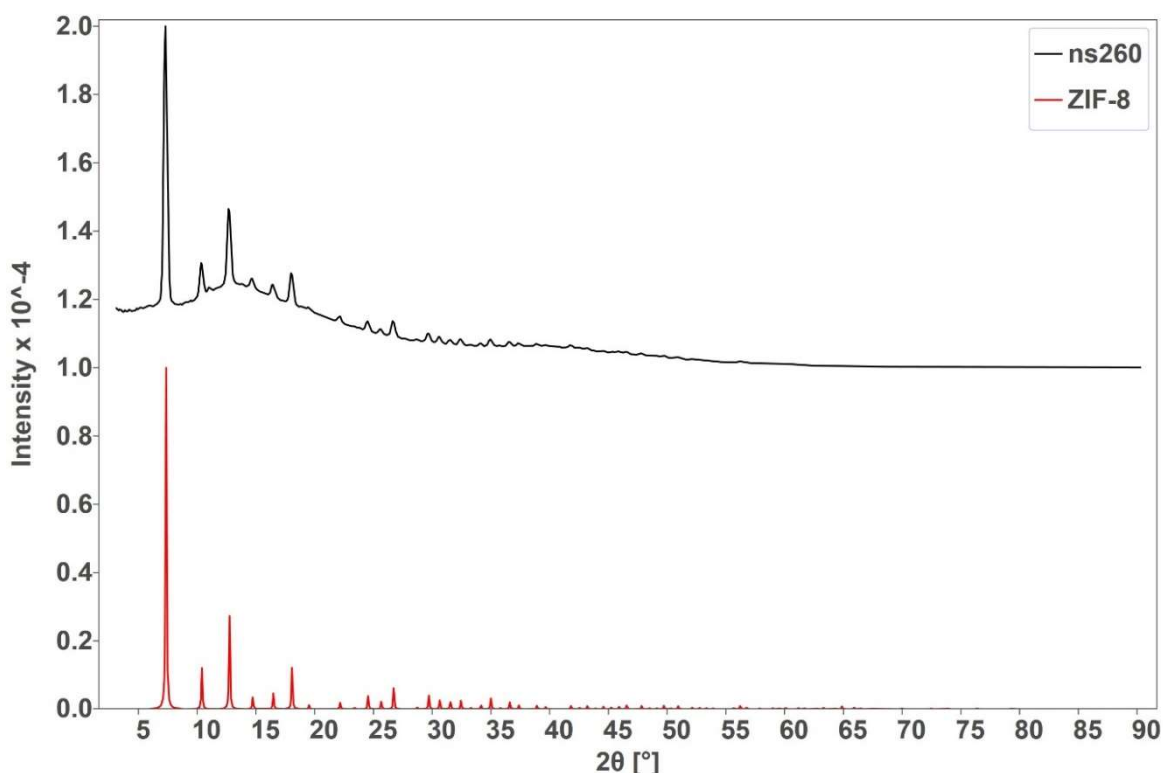


Figure S31 - PXRD pattern of ns260 compared to simulated ZIF-8.

5.0 mg of palladium acetate was dissolved in 50 mL of tetrahydrofuran by sonication. 1.86 mL and 2.73 mL of this solution were distributed into 2 fresh round bottom flasks, labelled a and b respectively. 38 mL of tetrahydrofuran was added to each. 2 mL of ns264 (52.4 mg ZIF-8@K-TA) was added to 2 separate vessels. Solutions a and b were added to the ZIF-8@K-TA solutions while stirring and were labelled ns260a and ns260b respectively. After 2 hours of stirring, the stirrer bar was removed and the solutions were centrifuged at 5k rpm for 10 minutes in a swinging bucket rotor to separate out the product. The product was then washed 2 times with tetrahydrofuran and dried overnight under vacuum. The product was ground lightly with a spatula to create a powder.

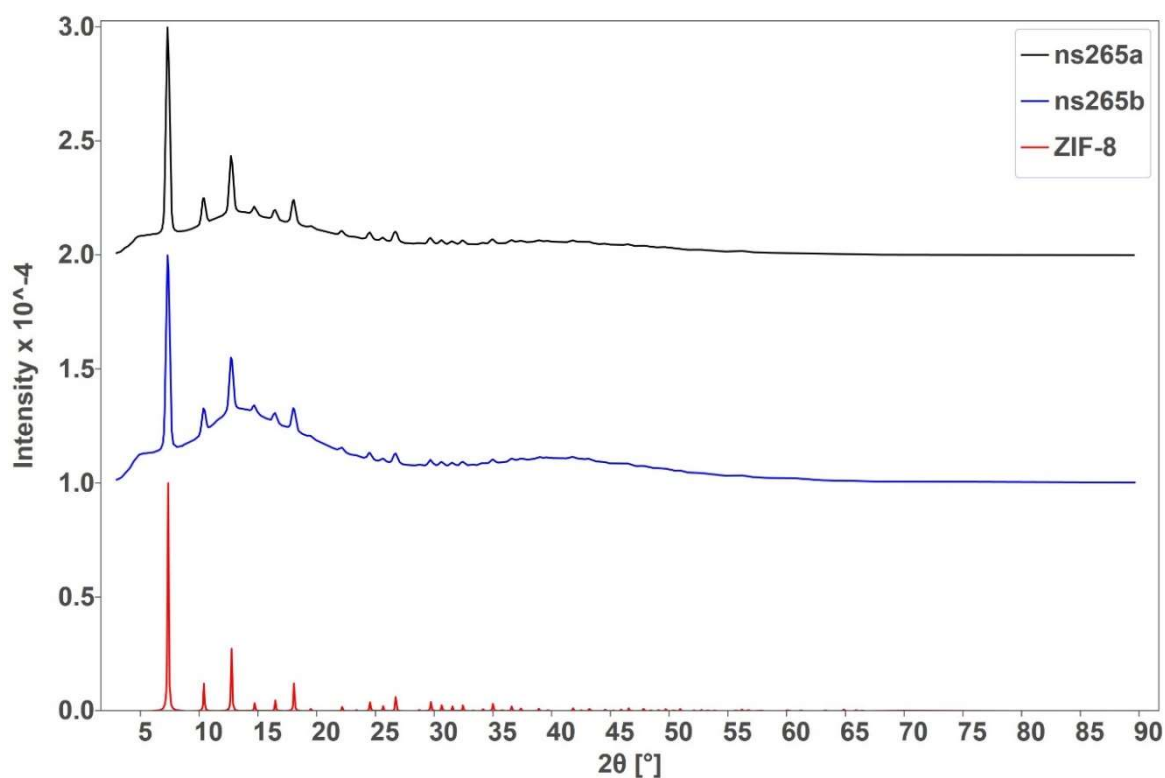


Figure S32 - PXRD pattern of ns265a and ns265b compared to simulated ZIF-8.

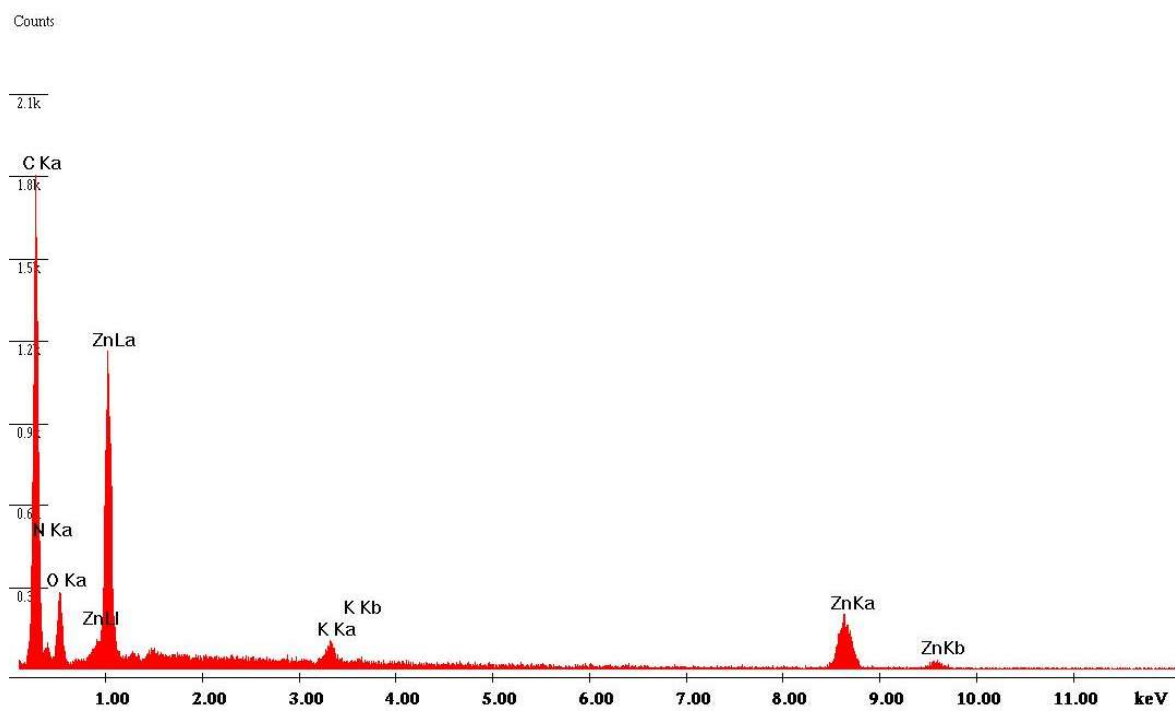


Figure S33 - EDX spectrum of ns256a.

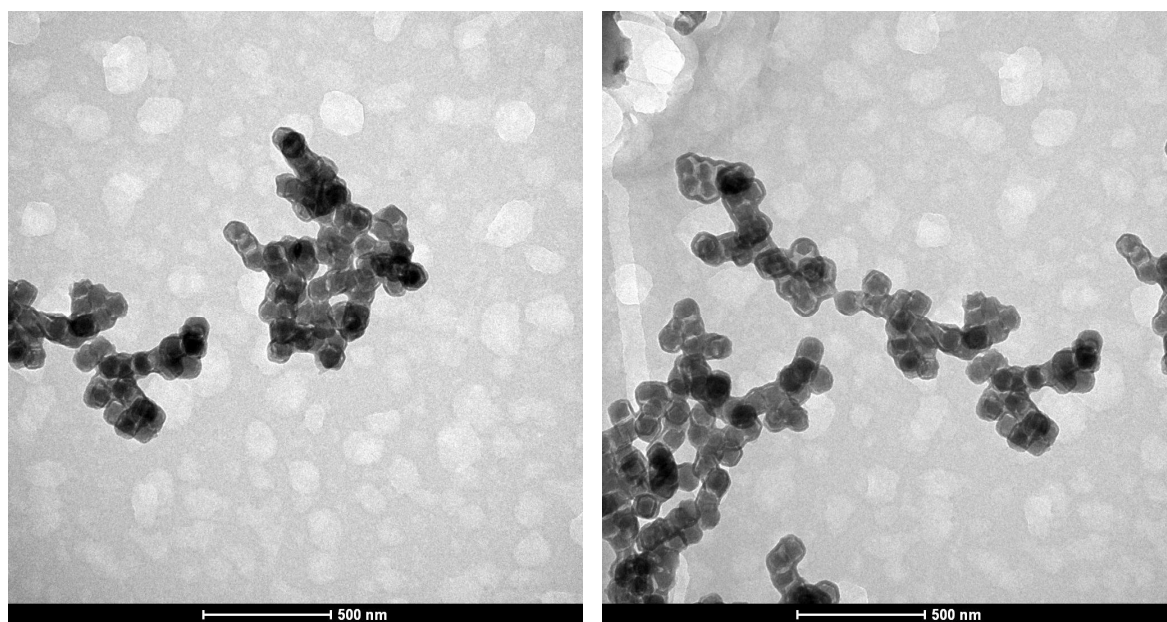


Figure S34 - TEM images of ns265a.

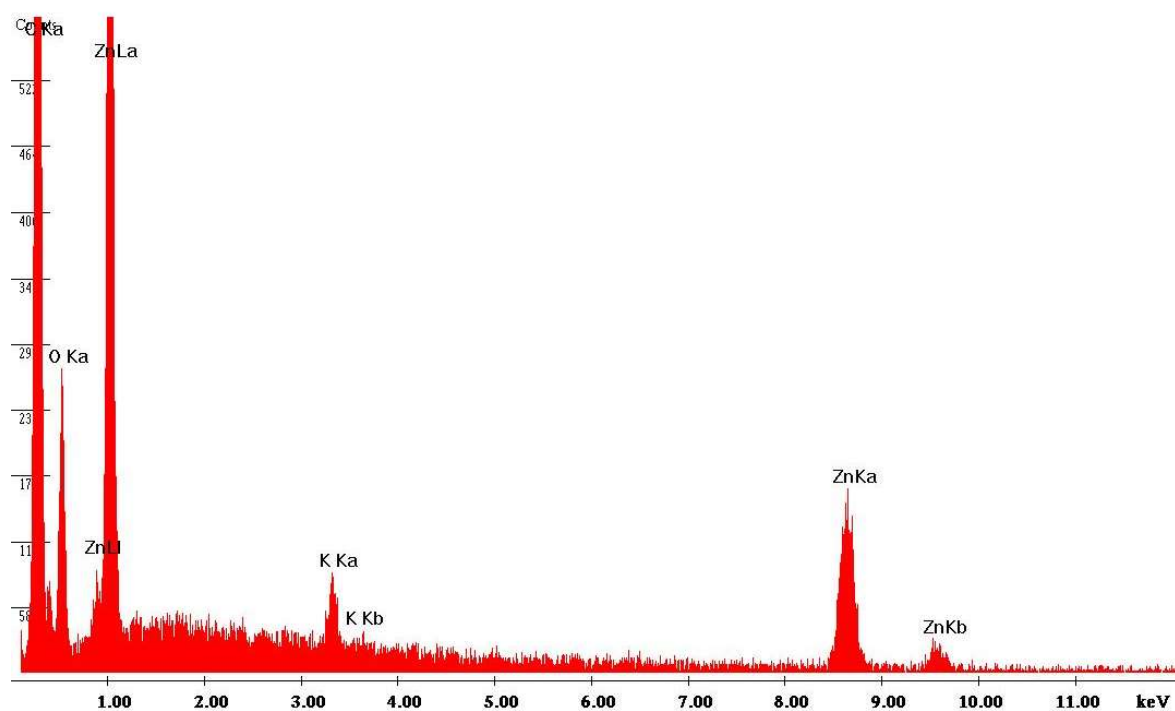


Figure S35 - EDX spectrum of ns256b.

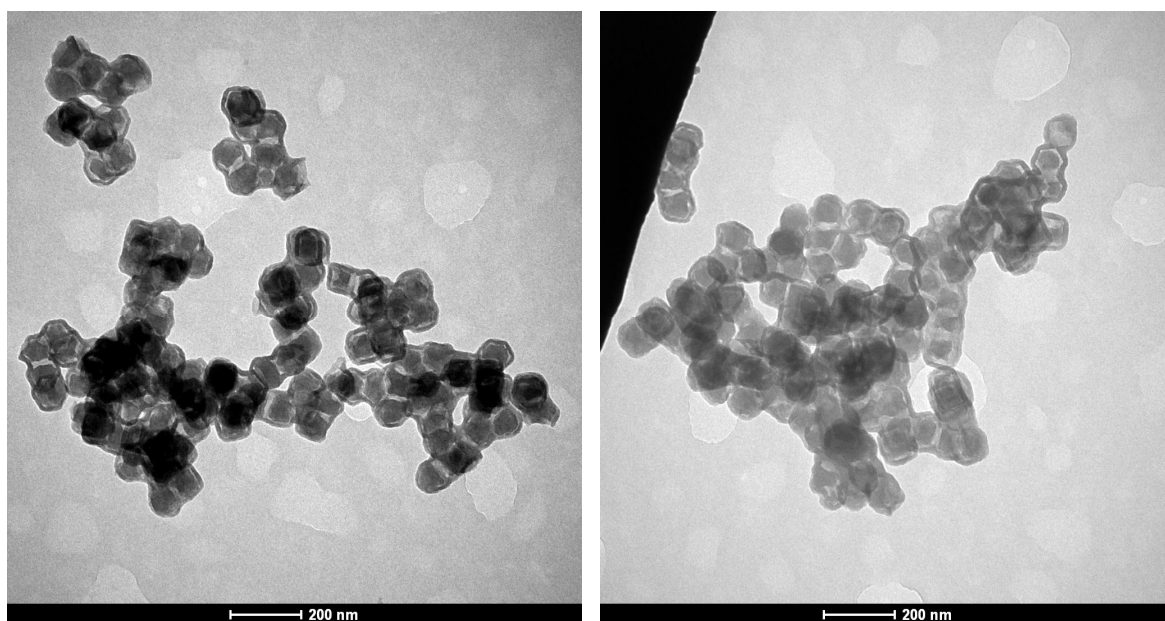


Figure S36 - TEM images of ns265b.

ns266

7.9 mg of palladium acetate was dissolved in 3 mL of tetrahydrofuran by sonication. 1.34 mL of this solution taken into a fresh vessel and the rest discarded. 940 mL of tetrahydrofuran added. 40 mL of ns264 (1048 mg ZIF-8@K-TA) added to a fresh vessel.

The palladium acetate solution was added to the ZIF-8@K-TA solution while stirring. After 2 hours of stirring, the stirrer bar was removed and the solutions were centrifuged at 5k rpm for 10 minutes in a swinging bucket rotor to separate out the product. The product was then washed 3 times with tetrahydrofuran and dried overnight under vacuum. The product was ground lightly with a mortar and pestle to create a powder. TEM images are shown in the main text.

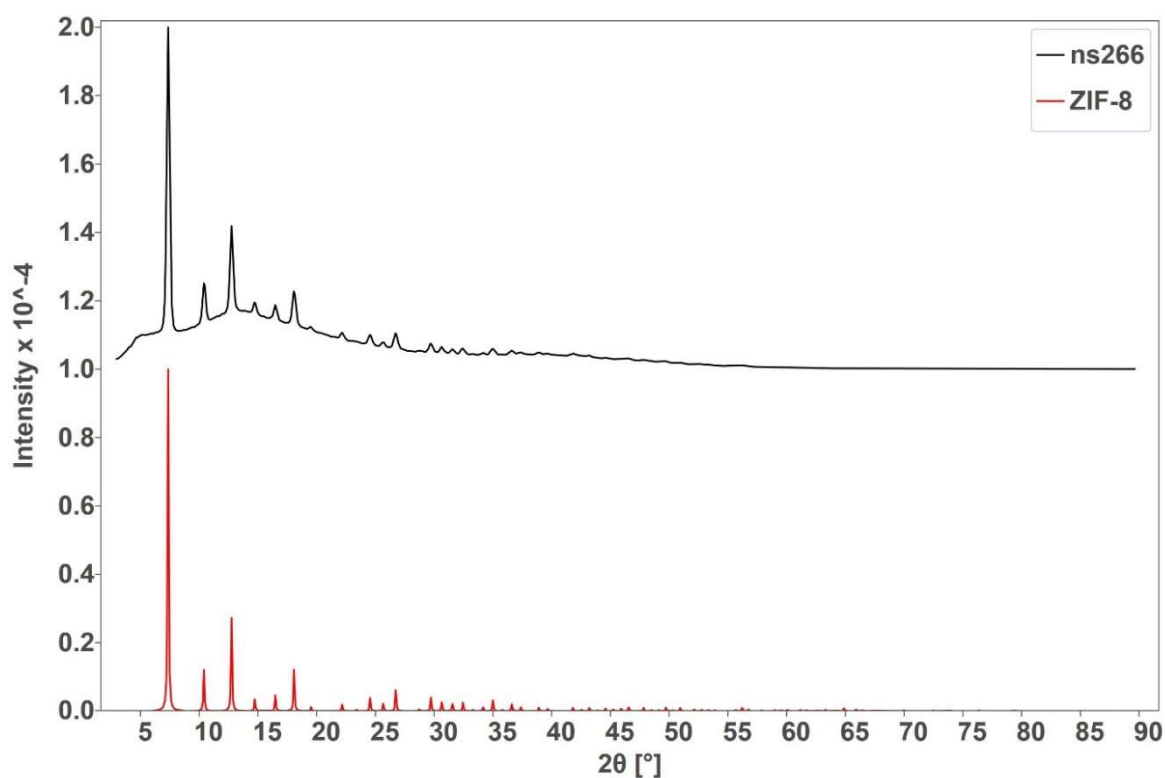


Figure S37 - PXRD pattern of ns266 compared to simulated ZIF-8.

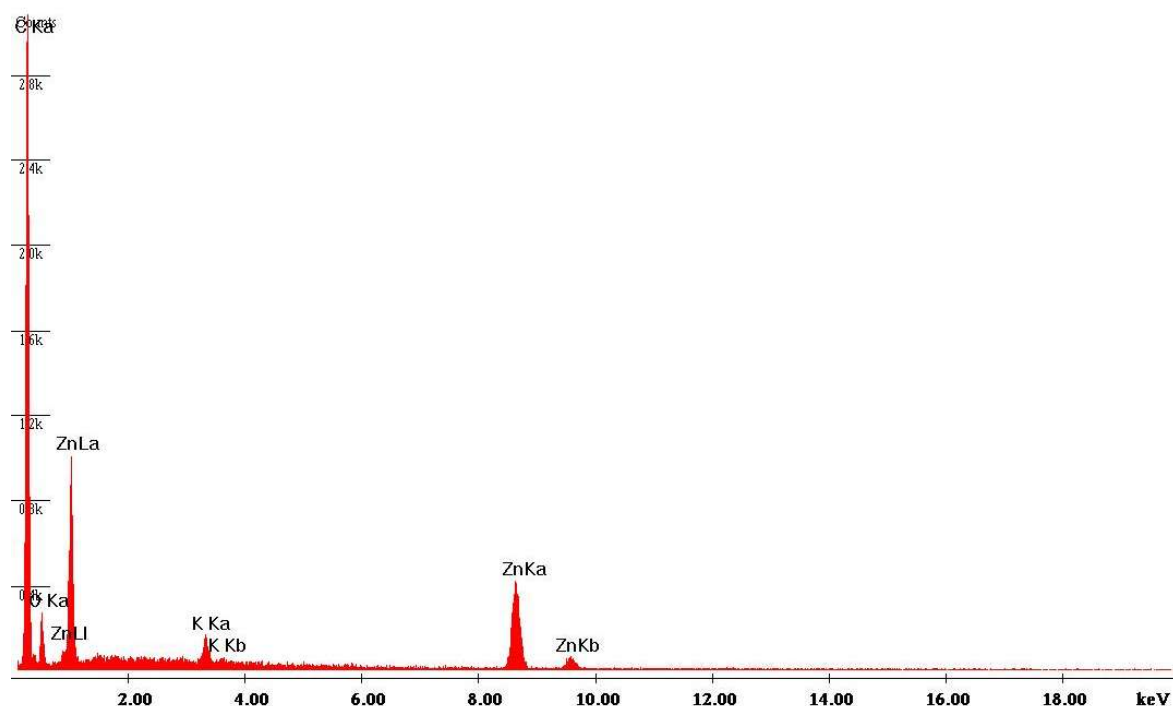


Figure S38 - EDX spectrum of ns266.

ns269

4.0 mg of palladium acetate was dissolved in 5 mL of tetrahydrofuran by sonication. 4.4 mL of this solution taken into a fresh vessel and the rest discarded. 940 mL of tetrahydrofuran added. 40 mL of ns264 (1048 mg ZIF-8@K-TA) added to a fresh vessel. The palladium acetate solution was added to the ZIF-8@K-TA solution while stirring. After 2 hours of stirring, the stirrer bar was removed and the solutions were centrifuged at 5k rpm for 10 minutes in a swinging bucket rotor to separate out the product. The product was then washed 3 times with tetrahydrofuran and dried overnight under vacuum. The product was ground lightly with a mortar and pestle to create a powder.

ns274

5.5 mg of palladium acetate was dissolved in 17 mL of tetrahydrofuran by sonication. 2.2 mL, 3.6 mL and 5.0 mL of this solution were distributed into 3 fresh round bottom flasks, labelled a, b and c respectively. 74, 73 and 71 mL of tetrahydrofuran was added respectively. 4 mL of ns264 (104.8 mg ZIF-8@K-TA) was added to 3 separate vessels. Solutions a, b and c were added to the ZIF-8@K-TA solutions while stirring and were labelled ns274a, ns274b and ns274c respectively. After 2 hours of stirring, the stirrer bar was removed and the

solutions were centrifuged at 5k rpm for 10 minutes in a swinging bucket rotor to separate out the product. The product was then washed 2 times with tetrahydrofuran and dried overnight under vacuum. The product was ground lightly with a spatula to create a powder.

Pyrolysis

Samples that were pyrolyzed before the second furnace arrived were simply named after their precursor. This follows the structure: [precursor]p. The 'p' after the precursor name stands for pyrolysis. These samples were pyrolyzed in a steel tube with Teflon seals as there were no quartz tubes available. After the second furnace arrived it was necessary to distinguish between the 2 furnaces easily, hence the furnace that was already here was named 'Y' and the new furnace was named 'X'. From then on product samples from pyrolysis were named by their precursor, the furnace it was pyrolyzed in and the date on which they were synthesized. This follows the structure: [precursor]p_[furnace]_[date]. Along with the new furnace, quartz tubes that fit both the old furnace and new furnace arrived. These were implemented as soon as they arrived. Therefore, it can be seen from the sample naming structure whether the sample was pyrolyzed in a steel or quartz tube as samples pyrolyzed in the steel tube will not have the furnace or date included in the sample name.

Iron

ns135

Sample ns134 was loaded into a ceramic crucible and inserted into the steel tube of 'furnace Y'. The tube was sealed with fresh Teflon seals. The tube was purged for 1 hour at a flow rate of 3 L/m of argon zero. The temperature of the furnace was raised to 900°C over 900 minutes and held at 900°C for 2 hours. TEM image and PXRD pattern shown in main text.

Cobalt

ns244p

Sample ns244pa was loaded into a ceramic crucible and inserted into the steel tube of 'furnace Y'. The tube was sealed with fresh Teflon seals. The tube was purged for 15 minutes at a flow rate of 12 L/m of argon zero. The flow rate was then lowered to 4 L/m and the temperature of the furnace was raised to 900°C at a rate of 5°C/m and held at 900°C for 2 hours.

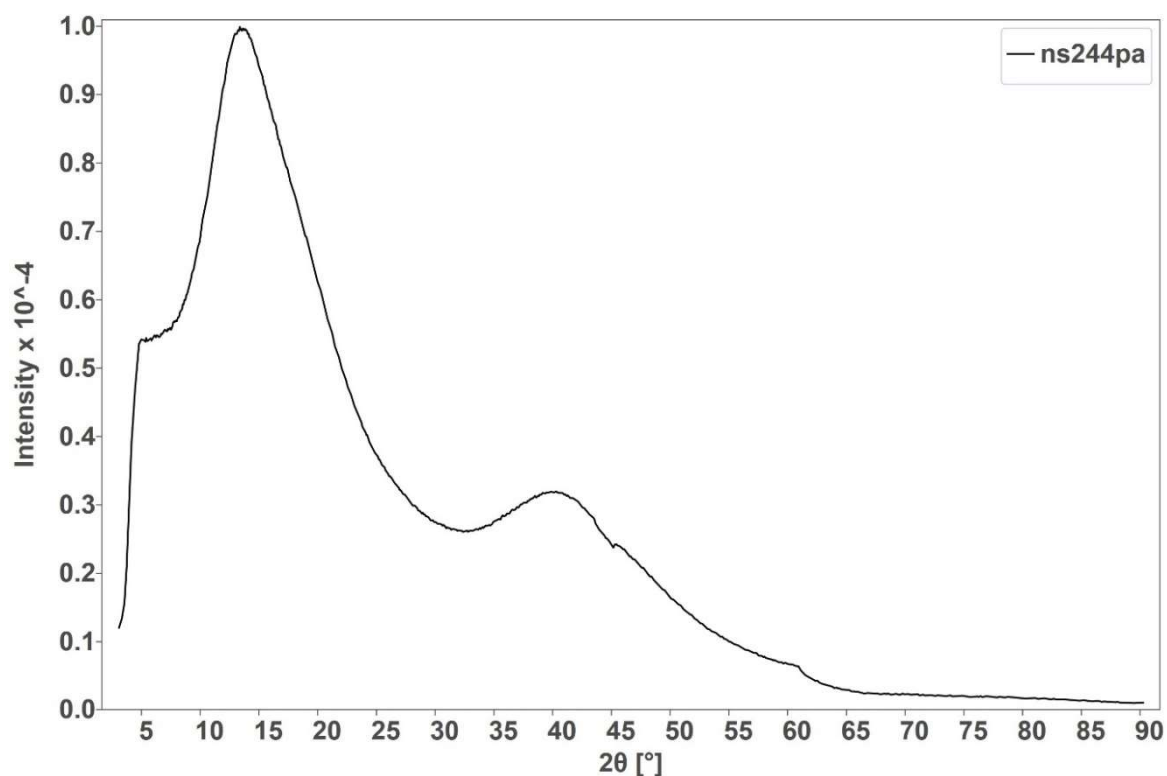


Figure S39 - PXRD pattern of ns244pa. Sample is completely amorphous.

Sample ns244pb was loaded into a ceramic crucible and inserted into the steel tube of ‘furnace Y’. The tube was sealed with fresh Teflon seals. The tube was purged for 15 minutes at a flow rate of 12 L/m of argon zero. The flow rate was then lowered to 4 L/m and the temperature of the furnace was raised to 900°C at a rate of 5°C/m and held at 900°C for 2 hours.

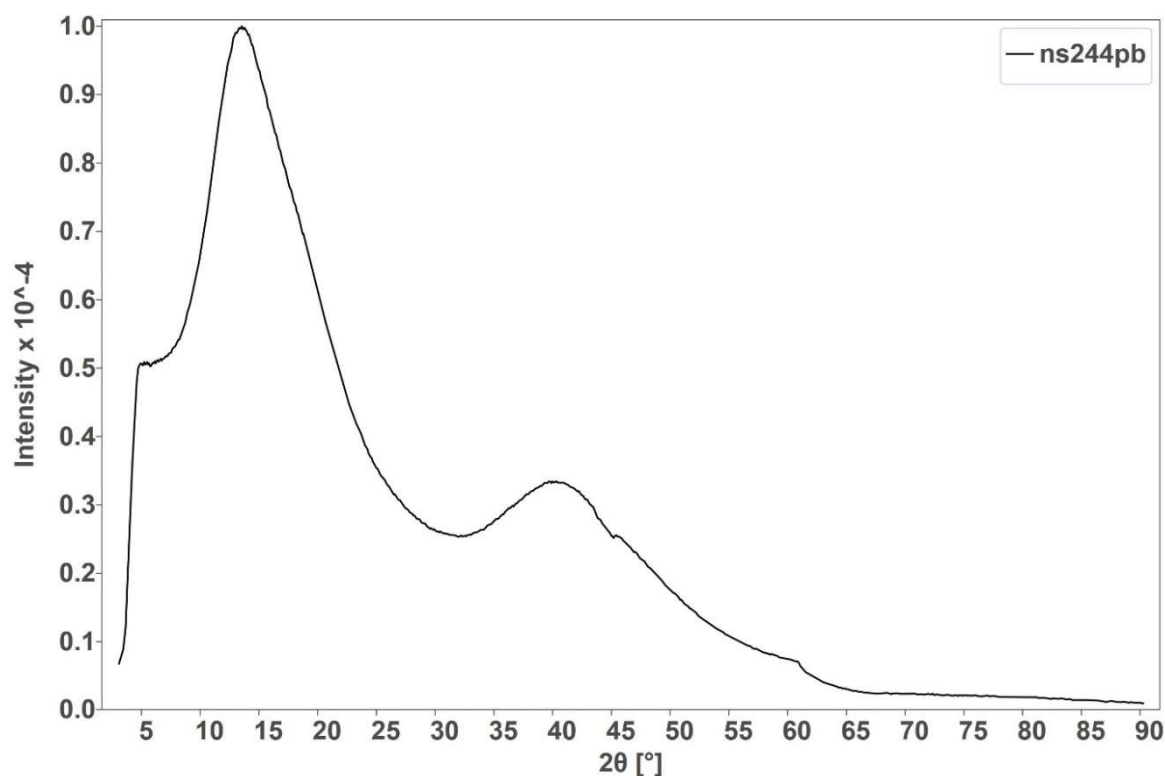


Figure S40 - PXRD pattern of ns244pb. Sample is completely amorphous.

ns252p

Sample ns252 was pyrolyzed 2 times, once purging by a set flow for a set time and once by purge/vac cycling (see purge/vac cycling description under Pyrolysis heading on page 32).

Sample ns252 was loaded into a ceramic crucible and inserted into the quartz tube of furnace X. The insulation blocks were inserted and the tube was sealed. The tube was purged for 25 minutes at a flow rate 12 L/m of argon zero. The flow was then lowered to 4 L/m and the temperature of the furnace was raised to 900°C over 3 hours and held at 900°C for 2 hours. The temperature was controlled down to 500°C over 80 minutes. This sample was labelled ns252p_X_23/6. PXRD pattern shown in the main text.

Sample ns252 was loaded into a ceramic crucible and inserted into the quartz tube of furnace X. The insulation blocks were inserted and the tube was sealed. The tube was purged by purge/vac cycling 3 times using argon zero. The flow was then set to 4 L/m and the temperature of the furnace was raised to 900°C over 3 hours and held at 900°C for 2 hours. The temperature was controlled down to 500°C over 80 minutes. This sample was labelled ns252p_X_25/6. The PXRD pattern is shown in the main text.

ns255p

Sample ns255e was loaded into a ceramic crucible and inserted into the quartz tube of furnace X. The insulation blocks were inserted and the tube was sealed. The tube was purged by purge/vac cycling 3 times using argon zero. The flow was then set to 2 L/m and the temperature of the furnace was raised to 900°C over 3 hours and held at 900°C for 2 hours. The temperature was controlled down to 500°C over 80 minutes. This sample was labelled ns255pe_X_1/7.

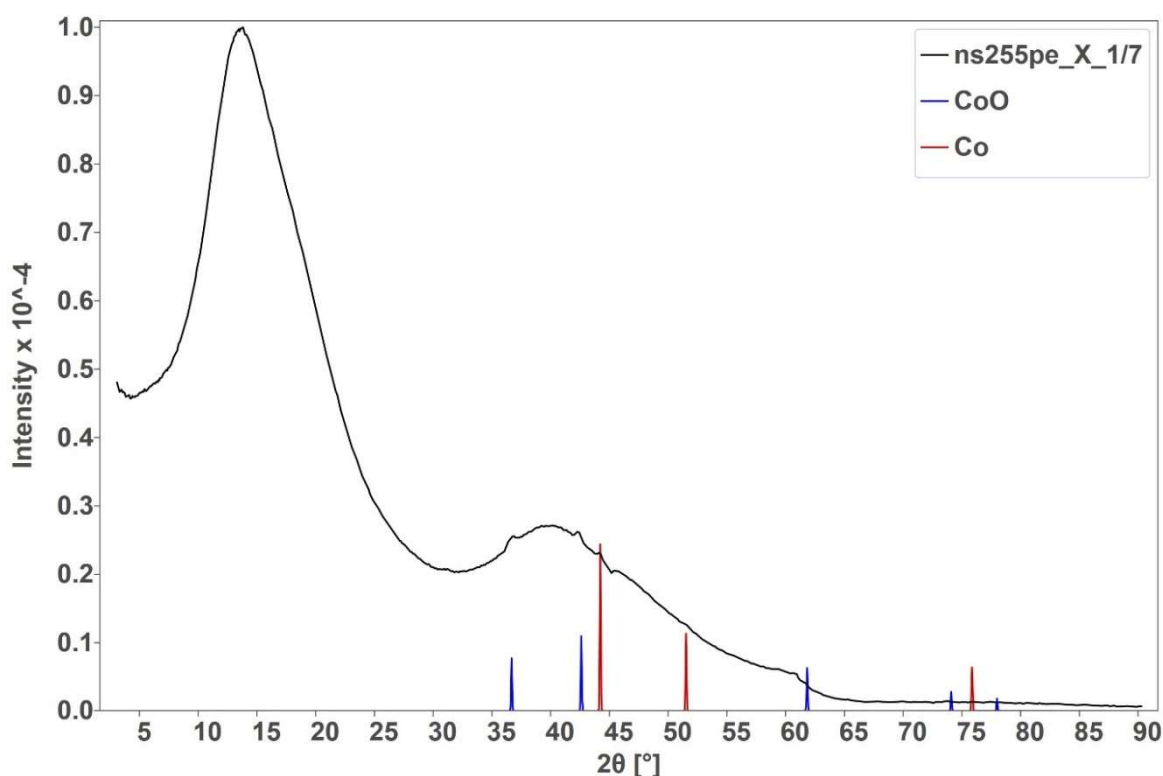


Figure S41 - PXRD pattern of ns255pe_X_1/7 compared to simulated cobalt oxide (CoO)^[7] and cobalt metal (Co)^[8]. Crystalline peaks are apparent in the PXRD pattern of ns255pe_X_1/7.

Sample ns255e was loaded into a ceramic crucible and inserted into the quartz tube of furnace X. The insulation blocks were inserted and the tube was sealed. The gas line from the cylinder to the inlet valve was purged by flowing argon zero through the line for 10 minutes. The tube was purged by purge/vac cycling 3 times using argon zero. The flow was then set to 2 L/m and the temperature of the furnace was raised to 900°C over 300 minutes and held at 900°C for 3 hours. The temperature was controlled down to 500°C over 80 minutes. This sample was labelled ns255pe_X_5/7.

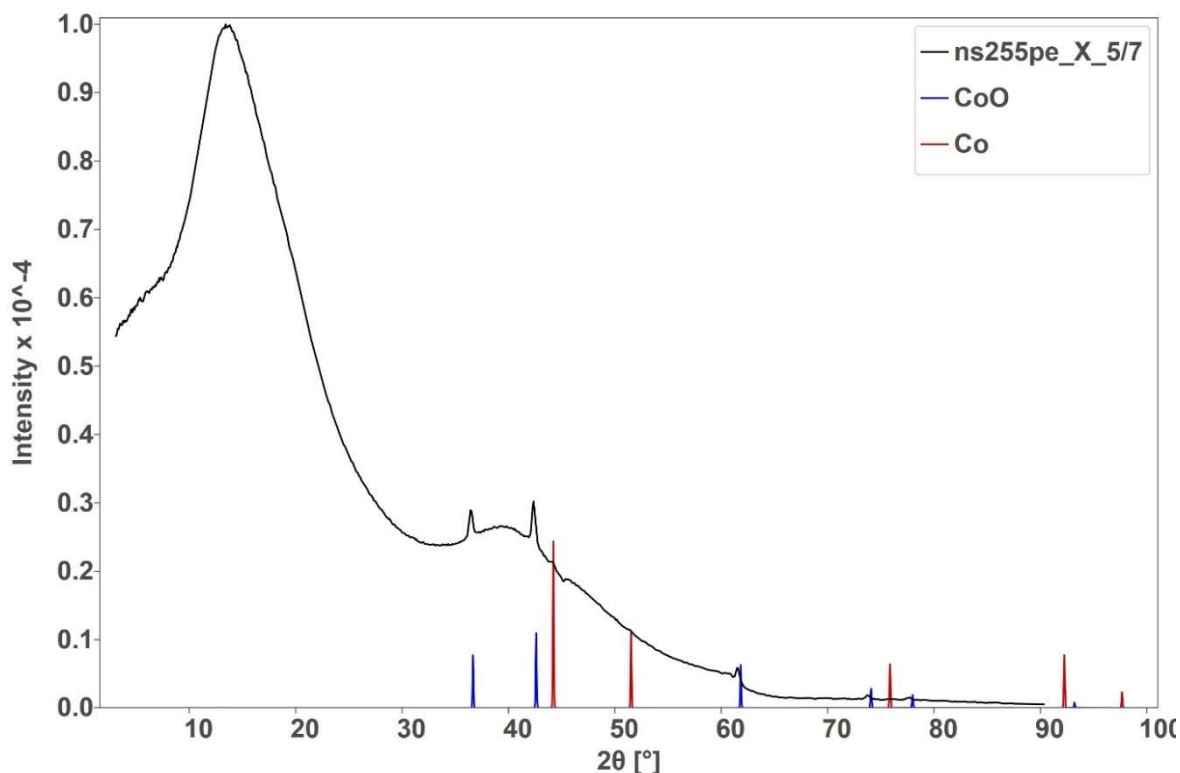


Figure S42 - PXRD pattern of ns255pe_X_5/7 compared to simulated cobalt oxide (CoO)^[7] and cobalt metal (Co)^[8]. Crystalline peaks are apparent in the PXRD pattern of ns255pe_X_5/7.

Sample ns255c was loaded into a ceramic crucible and inserted into the quartz tube of furnace X. The insulation blocks were inserted and the tube was sealed. The gas line from the cylinder to the inlet valve was purged by flowing argon zero through the line for 10 minutes. The tube was purged by purge/vac cycling 3 times using argon zero. The flow was then set to 2 L/m and the temperature of the furnace was raised to 900°C over 300 minutes and held at 900°C for 3 hours. The temperature was controlled down to 500°C over 80 minutes. This sample was labelled ns255pc_X_6/7.

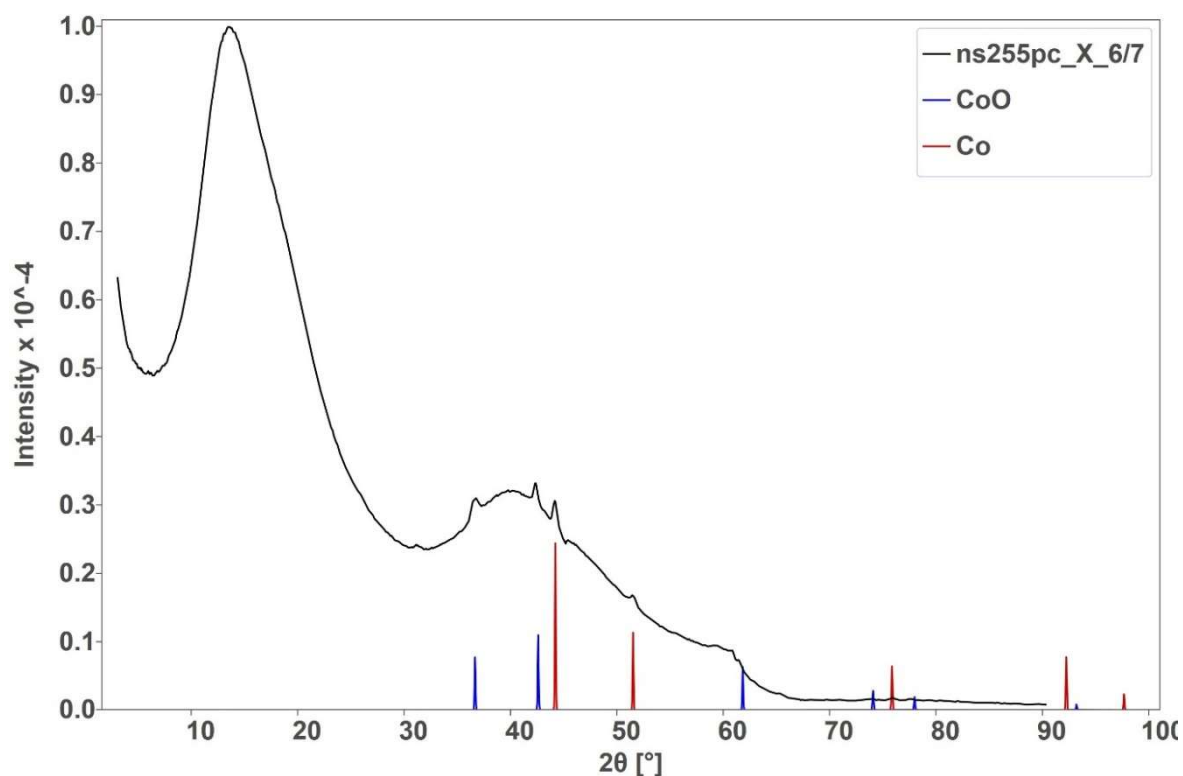


Figure S43 - PXRD pattern of ns255pc_X_6/7 compared to simulated cobalt oxide (CoO)^[7] and cobalt metal (Co)^[8]. Crystalline peaks are apparent in the PXRD pattern of ns255pc_X_6/7.

Sample ns255e was loaded into a ceramic crucible and inserted into the quartz tube of furnace X. The insulation blocks were inserted and the tube was sealed. The tube was purged by purge/vac cycling 5 times using argon zero. The flow was then set to 2 L/m and the temperature of the furnace was raised to 900°C over 3 hours and held at 900°C for 2 hours. The temperature was controlled down to 500°C over 80 minutes. This sample was labelled ns255pe_X_7/7.

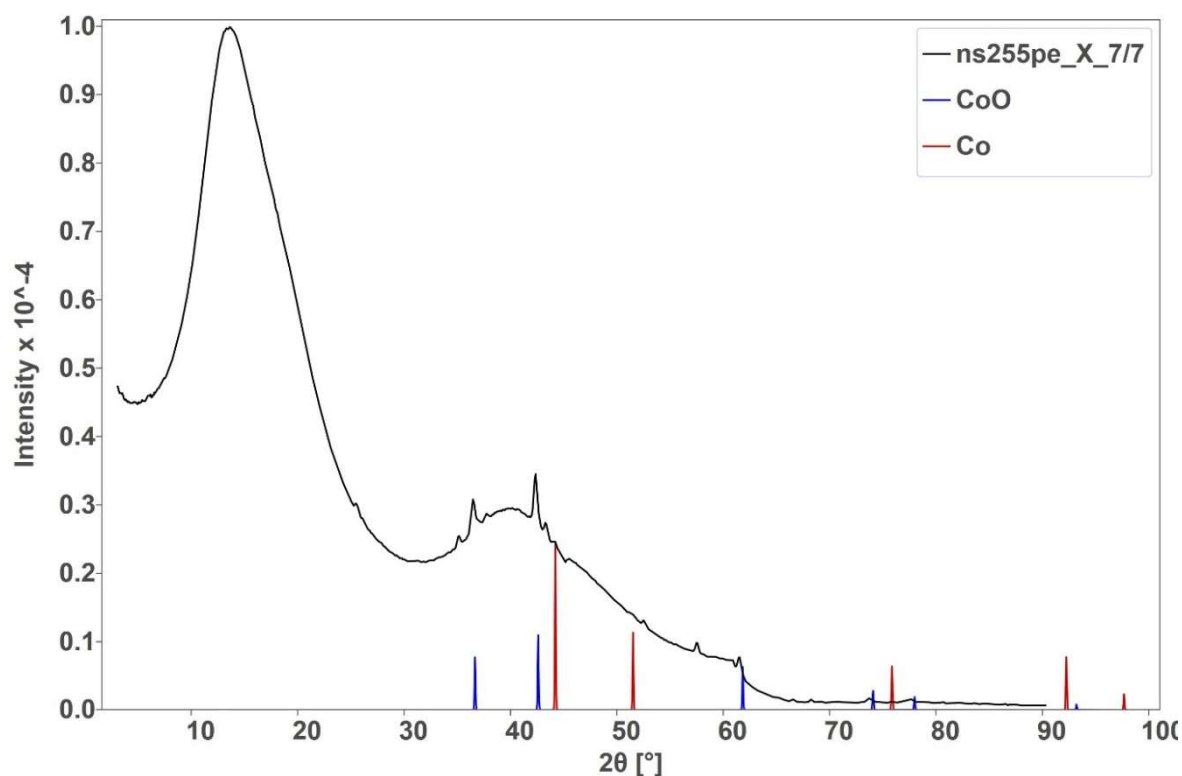


Figure S44 - PXRD pattern of ns255pe_X_7/7 compared to simulated cobalt oxide (CoO)^[7] and cobalt metal (Co)^[8]. Crystalline peaks are apparent in the PXRD pattern of ns255pe_X_7/7. Peaks are present that are unable to be attributed to any known materials.

Sample ns255e was loaded into a ceramic crucible and inserted into the quartz tube of furnace X. The insulation blocks were inserted and the tube was sealed. The tube was purged by purge/vac cycling 3 times using argon zero. The flow was then set to 1 L/m and the temperature of the furnace was raised to 900°C over 3 hours and held at 900°C for 2 hours. The temperature was controlled down to 500°C over 80 minutes. This sample was labelled ns255pe_X_9/7.

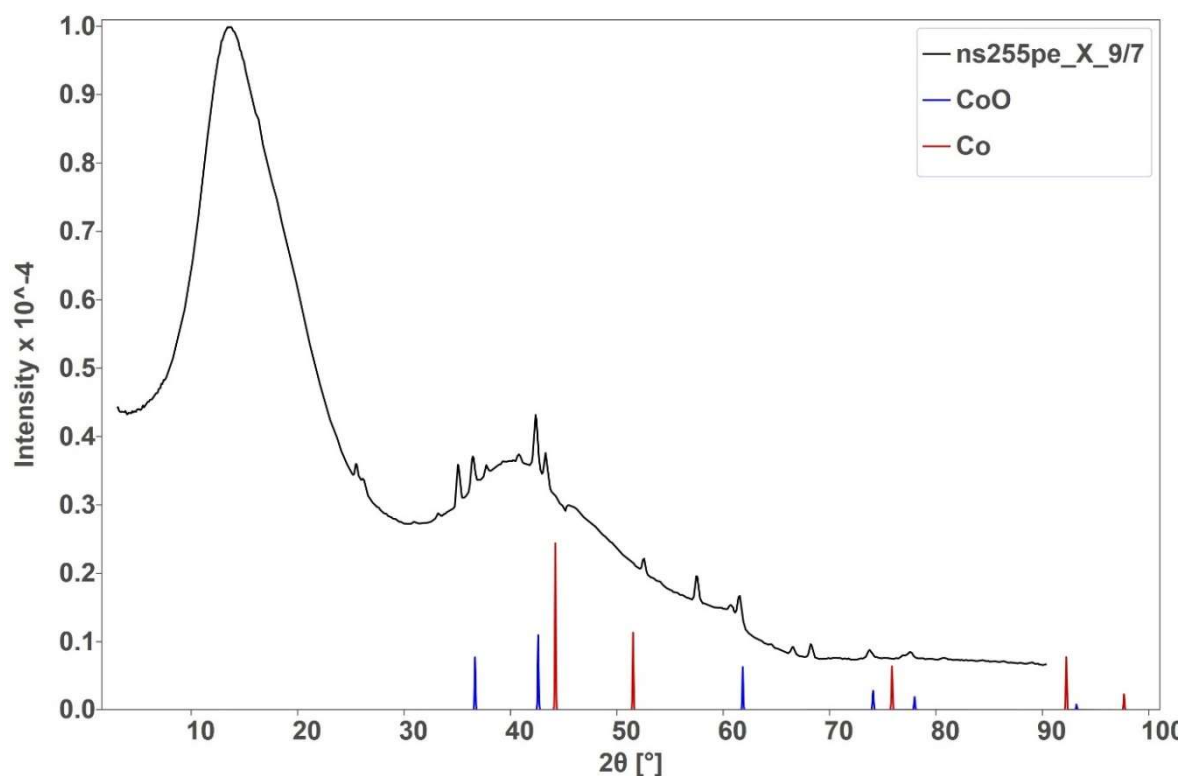


Figure S45 - PXRD pattern of ns255pe_X_9/7 compared to simulated cobalt oxide (CoO)^[7] and cobalt metal (Co)^[8]. Crystalline peaks are apparent in the PXRD pattern of ns255pe_X_9/7. Peaks are present that are unable to be attributed to any known materials.

Sample ns255d was loaded into a ceramic crucible and inserted into the quartz tube of furnace X. The insulation blocks were inserted and the tube was sealed. The tube was purged by purge/vac cycling 3 times using argon zero. The flow was then set to 1 L/m and the temperature of the furnace was raised to 900°C over 3 hours and held at 900°C for 2 hours. The temperature was controlled down to 500°C over 80 minutes. This sample was labelled ns255pd_X_10/7.

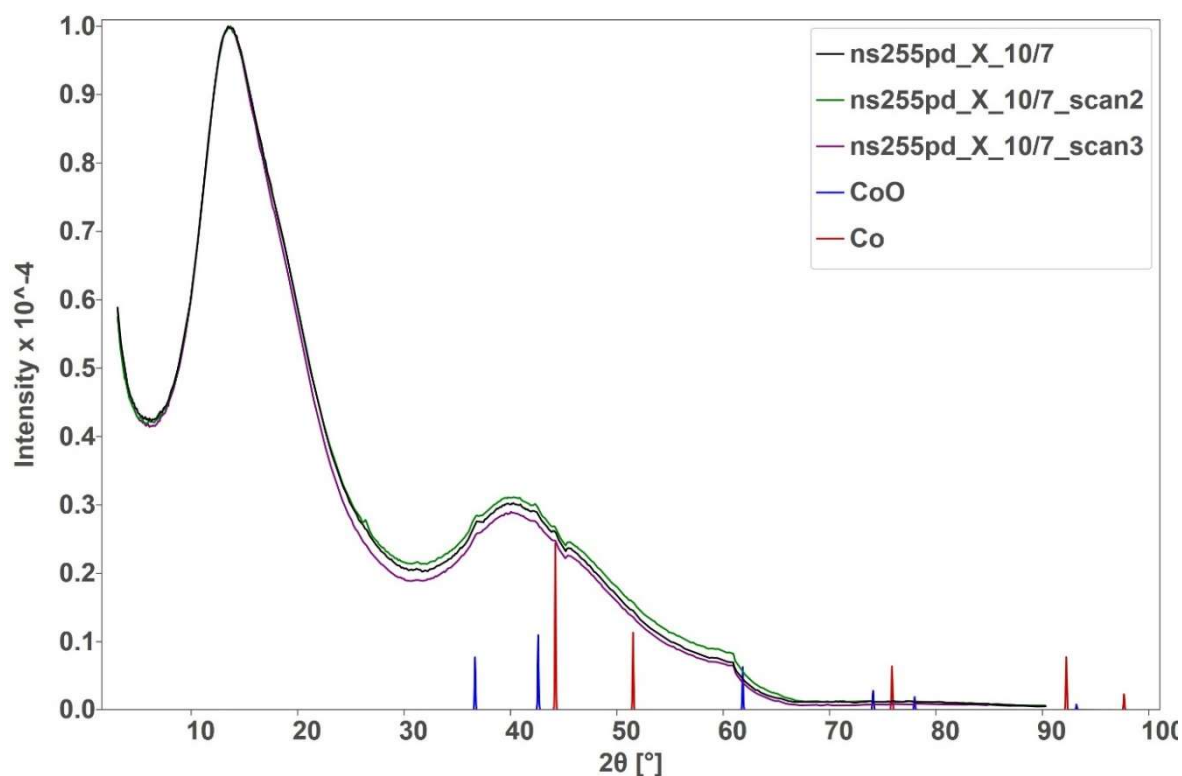


Figure S46 – PXRD patterns of ns255pd_X_10/7 over multiple scans compared to simulated cobalt oxide (CoO)^[7] and cobalt metal (Co)^[8]. Crystalline peaks are apparent in the PXRD pattern of ns255pd_X_10/7.

Sample ns255c was loaded into a ceramic crucible and inserted into the quartz tube of furnace X. The insulation blocks were inserted and the tube was sealed. The tube was purged by purge/vac cycling 3 times using argon zero. The flow was then set to 1 L/m and the temperature of the furnace was raised to 900°C over 3 hours and held at 900°C for 2 hours. The temperature was controlled down to 500°C over 80 minutes. This sample was labelled ns255pc_X_10/7.

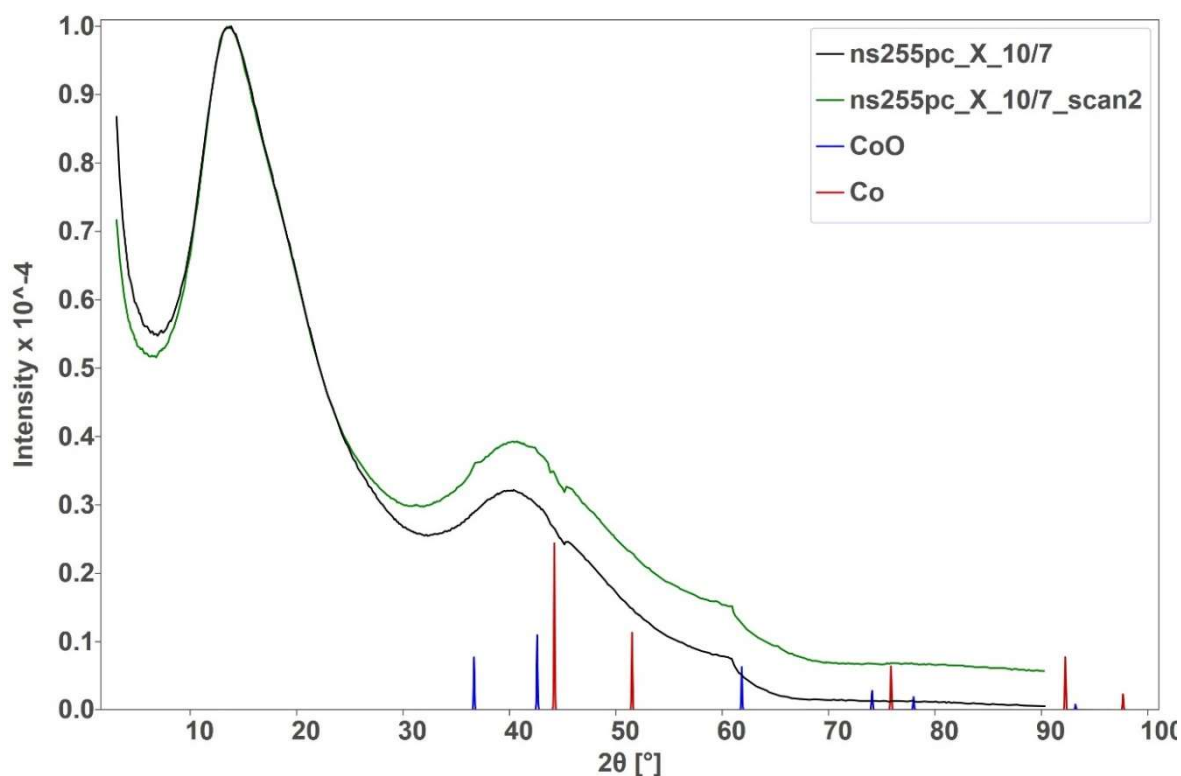


Figure S47 - PXRD patterns of ns255pc_X_10/7 over multiple scans compared to simulated cobalt oxide (CoO)^[7] and cobalt metal (Co)^[8]. Crystalline peaks are apparent in the PXRD pattern of ns255pc_X_10/7.

Nickel

ns245p

Sample ns245pa was loaded into a ceramic crucible and inserted into steel tube of ‘furnace Y’. The tube was sealed with fresh Teflon seals. The tube was purged for 15 minutes at a flow rate of 12 L/m of argon zero. The flow rate was then lowered to 4 L/m and the temperature of the furnace was raised to 900°C at a rate of 5°C/m and held at 900°C for 2 hours. TEM image and EDX spectrum shown in the main text.

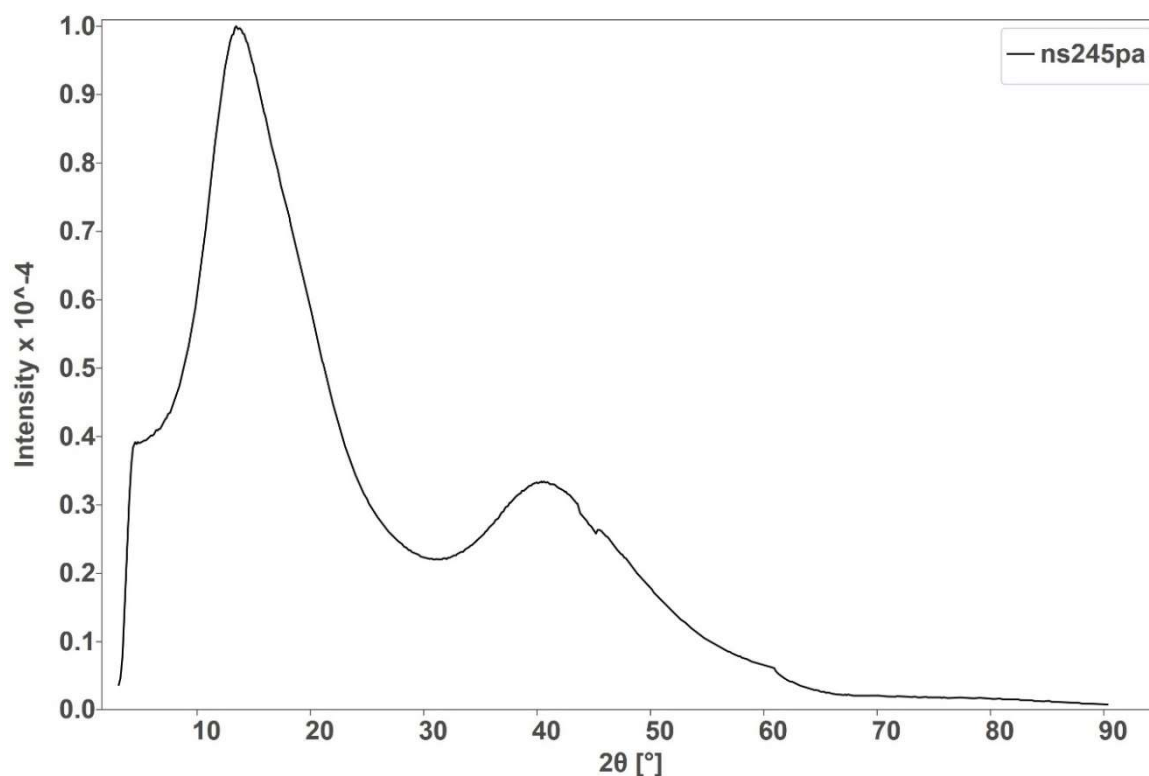


Figure S48 - PXRD pattern of ns245pa. Sample is completely amorphous.

Sample ns245pb was loaded into a ceramic crucible and inserted into steel tube of ‘furnace Y’. The tube was sealed with fresh Teflon seals. The tube was purged for 15 minutes at a flow rate of 12 L/m of argon zero. The flow rate was then lowered to 4 L/m and the temperature of the furnace was raised to 900°C at a rate of 5°C/m and held at 900°C for 2 hours. PXRD shown in the main text.

ns253p

Sample ns253 was pyrolyzed 2 times, once purging by a set flow for a set time and once by purge/vac cycling (see purge/vac cycling description under Pyrolysis heading on page 32).

Sample ns253 was loaded into a ceramic crucible and inserted into the quartz tube of furnace X. The insulation blocks were inserted and the tube was sealed. The tube was purged for 25 minutes at a flow rate 12 L/m of argon zero. The flow was then lowered to 4 L/m and the temperature of the furnace was raised to 900°C over 3 hours and held at 900°C for 2 hours. The temperature was controlled down to 500°C over 80 minutes. This sample was labelled ns253p_X_23/6.

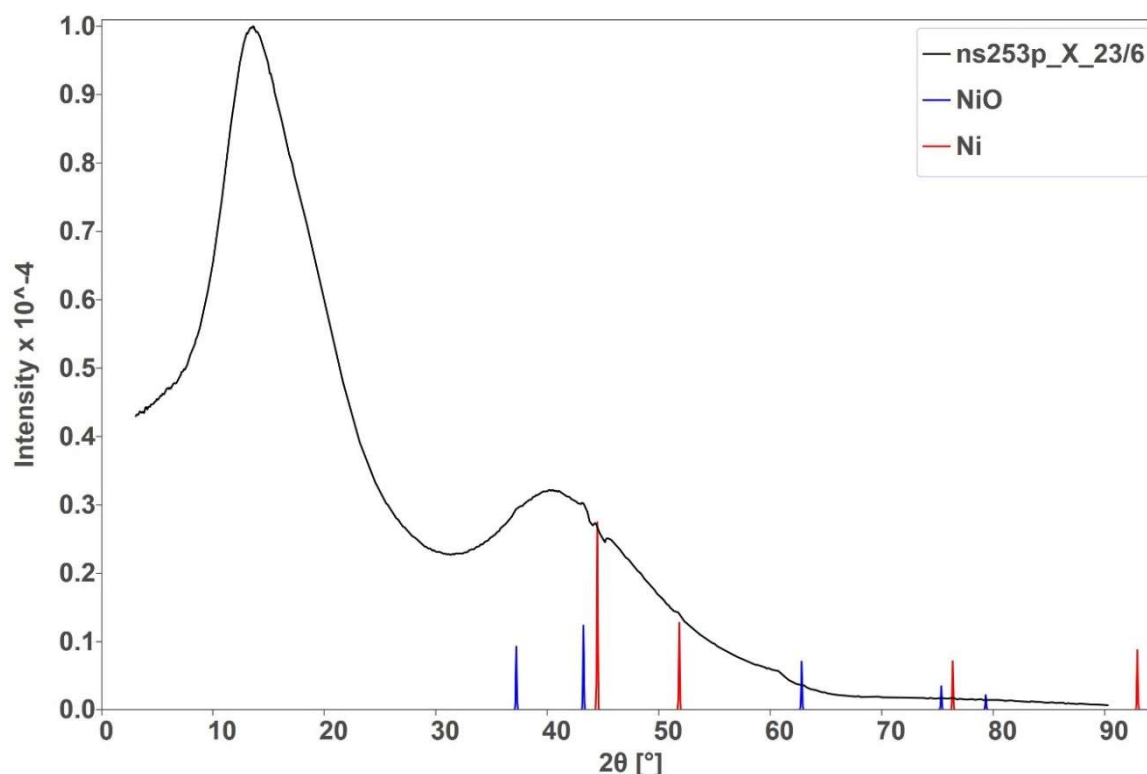


Figure S49 - PXRD pattern of ns253p_X_23/6 compared with simulated nickel oxide (NiO)^[9] and nickel metal (Ni)^[8]. Crystalline peaks are apparent in the PXRD pattern of ns253p_X_23/6.

Sample ns253 was loaded into a ceramic crucible and inserted into the quartz tube of furnace X. The insulation blocks were inserted and the tube was sealed. The tube was purged by purge/vac cycling 3 times using argon zero. The flow was then set to 4 L/m and the temperature of the furnace was raised to 900°C over 3 hours and held at 900°C for 2 hours. The temperature was controlled down to 500°C over 80 minutes. This sample was labelled ns253p_X_25/6. PXRD shown in the main text.

ns256p

Sample ns256e was loaded into a ceramic crucible and inserted into the quartz tube of furnace Y. The insulation blocks were inserted and the tube was sealed. The tube was purged by purge/vac cycling 3 times using argon zero. The flow was then set to 2 L/m and the temperature of the furnace was raised to 900°C over 3 hours and held at 900°C for 2 hours. The temperature was controlled down to 500°C over 80 minutes. This sample was labelled ns256pe_Y_29/6.

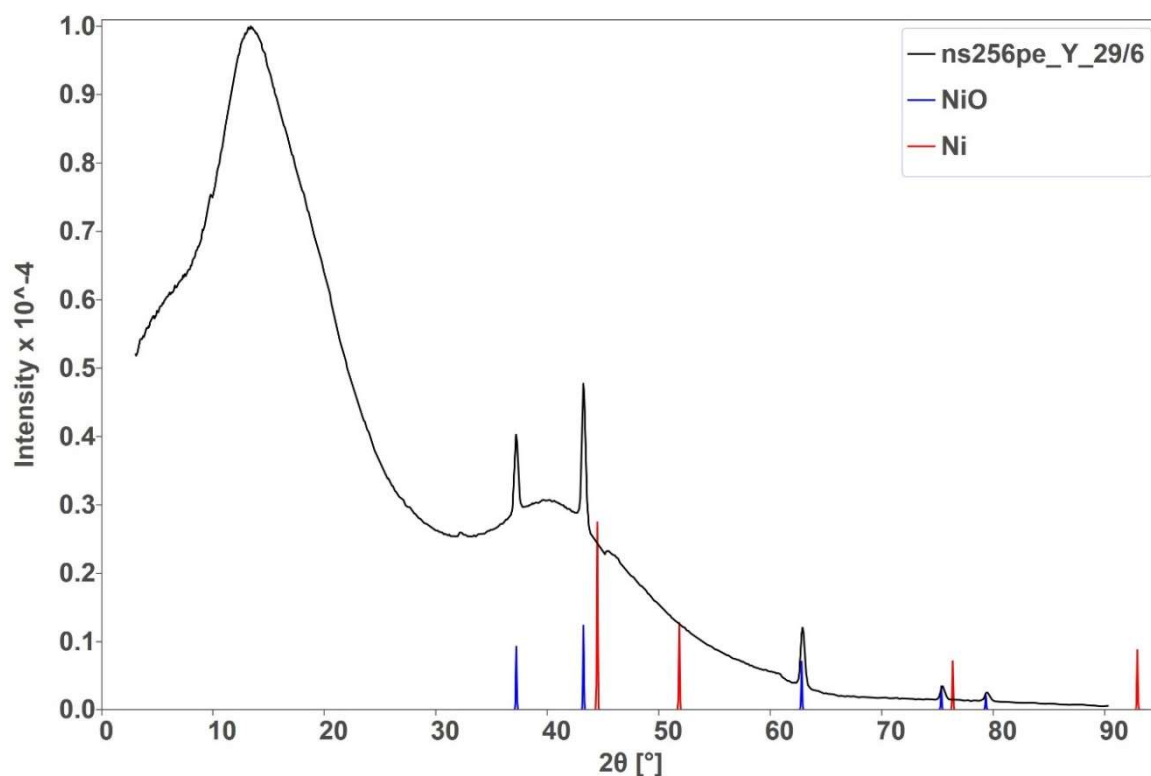


Figure S50 - PXRD pattern of ns256pe_Y_29/6 compared with simulated nickel oxide (NiO)^[9] and nickel metal (Ni)^[8]. Crystalline peaks are apparent in the PXRD pattern of ns256pe_Y_29/6.

Sample ns256d was loaded into a ceramic crucible and inserted into the quartz tube of furnace Y. The insulation blocks were inserted and the tube was sealed. The tube was purged by purge/vac cycling 5 times using argon zero. The flow was then set to 3 L/m and the temperature of the furnace was raised to 900°C over 3 hours and held at 900°C for 2 hours. The temperature was controlled down to 500°C over 80 minutes. This sample was labelled ns256pd_Y_29/6.

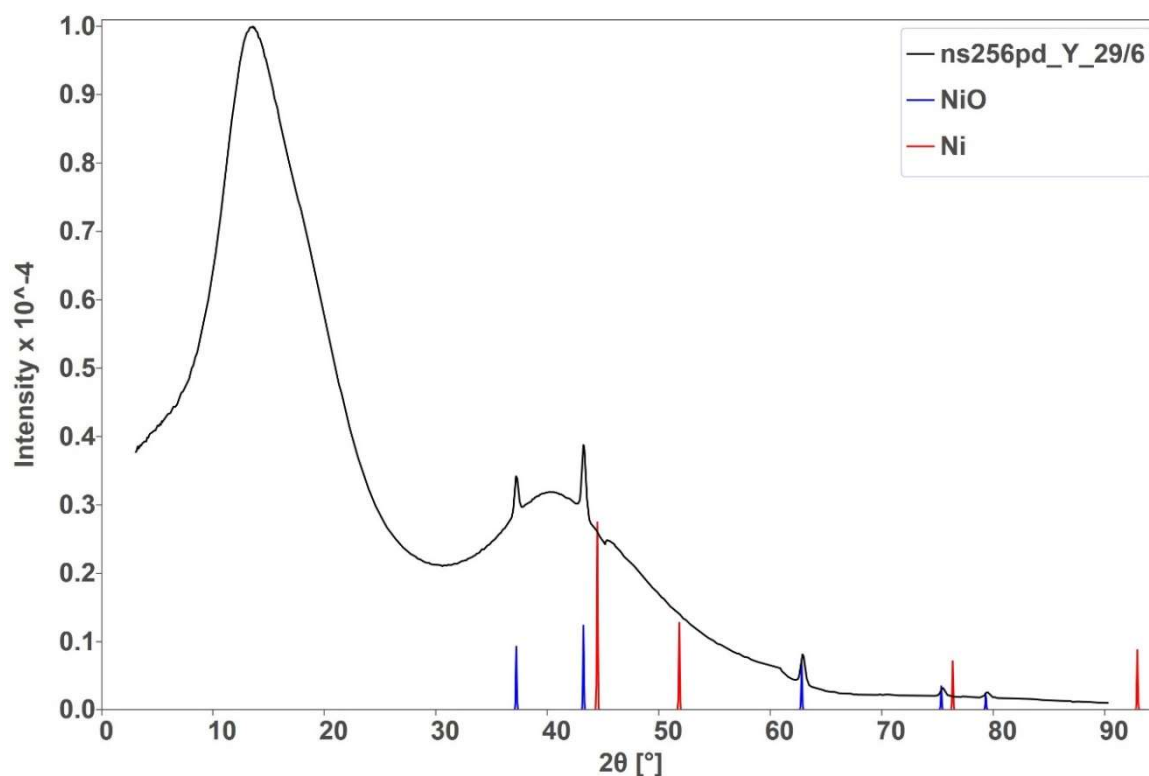


Figure S51 - PXRD pattern of ns256pd_Y_29/6 compared with simulated nickel oxide (NiO)^[9] and nickel metal (Ni)^[8]. Crystalline peaks are apparent in the PXRD pattern of ns256pd_Y_29/6.

Sample ns256a was loaded into a ceramic crucible and inserted into the quartz tube of furnace X. The insulation blocks were inserted and the tube was sealed. The tube was purged by purge/vac cycling 3 times using argon zero. The flow was then set to 2 L/m and the temperature of the furnace was raised to 900°C over 3 hours and held at 900°C for 2 hours. The temperature was controlled down to 500°C over 80 minutes. This sample was labelled ns256pa_X_6/7.

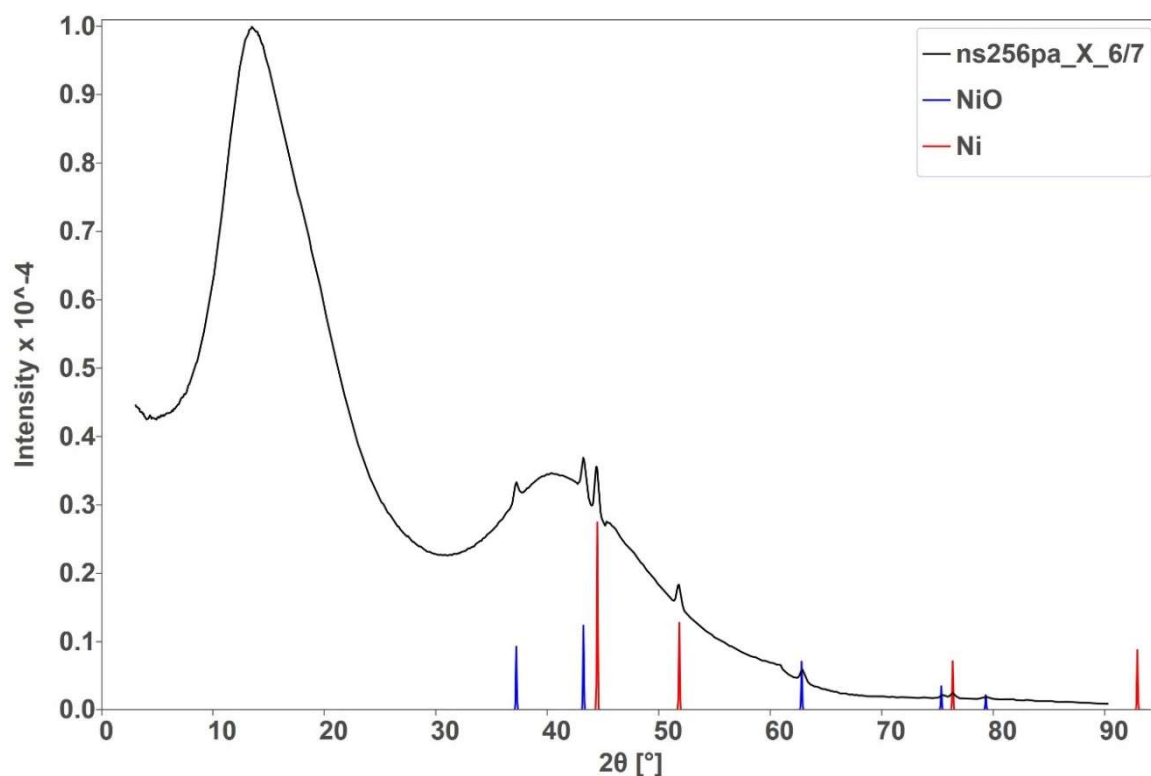


Figure S52 - PXRD pattern of ns256pa_X_6/7 compared with simulated nickel oxide (NiO)^[9] and nickel metal (Ni)^[8]. Crystalline peaks are apparent in the PXRD pattern of ns256pa_X_6/7.

Sample ns256c was loaded into a ceramic crucible and inserted into the quartz tube of furnace Y. The insulation blocks were inserted and the tube was sealed. The tube was purged by purge/vac cycling 3 times using argon zero. The flow was then set to 2 L/m and the temperature of the furnace was raised to 900°C over 300 minutes and held at 900°C for 3 hours. The temperature was controlled down to 500°C over 80 minutes. This sample was labelled ns256pc_Y_6/7.

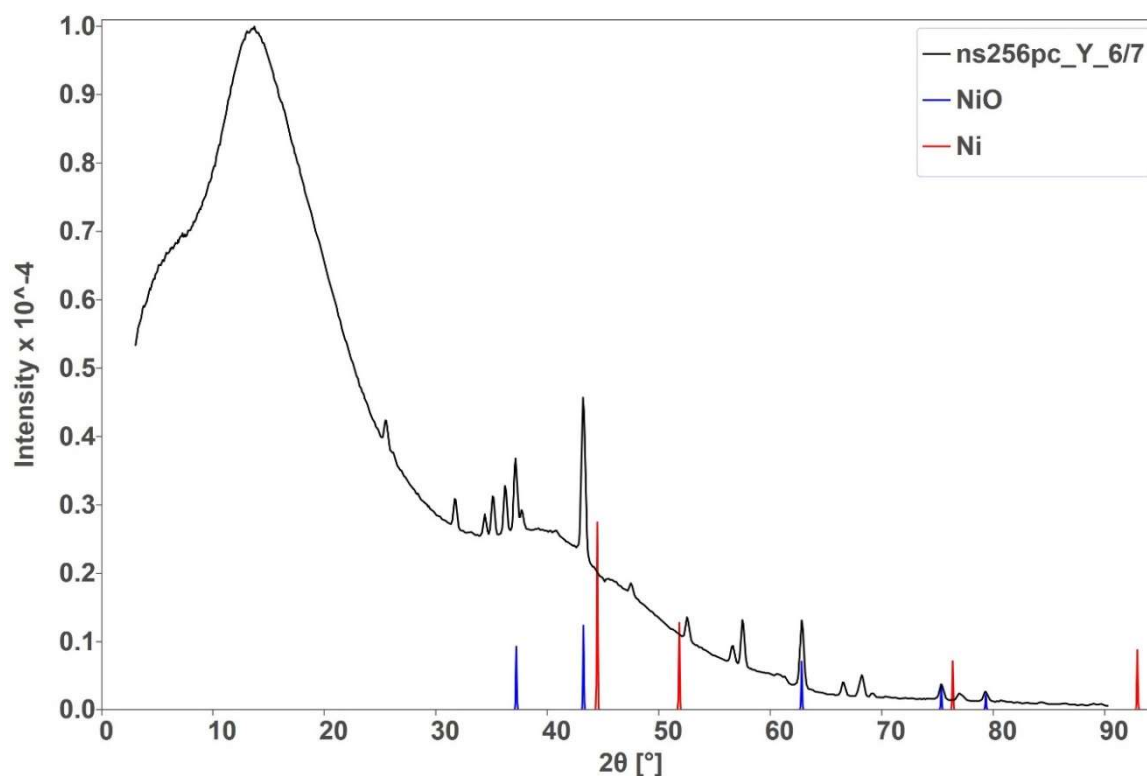


Figure S53 - PXRD pattern of ns256pc_Y_6/7 compared with simulated nickel oxide (NiO)^[9] and nickel metal (Ni)^[8]. Crystalline peaks are apparent in the PXRD pattern of ns256pc_Y_6/7.

Palladium

ns251p

Sample ns251a was loaded into a ceramic crucible and inserted into the quartz tube of furnace Y. The insulation blocks were inserted and the tube was sealed. The tube was purged by flowing argon zero at >12 L/m for 30 minutes. The flow was then set to 4 L/m and the temperature of the furnace was raised to 900°C over 3 hours and held at 900°C for 1 hour. The temperature was controlled down to 500°C over 80 minutes. This sample was labelled ns251pa_Y_22/6. TEM image and PXRD pattern shown in the main text.

Sample ns251b was loaded into a ceramic crucible and inserted into the quartz tube of furnace Y. The insulation blocks were inserted and the tube was sealed. The tube was purged by flowing argon zero at >12 L/m for 30 minutes. The flow was then set to 4 L/m and the temperature of the furnace was raised to 900°C over 3 hours and held at 900°C for 1 hour. The temperature was controlled down to 500°C over 80 minutes. This sample was labelled ns251pb_Y_22/6. TEM image and PXRD pattern shown in the main text.

ns254p

Sample ns254a was loaded into a ceramic crucible and inserted into the quartz tube of furnace X. The insulation blocks were inserted and the tube was sealed. The tube was purged by purge/vac cycling 3 times using argon zero. The flow was then set to 2 L/m and the temperature of the furnace was raised to 900°C over 3 hours and held at 900°C for 2 hours. The temperature was controlled down to 500°C over 80 minutes. This sample was labelled ns254pa_X_27/6. TEM image and PXRD pattern shown in the main text.

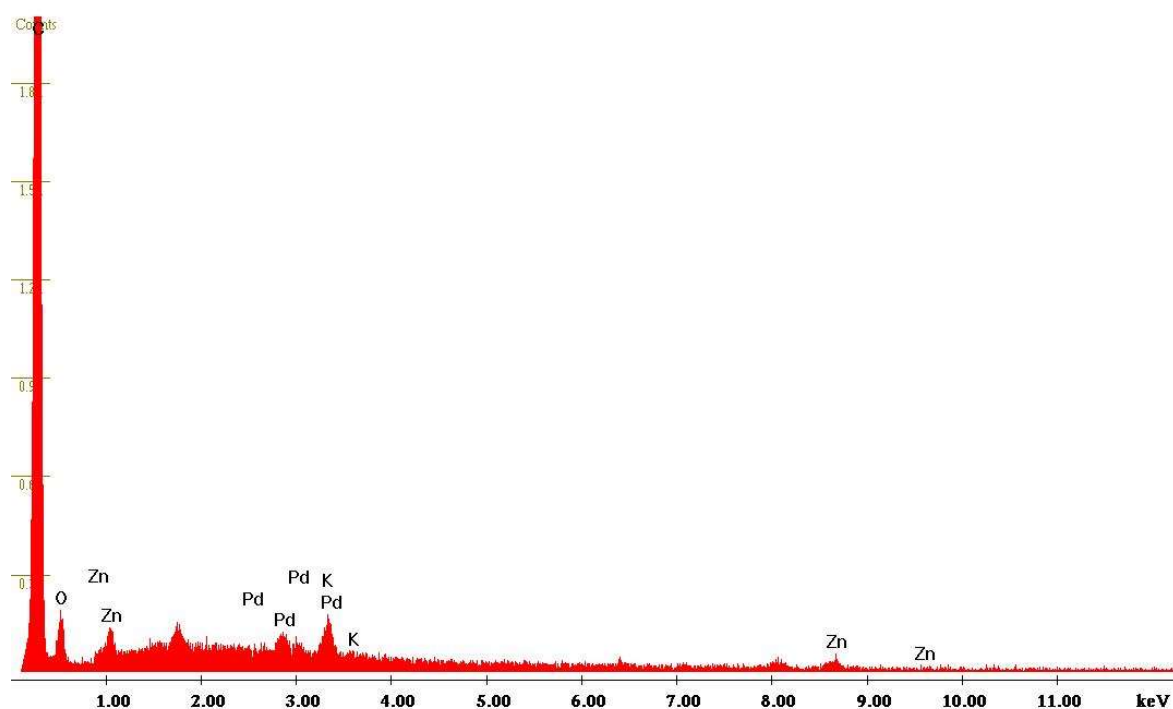


Figure S54 - EDX spectrum of ns254pa_X_27/6.

Sample ns254b was loaded into a ceramic crucible and inserted into the quartz tube of furnace Y. The insulation blocks were inserted and the tube was sealed. The tube was purged by purge/vac cycling 3 times using argon zero. The flow was then set to 2 L/m and the temperature of the furnace was raised to 900°C over 3 hours and held at 900°C for 2 hours. The temperature was controlled down to 500°C over 80 minutes. This sample was labelled ns254pb_Y_27/6. TEM image and PXRD pattern shown in the main text.

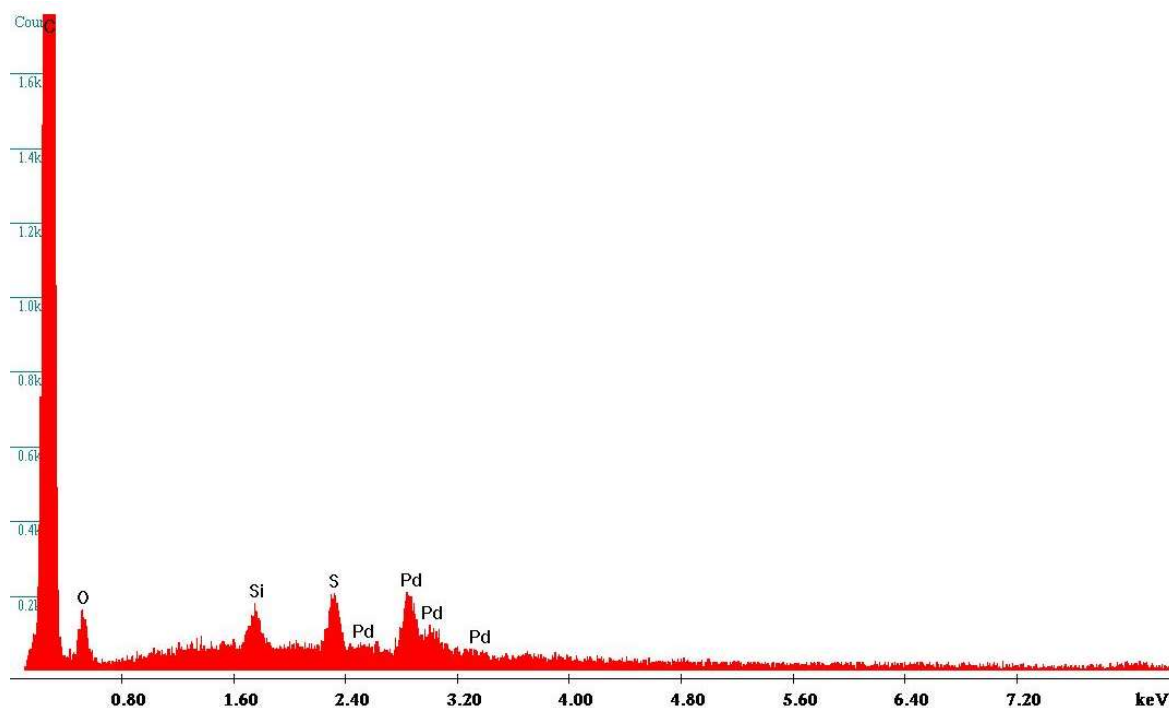


Figure S55 - EDX spectrum of ns254pb_Y_27/6.

Sample ns254b was loaded into a ceramic crucible and inserted into the quartz tube of furnace X. The insulation blocks were inserted and the tube was sealed. The tube was purged by purge/vac cycling 3 times using argon zero. The flow was then set to 2 L/m and the temperature of the furnace was raised to 900°C over 3 hours and held at 900°C for 2 hours. The temperature was controlled down to 500°C over 80 minutes. This sample was labelled ns254pb_X_2/7.

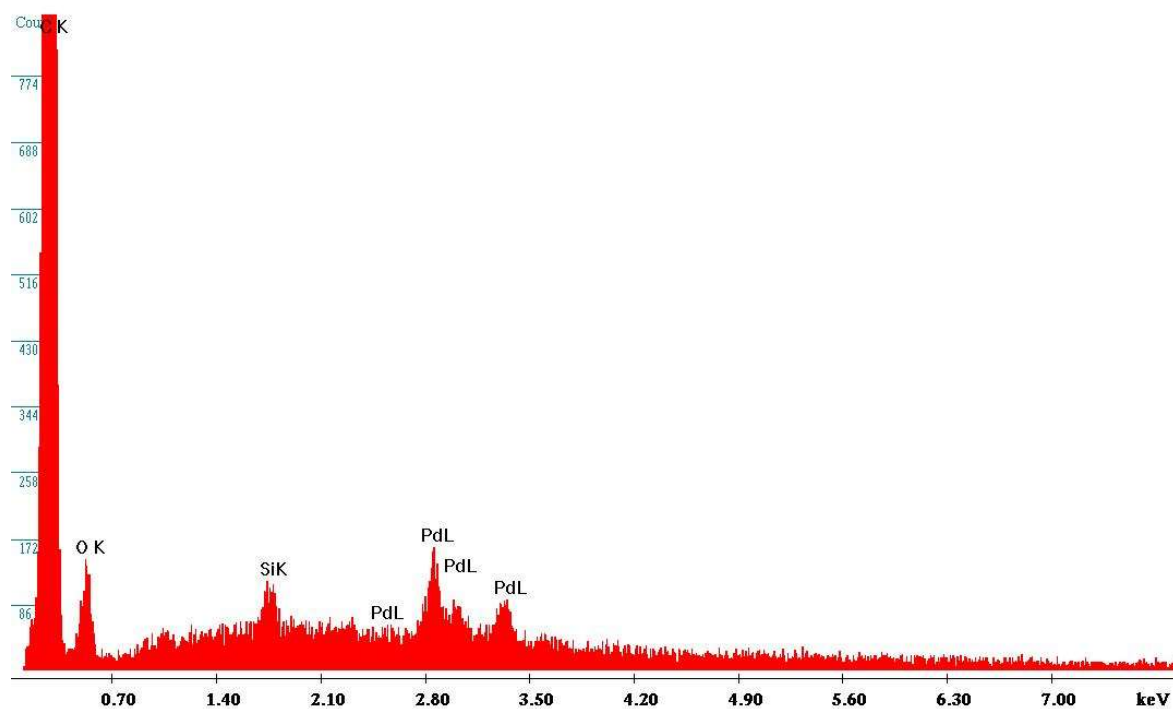


Figure S56 - EDX spectrum of ns254pb_X_2/7.

ns258p

Sample ns258a was loaded into a ceramic crucible and inserted into the quartz tube of furnace X. The insulation blocks were inserted and the tube was sealed. The tube was purged by purge/vac cycling 3 times using argon zero. The flow was then set to 2 L/m and the temperature of the furnace was raised to 900°C over 3 hours and held at 900°C for 2 hours. The temperature was controlled down to 500°C over 80 minutes. This sample was labelled ns258pa_X_18/7.

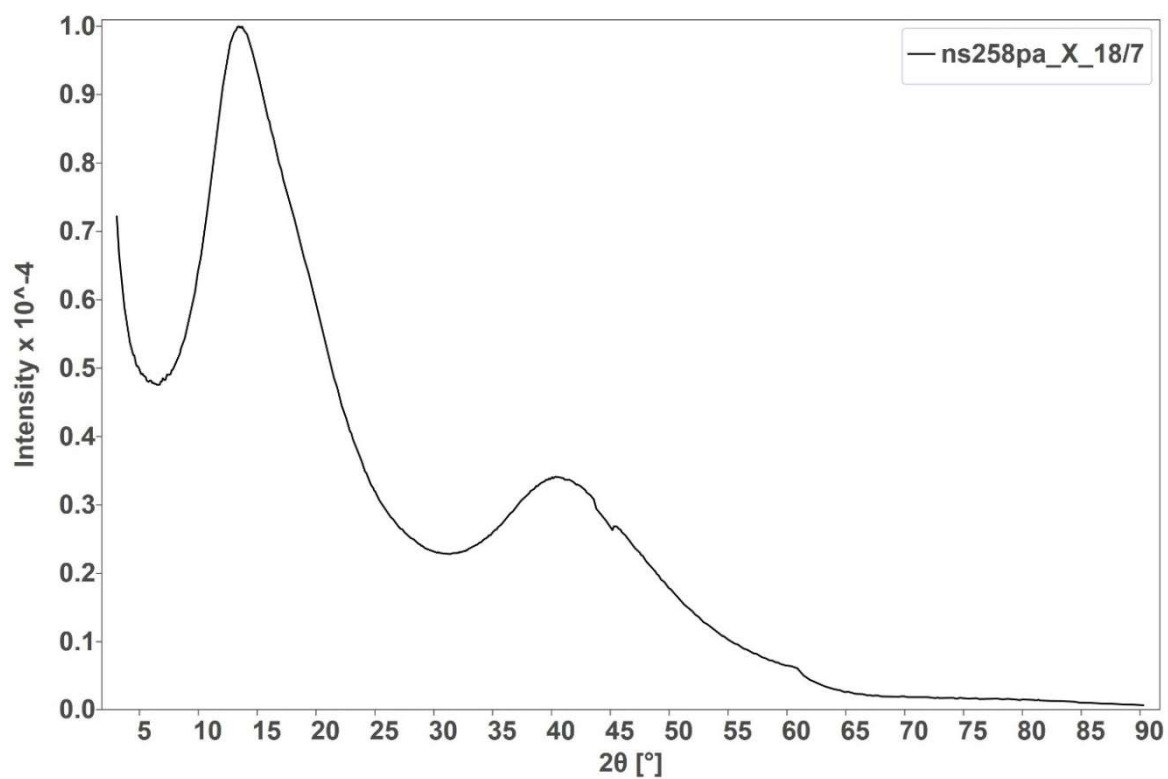


Figure S57 - PXRD pattern of ns258pa_X_18/7. Sample is completely amorphous.

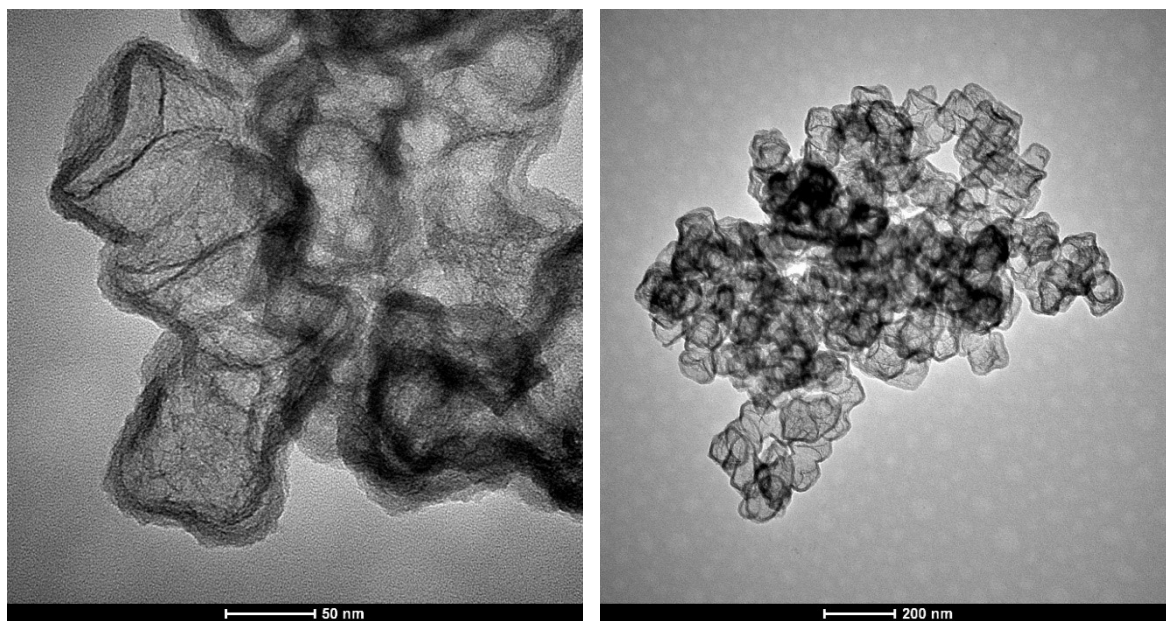


Figure S58 - TEM images of ns258pa_X_18/7.

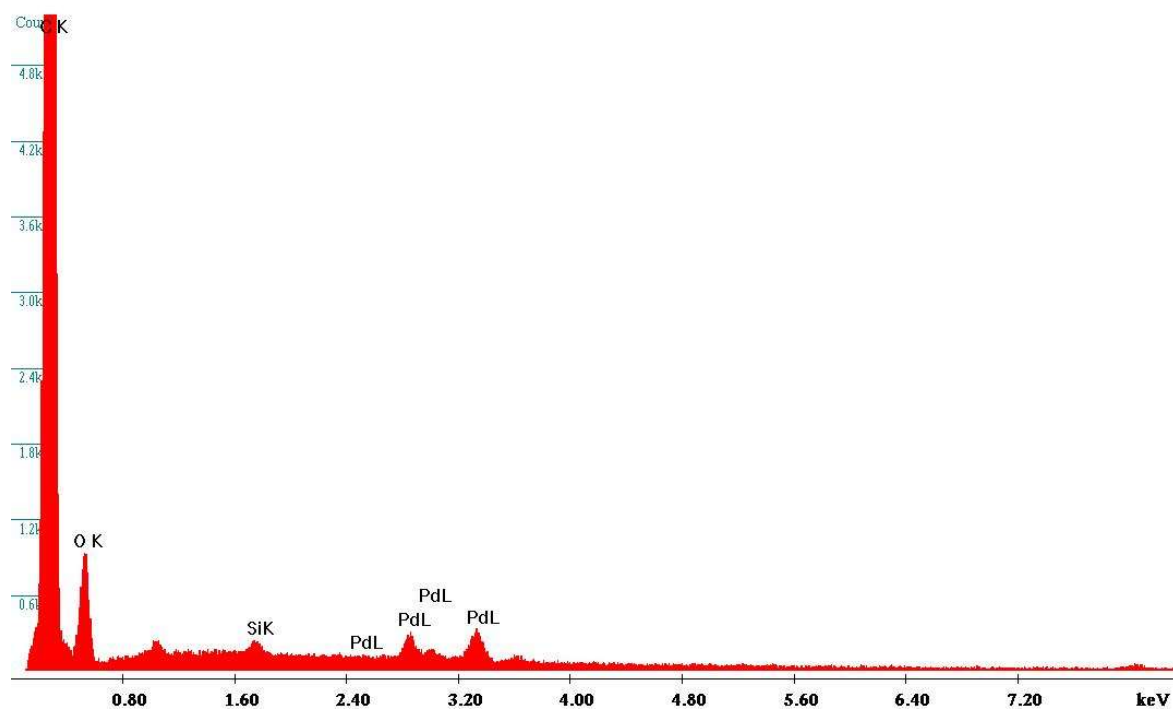


Figure S59 - EDX spectrum of ns258pa_X_18/7.

Sample ns258b was loaded into a ceramic crucible and inserted into the quartz tube of furnace X. The insulation blocks were inserted and the tube was sealed. The tube was purged by purge/vac cycling 3 times using argon zero. The flow was then set to 2 L/m and the temperature of the furnace was raised to 900°C over 3 hours and held at 900°C for 2 hours. The temperature was controlled down to 500°C over 80 minutes. This sample was labelled ns258pb_X_19/7.

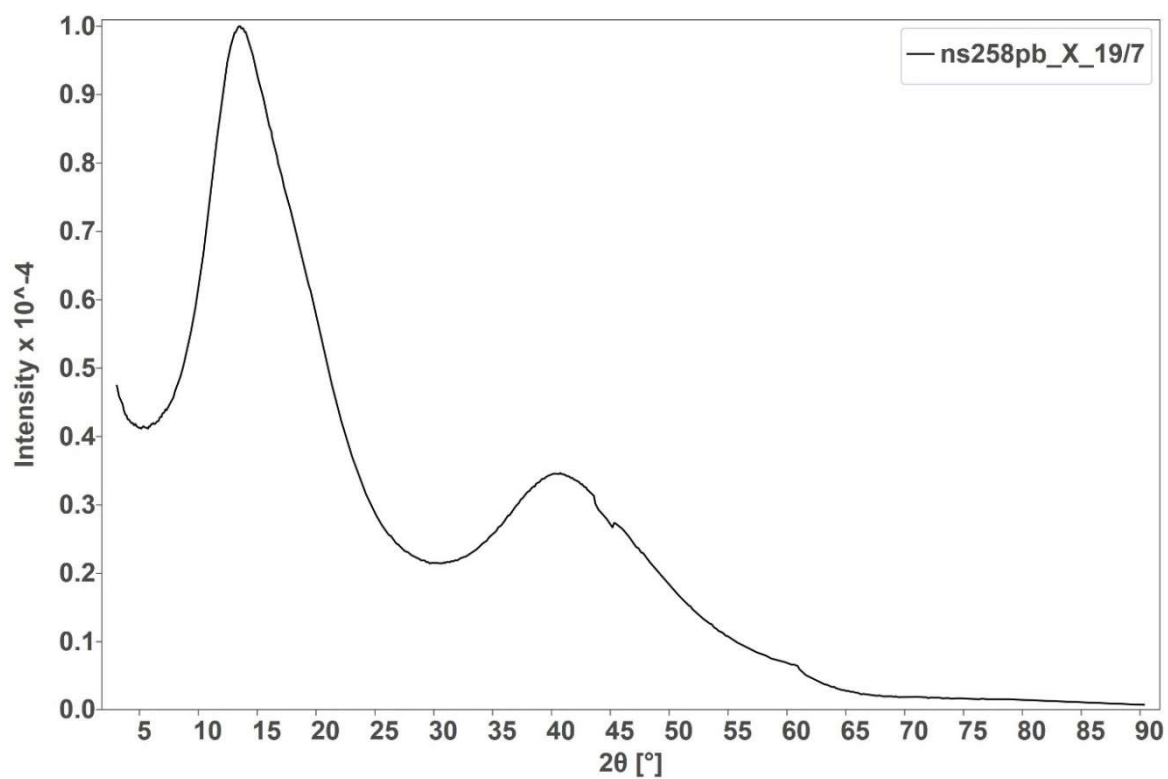


Figure S60 - PXRD pattern of ns258pb_X_19/7. Sample is completely amorphous.

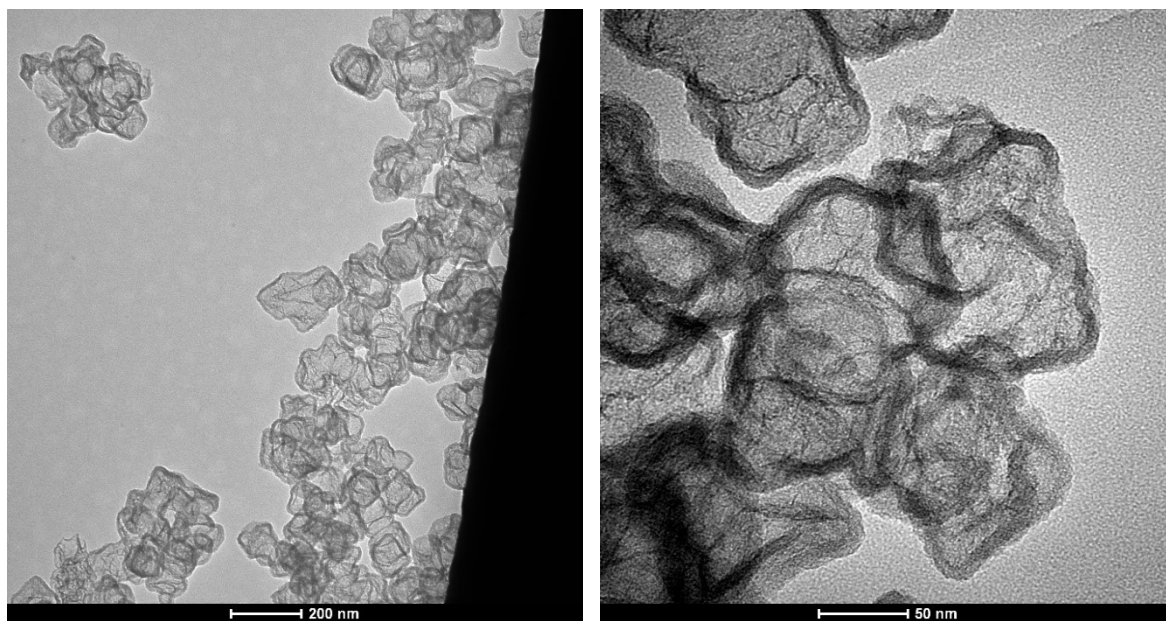


Figure S61 - TEM images of ns258pb_X_19/7.

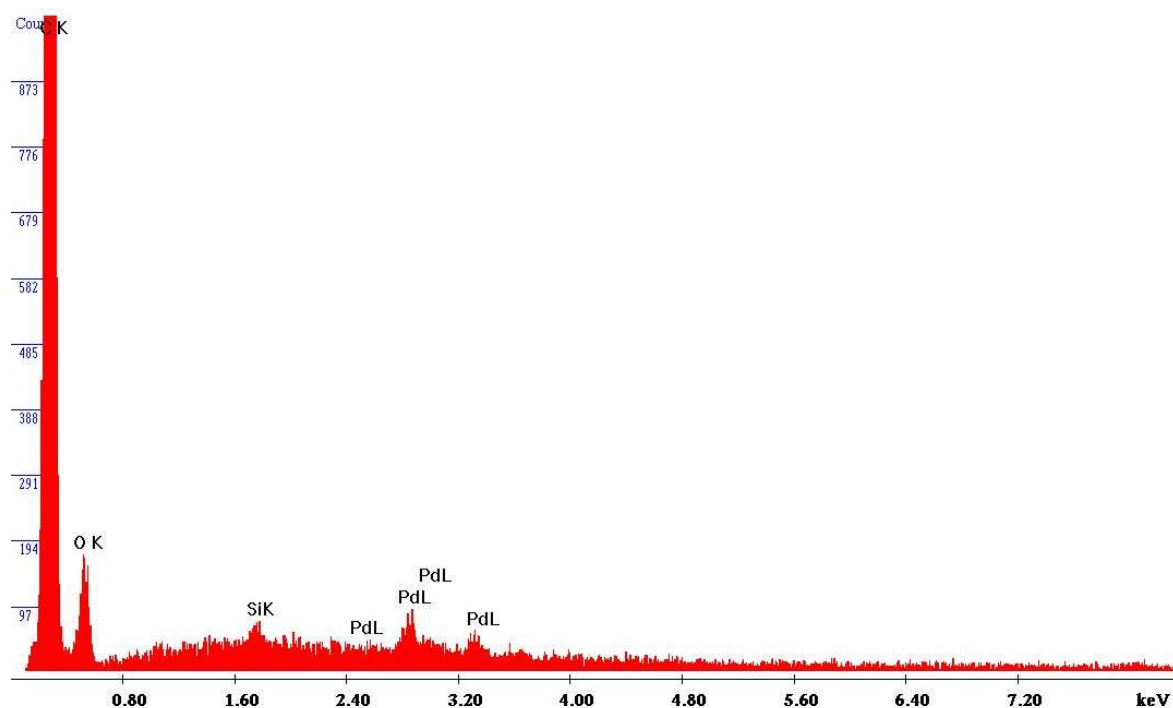


Figure S62 - EDX spectrum of ns258pb_X_19/7.

ns260p

A small portion of sample ns260 was loaded into a ceramic crucible and inserted into the quartz tube of furnace X. The insulation blocks were inserted and the tube was sealed. The tube was purged by purge/vac cycling 3 times using argon zero. The flow was then set to 1 L/m and the temperature of the furnace was raised to 900°C over 3 hours and held at 900°C for 2 hours. The temperature was controlled down to 500°C over 80 minutes. This sample was labelled ns260p_X_1/8.

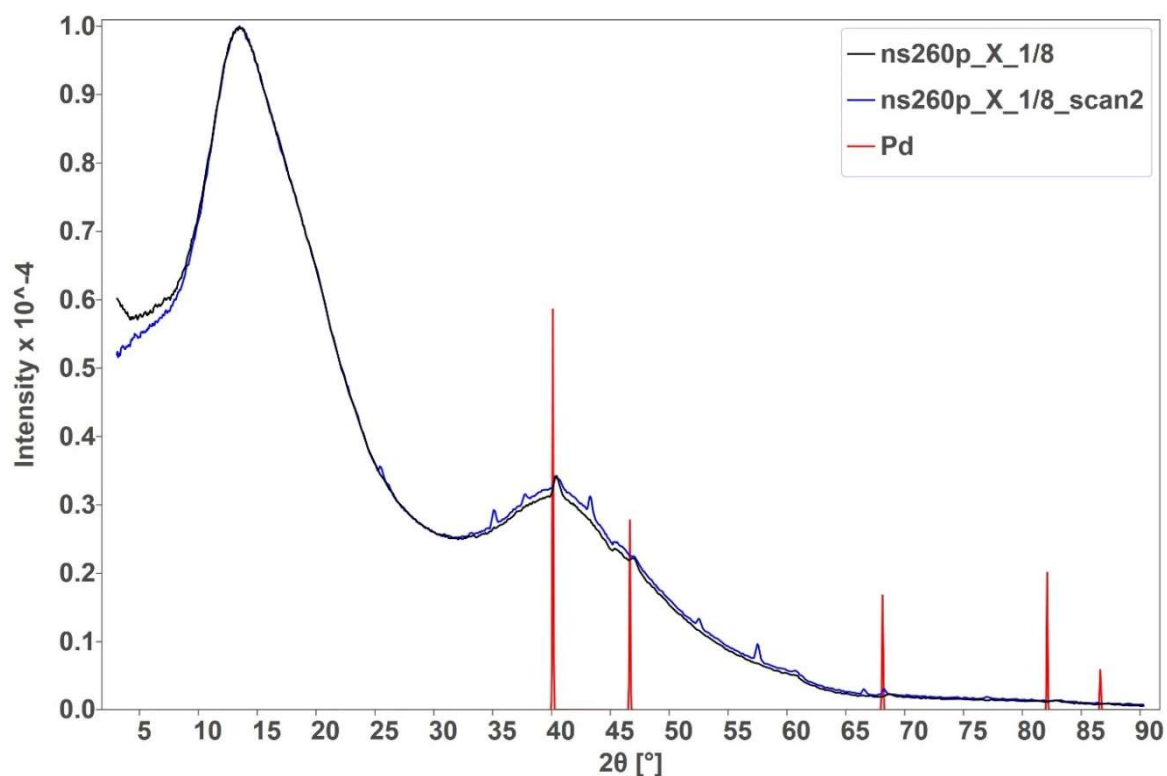


Figure S63 - PXRD patterns of ns260p_X_1/8 over multiple scans compared to simulated palladium (Pd)^[8]. Crystalline peaks are apparent in the PXRD patterns of ns260p_X_1/8 and ns260p_X_1/8_scan2. The PXRD pattern of ns260p_X_1/8_scan 2 has more PXRD pattern peaks than scan 1 (35° , 37° , 43° , 52° , 57°).

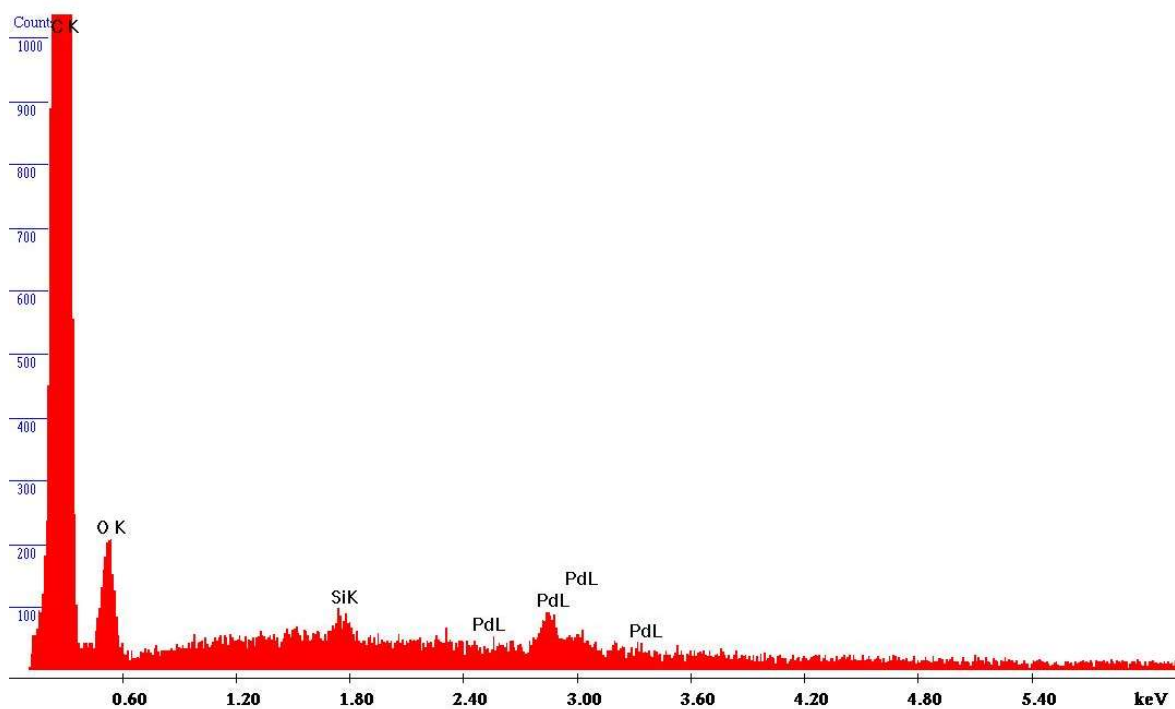


Figure S64 - EDX spectrum of ns260p_X_1/8.

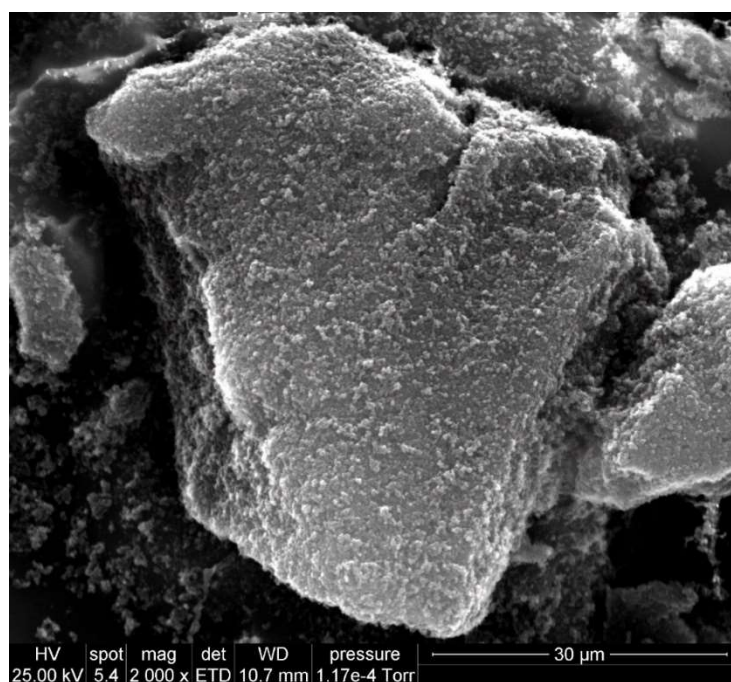


Figure S65 - SEM image of ns260p_X_1/8.

A small portion of sample ns260 was loaded into a large ceramic crucible and inserted into the quartz tube of furnace X. The insulation blocks were inserted and the tube was sealed. The tube was purged by purge/vac cycling 3 times using argon zero. The flow was then set to 1 L/m and the temperature of the furnace was raised to 900°C over 3 hours and held at 900°C for 2 hours. The temperature was controlled down to 500°C over 80 minutes. Material that was easily dislodged from the crucible by tapping lightly on the crucible was labelled ns260p_X_8/8_1, material that required hard tapping was labelled ns260p_X_8/8_2 and material that required a spatula to scrape the material free was labelled ns260p_X_8/8_3. These were stored separately. TEM image and PXRD pattern of ns260p_X_8/8_1 shown in the main text.

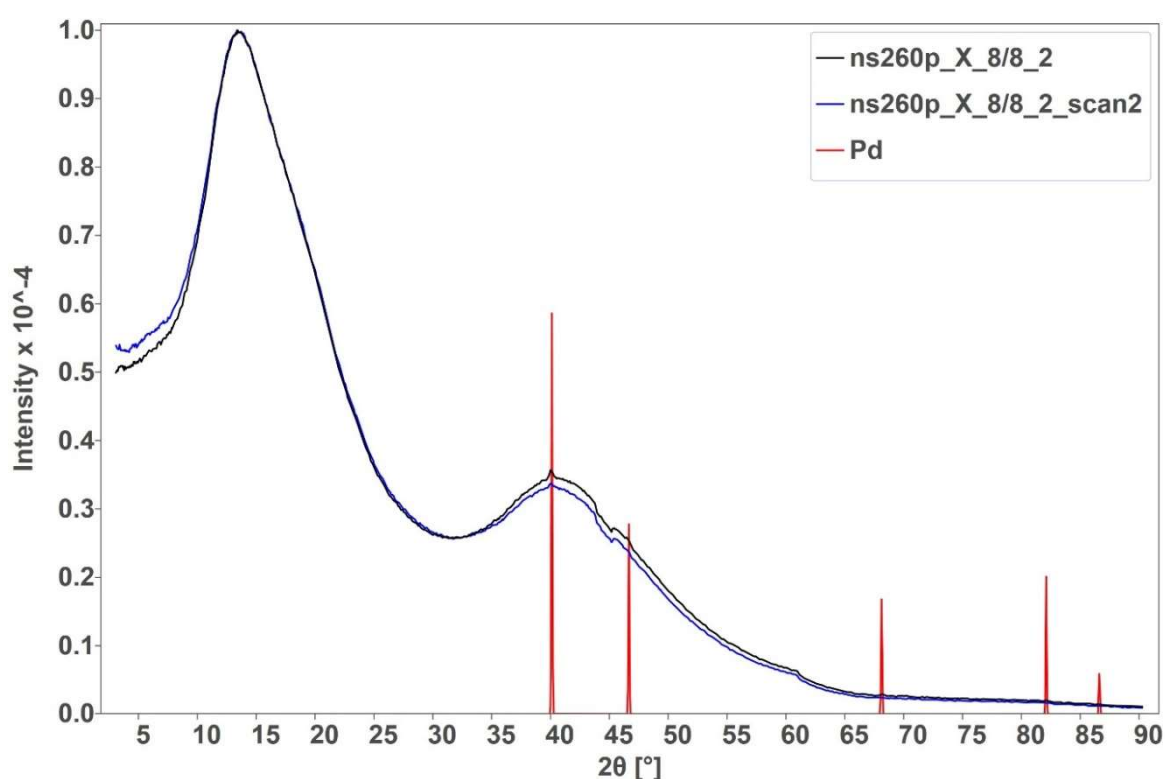


Figure S66 - PXRD patterns of ns260p_X_8/8_2 over multiple scans compared to simulated palladium (Pd)^[8]. Crystalline peaks are apparent in the PXRD patterns of ns260p_X_8/8_2 and ns260p_X_8/8_2_scan2.

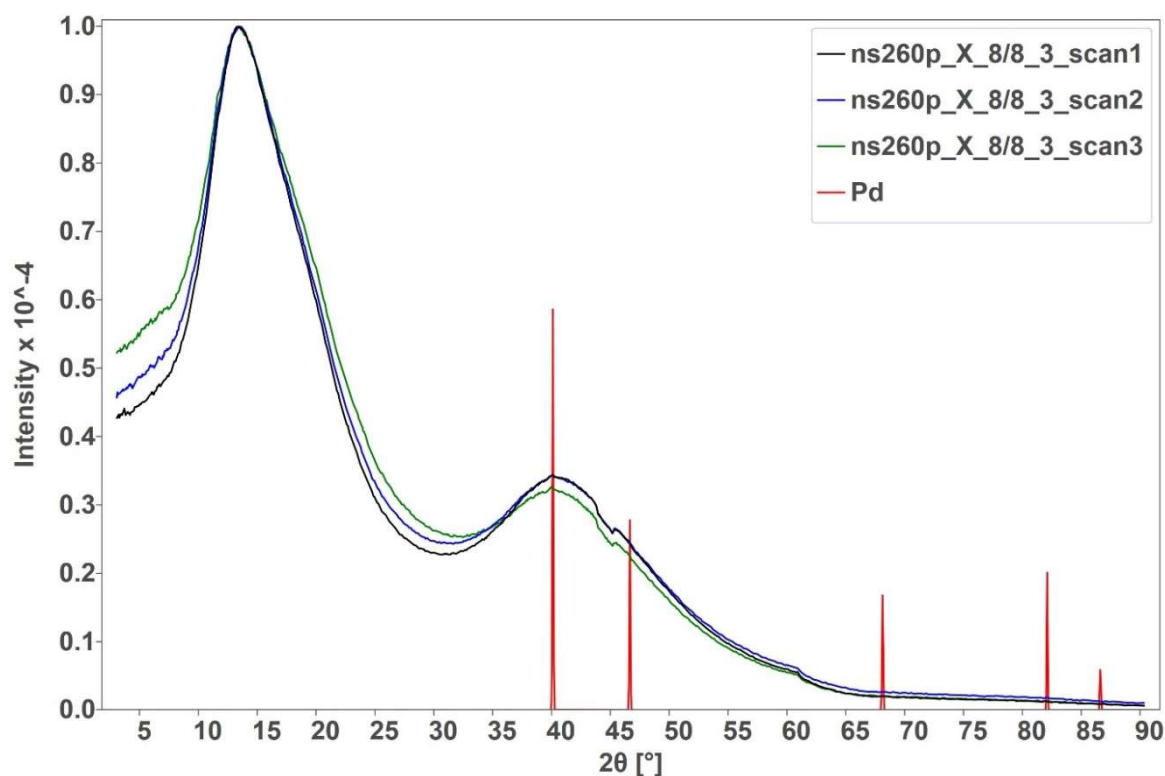


Figure S67 - PXRD patterns of ns260p_X_8/8_3 over multiple scans compared to simulated palladium (Pd)^[8]. Crystalline peaks are apparent in the PXRD patterns of ns260p_X_8/8_3, ns260p_X_8/8_3_scan2 and ns260p_X_8/8_3_scan3.

A small portion of sample ns260 was loaded into a platinum crucible and inserted into the simultaneous thermal analysis (STA) instrument. The instrument was supplied with argon zero at a flow rate of 70 mL/min to provide an inert atmosphere. The temperature was raised at 10°C/m until the temperature reached 1000°C. Some material had clumped together while other parts remained as fine grains. Material that was clumped was measured for PXRD separately from the fine material, labelled ns260_STA_3/8_clump and ns260_STA_3/8_fine respectively. TEM image and PXRD pattern shown in the main text.

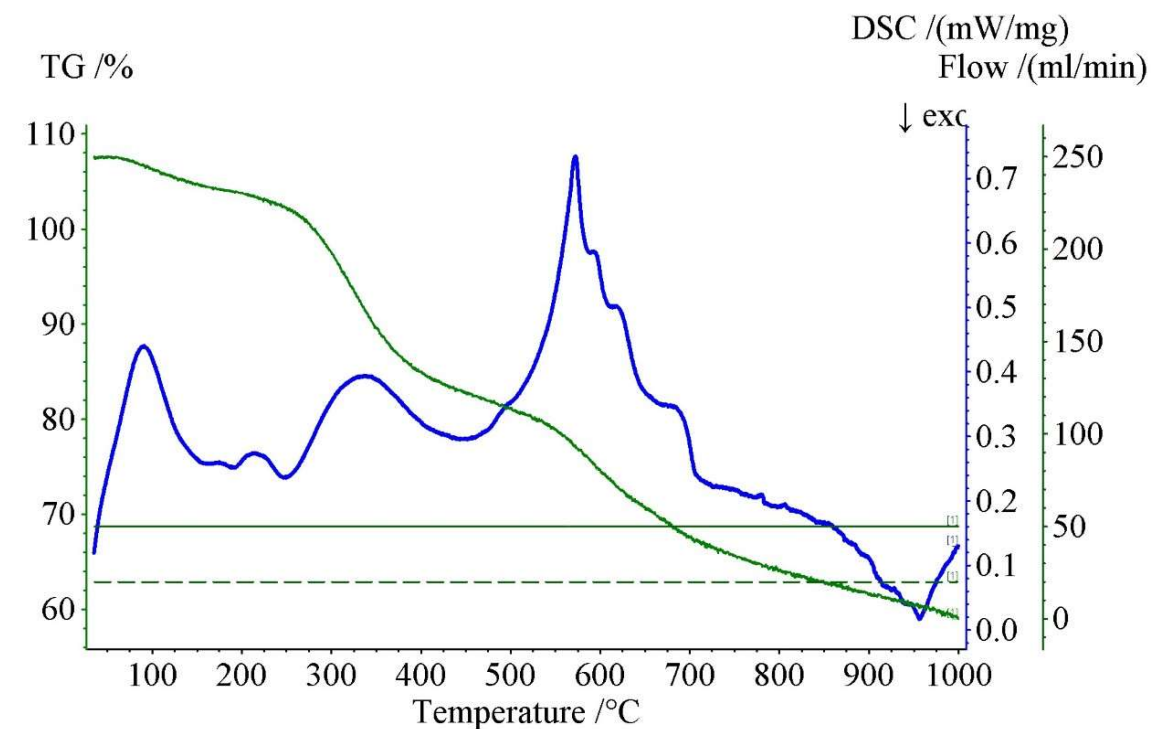


Figure S68 - Graph of results of STA of ns260P_STA_3/8.

Sample ns260 was loaded into a ceramic crucible and inserted into the quartz tube of furnace Y. The insulation blocks were inserted and the tube was sealed. The tube was purged by purge/vac cycling 3 times using argon zero. The flow was switched to a 40%/60% hydrogen/argon atmosphere and then lowered to a flowrate of 25 bubbles/minute (measured by a bubbler). Argon zero was then introduced to increase the flowrate to approximately 200 bubbles/minute, achieving an approximate atmosphere composition of 5%/95% hydrogen/argon. The temperature of the furnace was raised to 900°C over 3 hours and held at 900°C for 2 hours. The temperature was controlled down to 500°C over 80 minutes. TEM image, EDX spectrum and PXRD pattern shown in the main text.

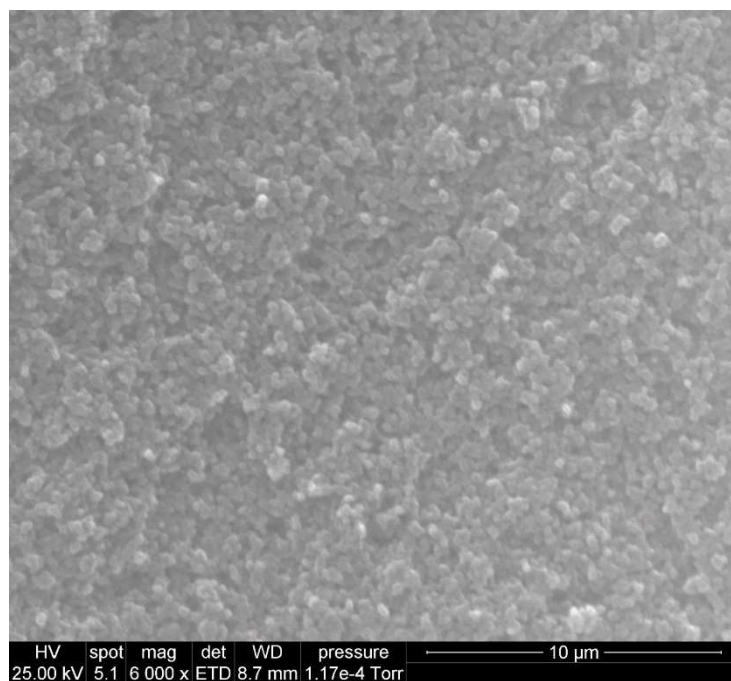


Figure S69 - SEM image of ns260p_Y_14/8.

ns265p

Sample ns265a was loaded into a ceramic crucible and inserted into the quartz tube of furnace X. The insulation blocks were inserted and the tube was sealed. The tube was purged by purge/vac cycling 3 times using argon zero. The flow was then set to 1 L/m and the temperature of the furnace was raised to 900°C over 3 hours and held at 900°C for 2 hours. The temperature was controlled down to 500°C over 80 minutes. TEM image and PXRD pattern shown in the main text.

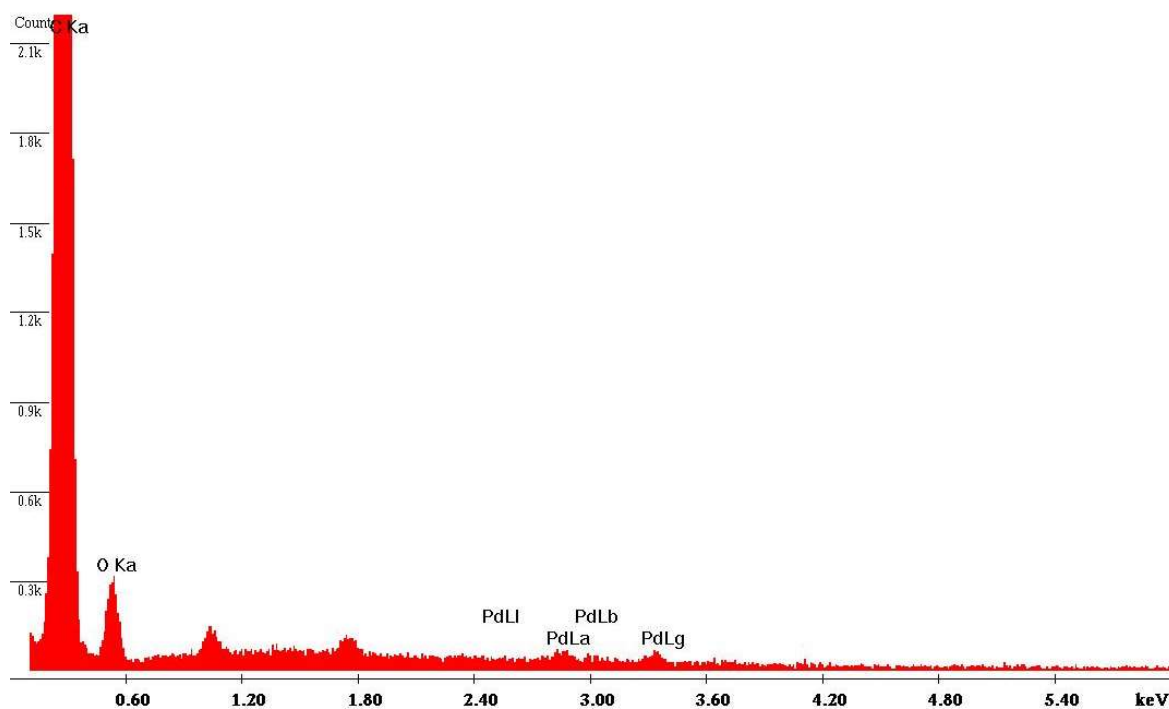


Figure S70 - EDX spectrum of ns265pa_X_19/8.

Sample ns265b was loaded into a ceramic crucible and inserted into the quartz tube of furnace X. The insulation blocks were inserted and the tube was sealed. The tube was purged by purge/vac cycling 3 times using argon zero. The flow was then set to 1 L/m and the temperature of the furnace was raised to 900°C over 3 hours and held at 900°C for 2 hours. The temperature was controlled down to 500°C over 80 minutes. TEM image and PXRD pattern shown in the main text.

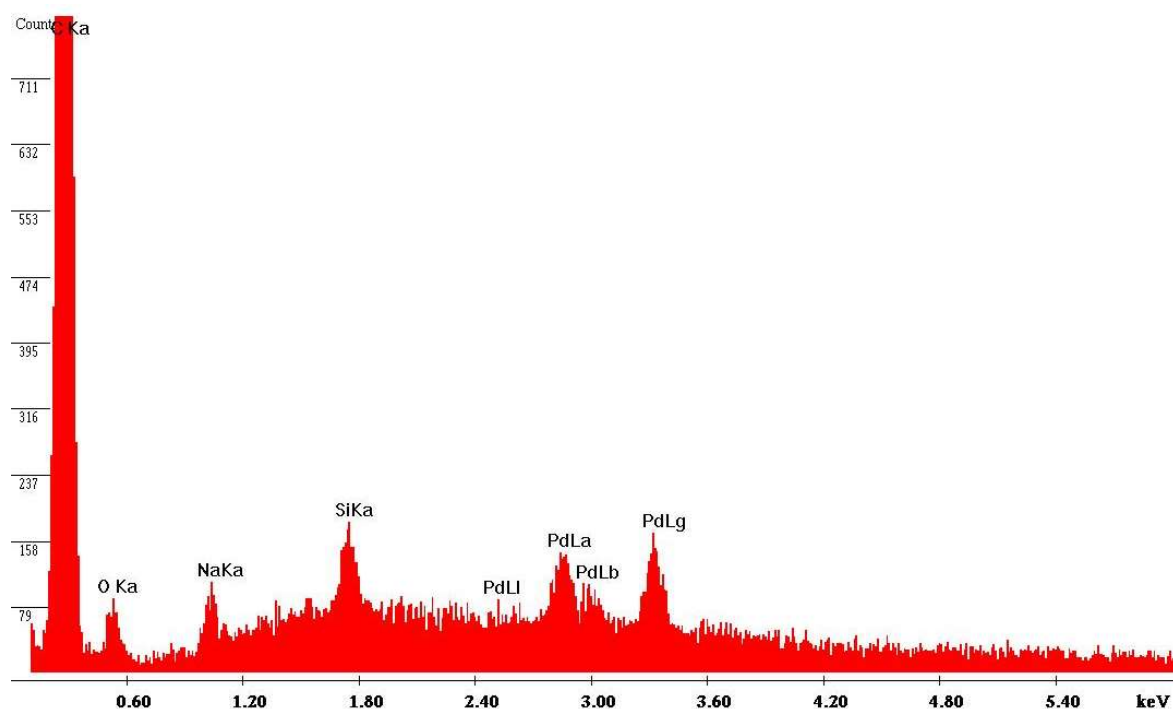


Figure S71 - EDX spectrum of ns265pb_X_20/8.

ns266p

Roughly equal amounts of sample ns266 was loaded into 2 large ceramic crucibles, totalling 0.89 g of sample ns266 in total. The crucibles were shaken back and forth lightly to spread the material thin over the surface of the crucibles. The large ceramic crucibles were then inserted into the quartz tube of furnace X at equal distances from the middle of the furnace, one crucible being downstream of the other. The insulation blocks were inserted and the tube was sealed. The tube was purged by purge/vac cycling 7 times using argon zero. The flow was then set to 2 L/m and the temperature of the furnace was raised to 900°C over 3 hours and held at 900°C for 2 hours. The temperature was controlled down to 500°C over 80 minutes. A small sample of material from the most upstream side of the upstream crucible was taken and labelled ns266p_X_25/8_front. A small sample of material was also taken from the middle of the downstream crucible that was labelled ns266p_X_25/8_mid as well as a sample from the most downstream side of the downstream crucible that was labelled ns266p_X_25/8_end. The remaining material was labelled ns266p_X_25/8. TEM image, EDX spectrum and PXRD pattern shown in the main text.

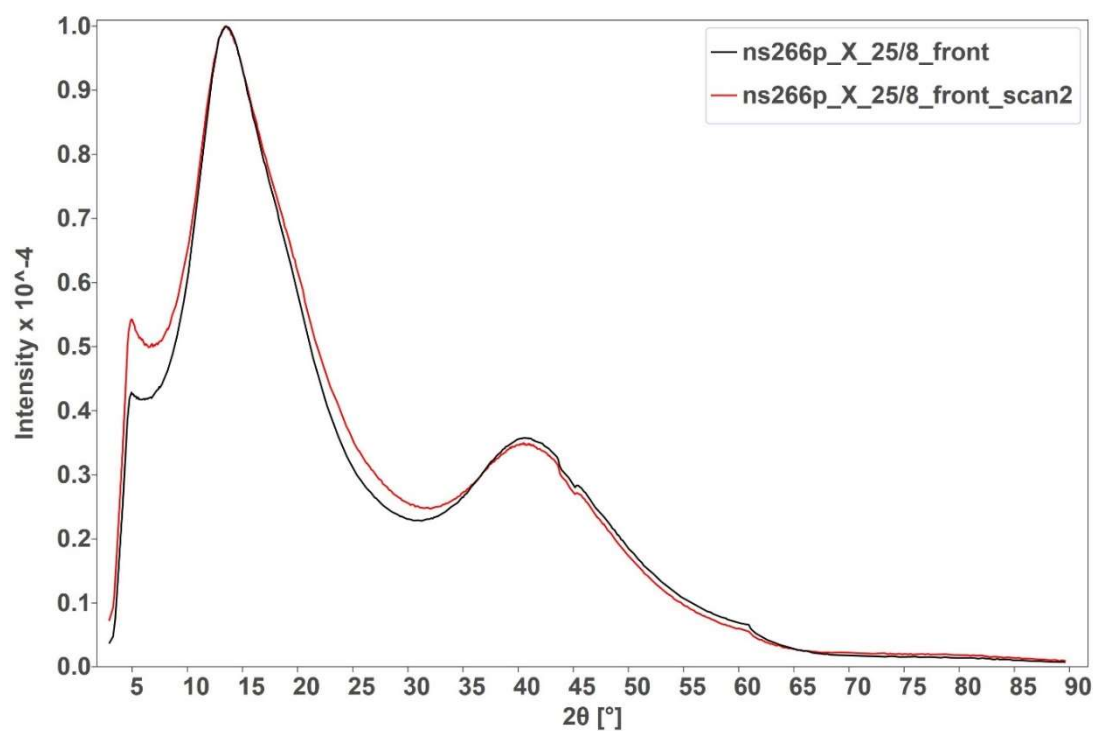


Figure S72 - PXRD pattern of ns266p_X_25/8_front over multiple scans. Sample ns266p_X_25/8_front is completely amorphous.

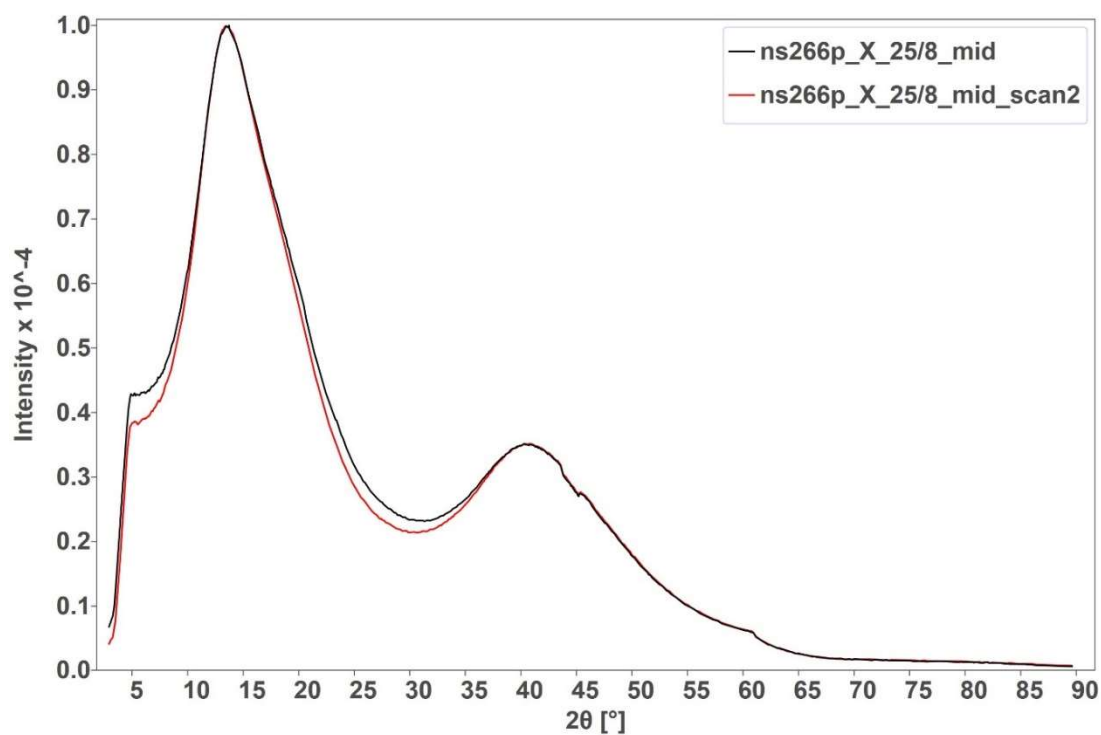


Figure S73 - PXRD pattern of ns266p_X_25/8_mid over multiple scans. Sample ns266p_X_25/8_mid is completely amorphous.

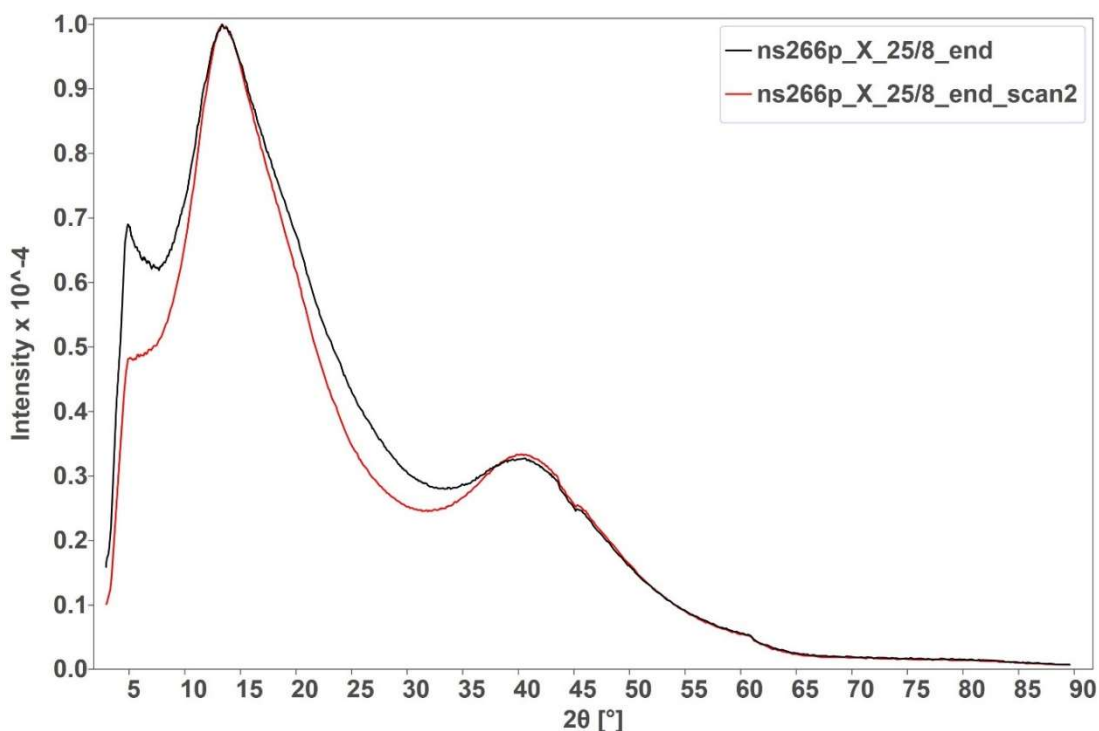


Figure S74 - PXRD pattern of ns266p_X_25/8_end over multiple scans. Sample ns266p_X_25/8_end is completely amorphous.

All of sample ns266p_X_25/8 was loaded into a large ceramic crucible and inserted into the quartz tube of furnace X. The insulation blocks were inserted and the tube was sealed. The tube was purged by purge/vac cycling 7 times using argon zero. The flow was then set to 1.5 L/m and the temperature of the furnace was raised to 900°C over 3 hours and held at 900°C for 2 hours. The temperature was controlled down to 500°C over 80 minutes. The product was labelled ns266pp. EDX spectrum shown in main text.

Sample ns266pp was washed by dispersing in a roughly equal parts methanol and distilled water mixture and storing this solution in a dialysis membrane suspended in distilled water. After the system was given ~12 hours to pull contaminants out of the sample into the surrounding distilled water, the distilled water was exchanged with fresh distilled water. This was repeated 2 times. The product was then centrifuged to remove the solvent and dried under vacuum. The product was labelled ns266pp_washed. EDX spectrum shown in main text.

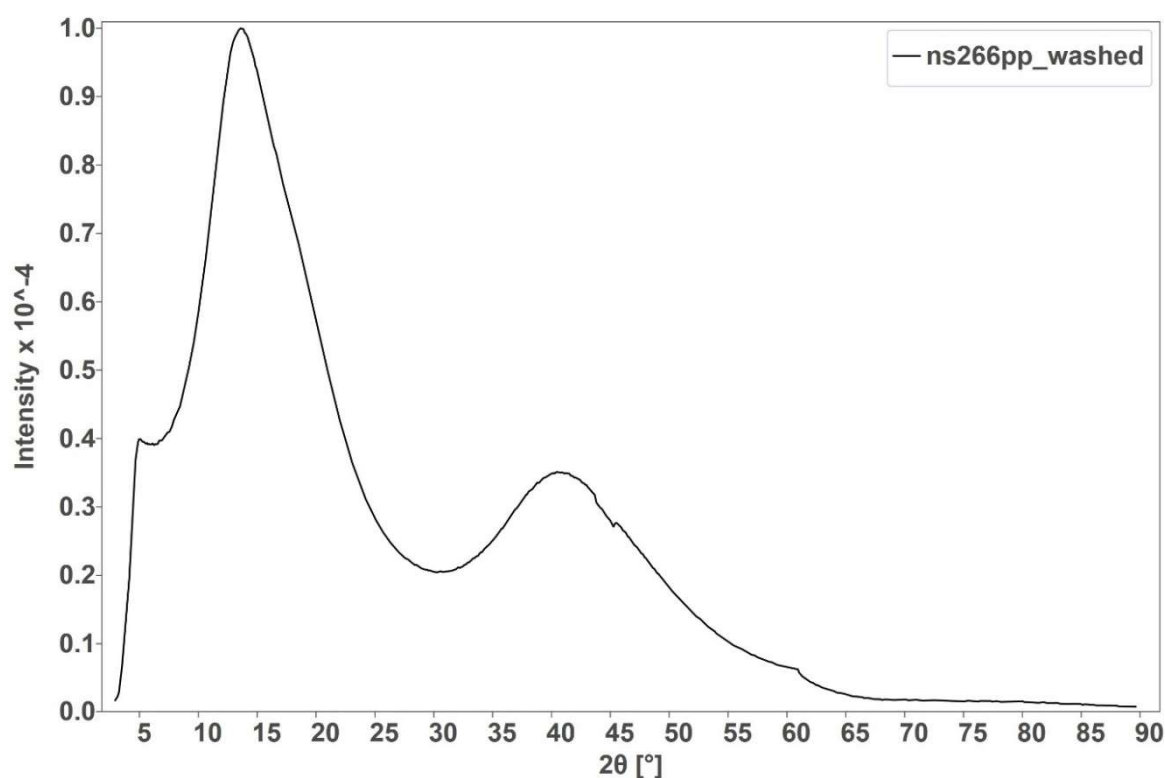


Figure S75 - PXRD pattern of ns266pp_washed. Sample ns266pp_washed is completely amorphous.

ns269p

Roughly equal amounts of sample ns269 was loaded into 2 large ceramic crucibles, totalling 0.87 g of sample ns266 in total. The crucibles were shaken back and forth lightly to spread the material thin over the surface of the crucibles. The large ceramic crucibles were then inserted into the quartz tube of furnace X at equal distances from the middle of the furnace, one crucible being downstream of the other. The insulation blocks were inserted and the tube was sealed. The tube was purged by purge/vac cycling 5 times using argon zero. The flow was then set to 2 L/m and the temperature of the furnace was raised to 900°C over 3 hours and held at 900°C for 2 hours. The temperature was controlled down to 500°C over 80 minutes. The product weighed 0.24 g for a yield of 27.6 wt.%. The product was washed by suspending in a roughly equal parts methanol and distilled water mixture and storing this solution in a dialysis membrane suspended in distilled water. After the system was given ~12 hours to pull contaminants out of the sample into the surrounding distilled water, the distilled water was exchanged with fresh distilled water. This was repeated 2 times. The product was then centrifuged to remove the solvent and dried under vacuum. TEM image, EDX spectrum and PXRD pattern shown in the main text.

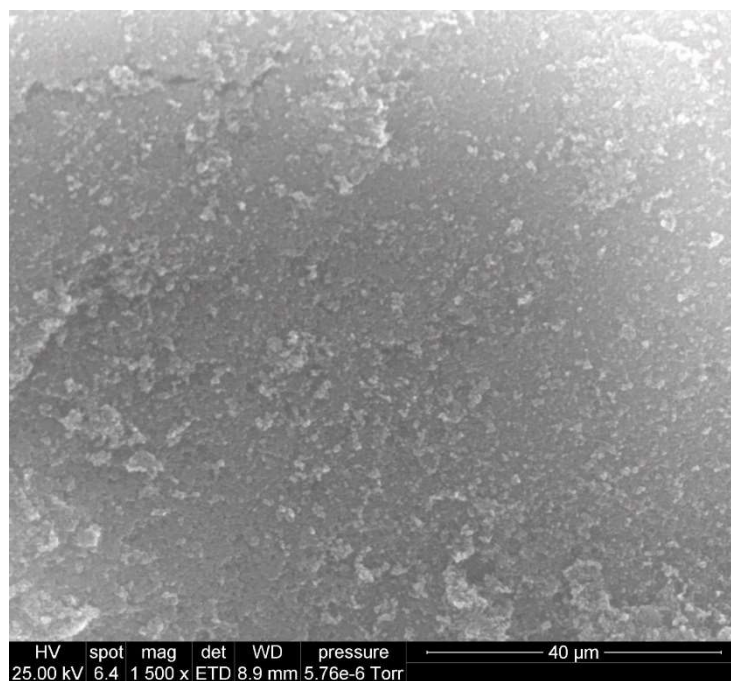


Figure S76 - SEM image of ns269p.

ns274p

Sample ns274a was loaded into a large ceramic crucible. The crucible was shaken back and forth lightly to spread the material thin over the surface of the crucible. The large ceramic crucible was then inserted into the quartz tube of furnace X. The insulation blocks were inserted and the tube was sealed. The tube was purged by purge/vac cycling 4 times using argon zero. The flow was then set to 1 L/m and the temperature of the furnace was raised to 900°C over 3 hours and held at 900°C for 2 hours. The temperature was controlled down to 500°C over 80 minutes. The product was washed by suspending in a roughly equal parts methanol and distilled water mixture and storing this solution in a dialysis membrane suspended in distilled water. After the system was given ~12 hours to pull contaminants out of the sample into the surrounding distilled water, the distilled water was exchanged with fresh distilled water. This was repeated 2 times. The product was then centrifuged to remove the solvent and dried under vacuum. TEM image and PXRD pattern shown in the main text.

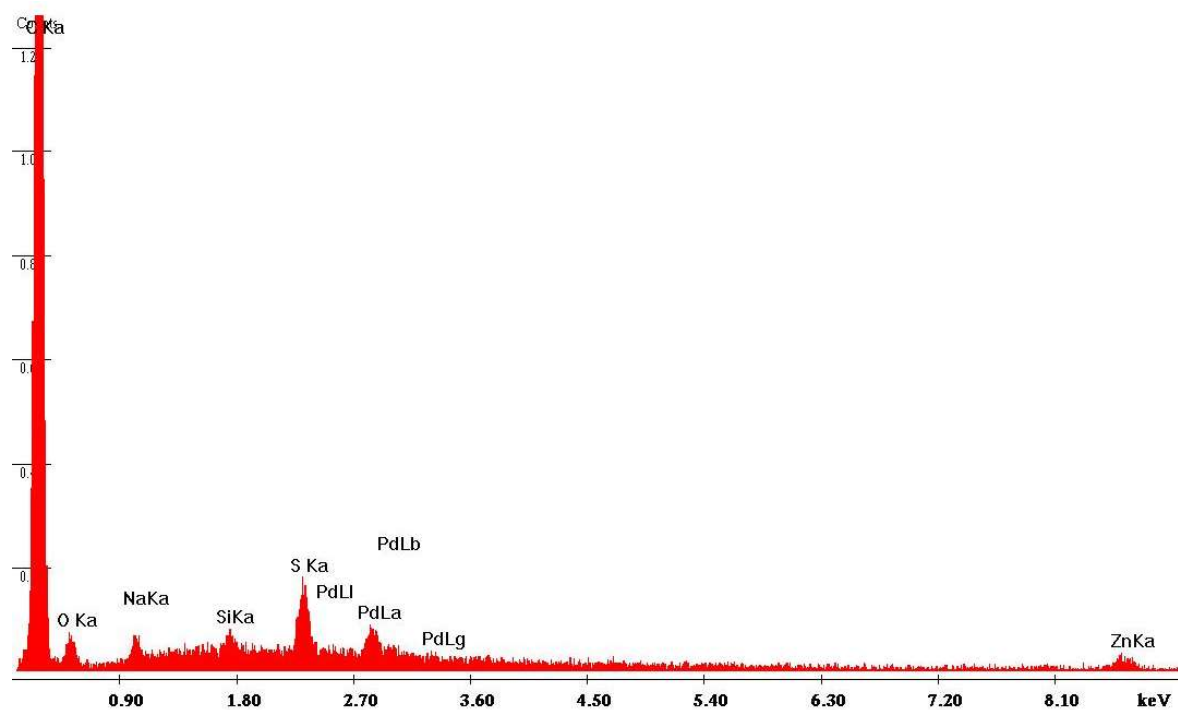


Figure S77 - EDX spectrum of ns274pa_X_6/9.

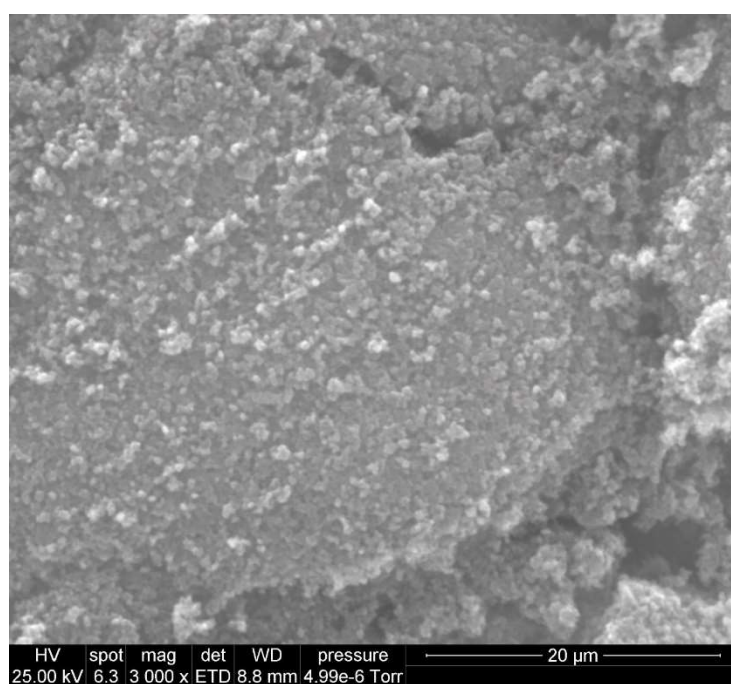


Figure S78 - SEM image of ns274pa_X_6/9.

Sample ns274b was loaded into 2 ceramic crucibles. The crucibles were shaken back and forth lightly to spread the material thin over the surface of the crucibles. The ceramic crucibles were then inserted into the quartz tube of furnace X at equal distances from the middle of the furnace, one crucible being downstream of the other. The insulation blocks were inserted and the tube was sealed. The tube was purged by purge/vac cycling 5 times using argon zero. The flow was then set to 1 L/m and the temperature of the furnace was raised to 900°C over 3 hours and held at 900°C for 2 hours. The temperature was controlled down to 500°C over 80 minutes. The product was washed by dispersing in a roughly equal parts methanol and distilled water mixture and storing this solution in a dialysis membrane suspended in distilled water. After the system was given ~12 hours to pull contaminants out of the sample into the surrounding distilled water, the distilled water was exchanged with fresh distilled water. This was repeated 2 times. The product was then centrifuged to remove the solvent and dried under vacuum. TEM image and PXRD pattern shown in the main text.

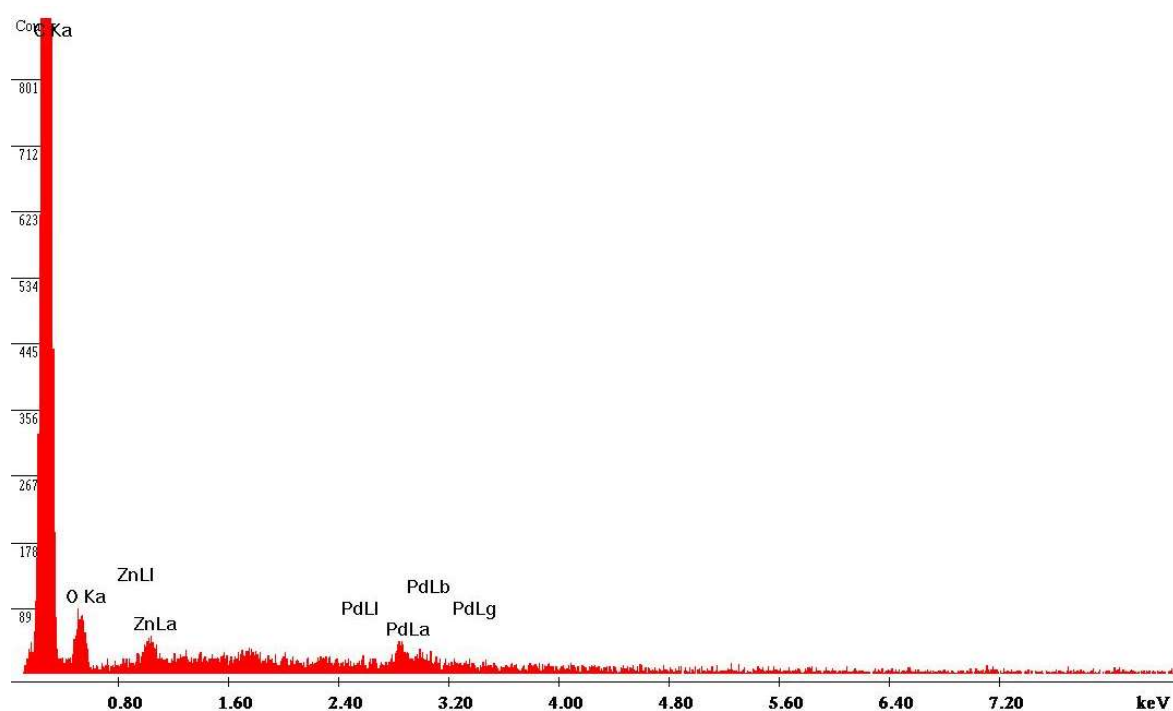


Figure S79 - EDX spectrum of ns274pb_X_8/9.

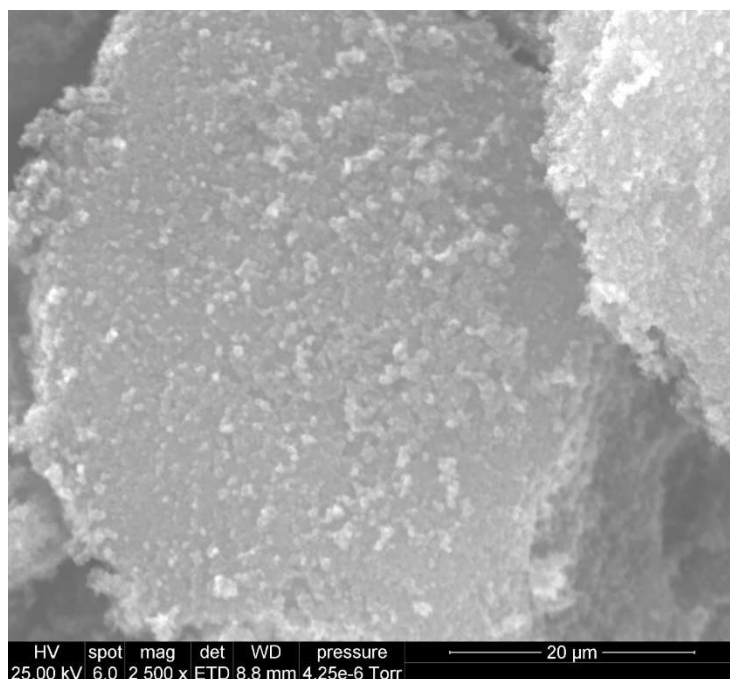


Figure S80 - SEM image of ns274pb_X_8/9.

Sample ns274c was loaded into a large ceramic crucible. The crucible was shaken back and forth lightly to spread the material thin over the surface of the crucible. The large ceramic crucible was then inserted into the quartz tube of furnace X. The insulation blocks were inserted and the tube was sealed. The tube was purged by purge/vac cycling 4 times using argon zero. The flow was then set to 1 L/m and the temperature of the furnace was raised to 900°C over 3 hours and held at 900°C for 2 hours. The temperature was controlled down to 500°C over 80 minutes. The product was washed by dispersing in a roughly equal parts methanol and distilled water mixture and storing this solution in a dialysis membrane suspended in distilled water. After the system was given ~12 hours to pull contaminants out of the sample into the surrounding distilled water, the distilled water was exchanged with fresh distilled water. This was repeated 2 times. The product was then centrifuged to remove the solvent and dried under vacuum. TEM image and PXRD pattern shown in the main text.

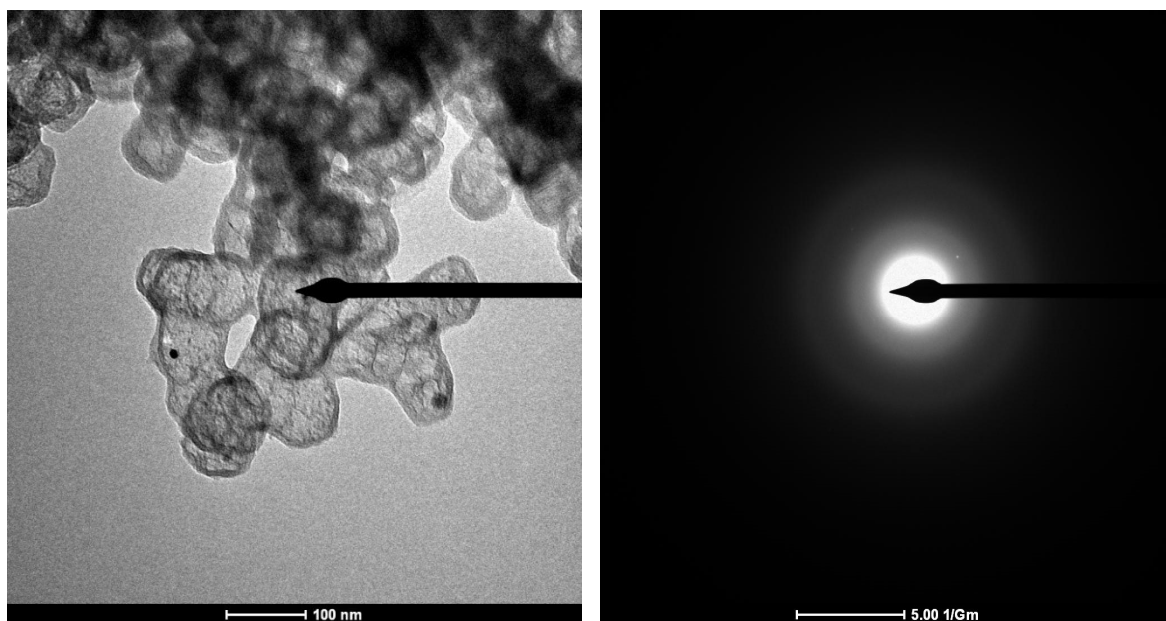


Figure S81 - Images of electron diffraction of sample ns274pc_X_9/9 using TEM.

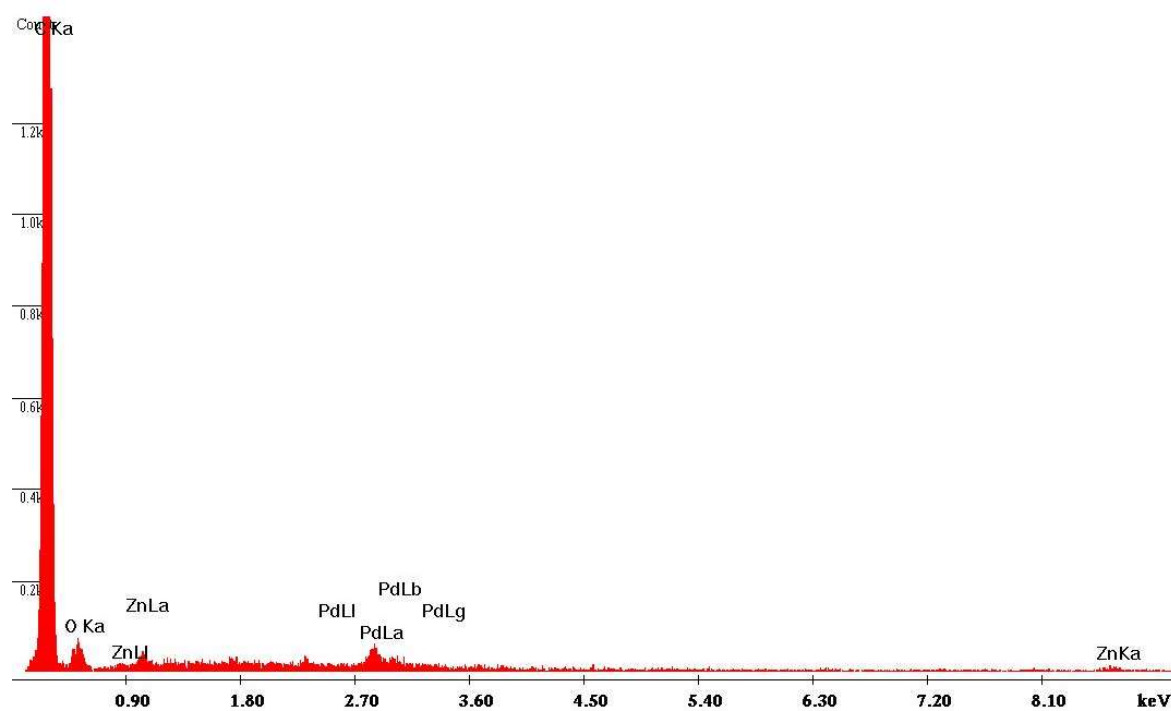


Figure S82 - EDX spectrum of ns274pc_X_9/9.

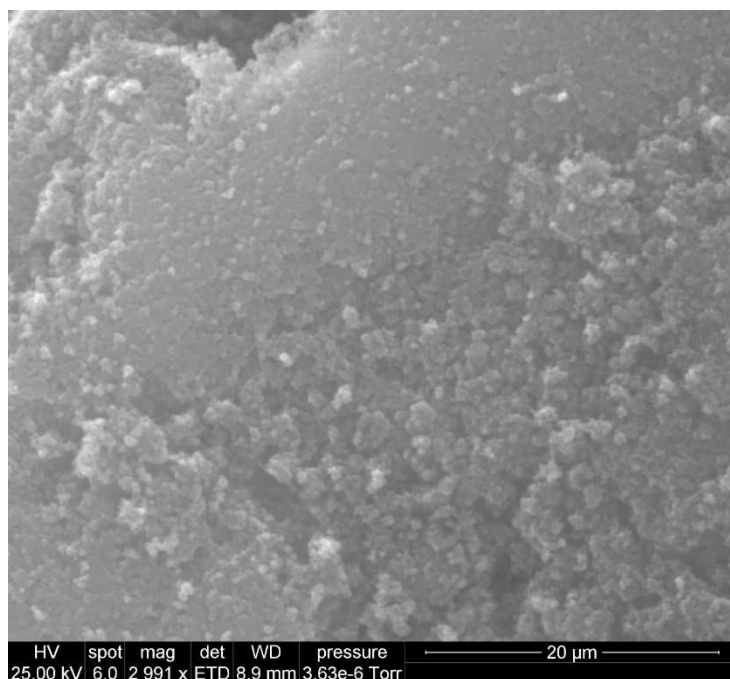


Figure S83 - SEM image of ns274pc_X_9/9.

Control

ns264p

Roughly equal amounts of sample ns264 was loaded into 2 large ceramic crucibles, totalling 0.52 g of sample ns264 in total. The crucibles were shaken back and forth lightly to spread the material thin over the surface of the crucibles. The large ceramic crucibles were then inserted into the quartz tube of furnace X at equal distances from the middle of the furnace, one crucible being downstream of the other. The insulation blocks were inserted and the tube was sealed. The tube was purged by purge/vac cycling 5 times using argon zero. The flow was then set to 2 L/m and the temperature of the furnace was raised to 900°C over 3 hours and held at 900°C for 2 hours. The temperature was controlled down to 500°C over 80 minutes. The product was washed by dispersing in a roughly equal parts methanol and distilled water mixture and storing this solution in a dialysis membrane suspended in distilled water. After the system was given ~12 hours to pull contaminants out of the sample into the surrounding distilled water, the distilled water was exchanged with fresh distilled water. This was repeated 2 times. The product was then centrifuged to remove the solvent and dried under vacuum. The PXRD pattern, TEM images and EDX spectrum obtained from ns264p are shown in the main text.

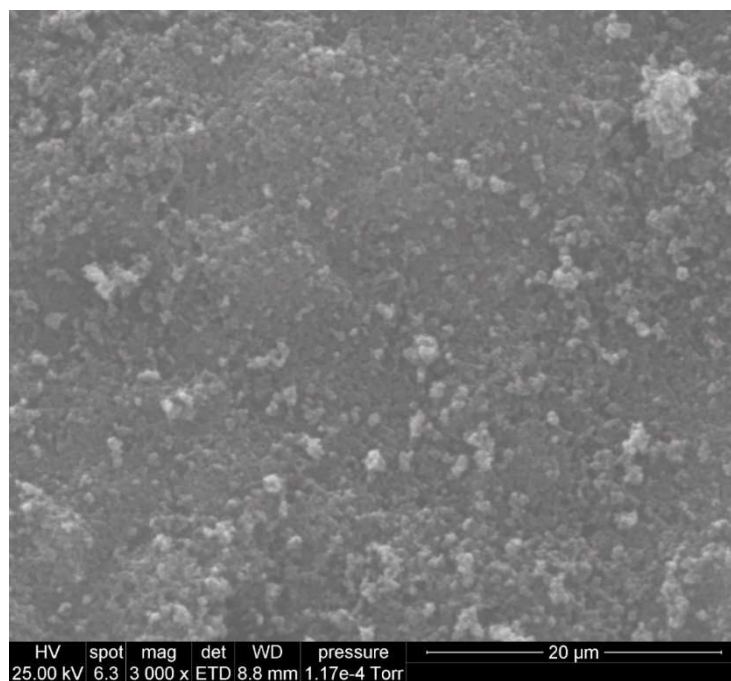


Figure S84 - SEM image of ns264p_X_7/9.

Catalysis

Biomass conversion (Furfural to cyclopentanone)

Gas chromatography method

The temperature was raised from 30.0°C at a rate of 0.50°C/min to 40.0°C, raised further at a rate of 3.00°C/min until 50.0°C, and finally raised further at a rate of 70.00°C/min until 270.0°C at which the temperature was held for 6 minutes. The injector was kept at 300°C and the detector at 280°C. Injection volume was 1.0 µL. Carrier gas flow through the column was 36.2 mL/min at a pressure of 101.0 kPa. The carrier gas used was nitrogen.

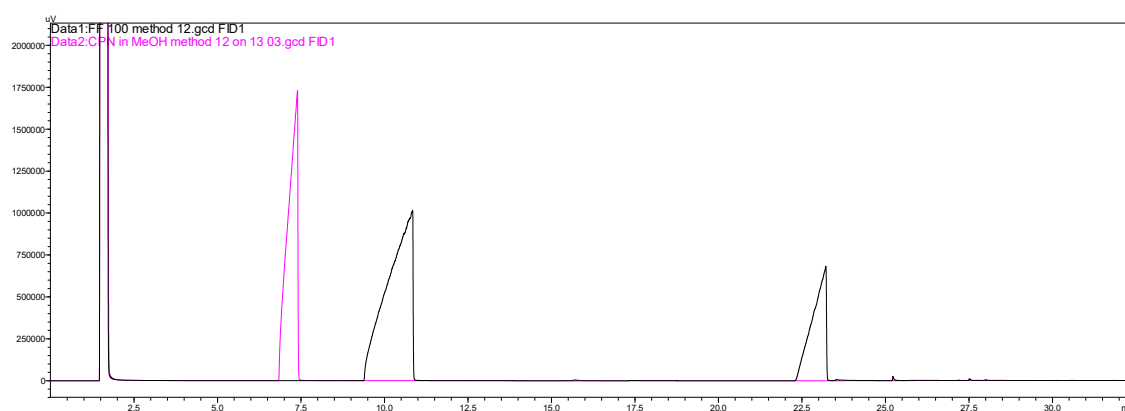


Figure S85 - Gas chromatograph of furfural (black) compared to cyclopentanone (pink). Peaks before 3 minutes are solvents.

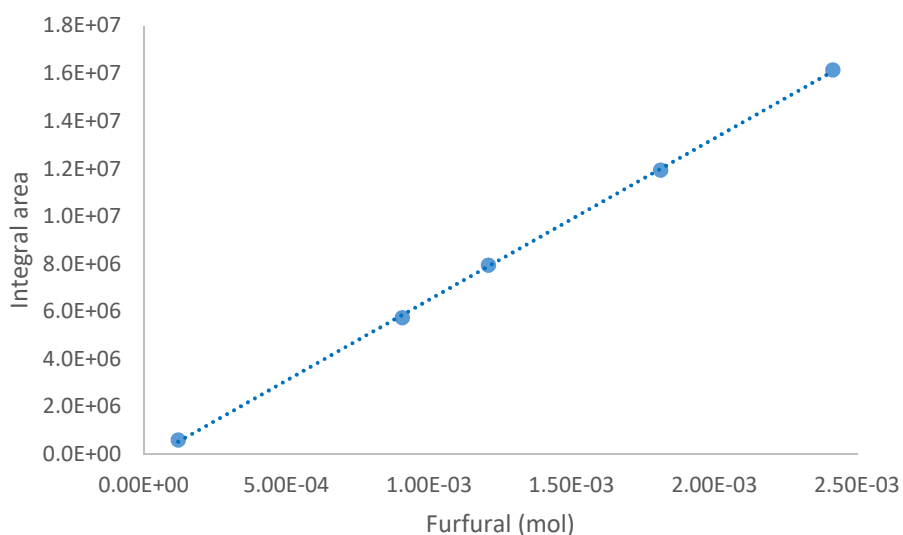


Figure S86 - Furfural gas chromatography calibration curve.

ns198

170 μL furfural ($2.05\text{E-}03$ mol), 4 mL distilled water, 10.8 mg commercial platinum on carbon (10 wt.%) and a stirrer bar were loaded into the Parr reactor in a glass lining. The vessel was sealed and pressurized with hydrogen to 5 bar, 7.6 bar and finally 7.6 bar with venting in-between to improve the atmosphere purity. The vessel was placed in an oil bath preheated to 200°C while stirring. After 24 hours the internal temperature of the vessel had reached 109°C . The vessel was then removed from the oil bath and allowed to cool. The reaction product was centrifuged and filtered to remove the catalyst and stored in the fridge.

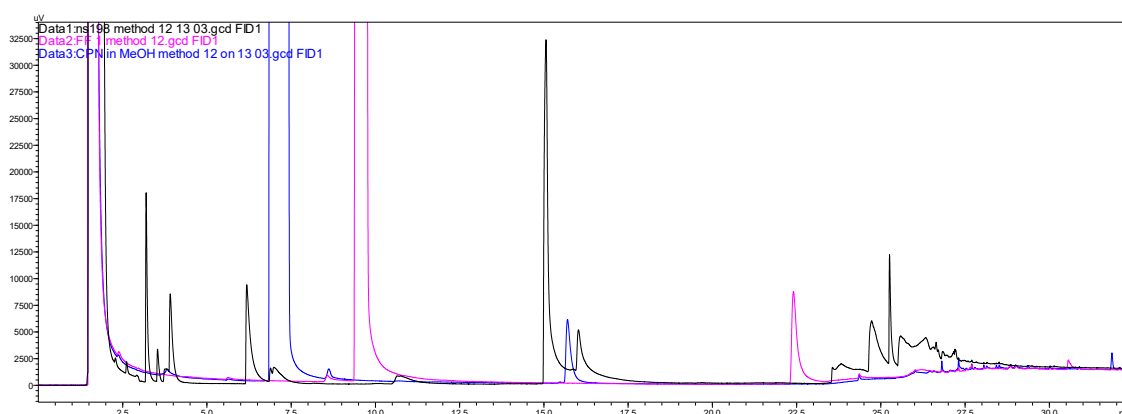


Figure S87 - Gas chromatograph of ns198 (black) compared to furfural (pink) and cyclopentanone (blue).

ns275

170 μL furfural ($2.05\text{E-}03$ mol), 4 mL distilled water, 3.6 mg ns266pp_washed ($1.87\text{E-}07$ mol Pd) and a stirrer bar were loaded into the Parr reactor in a glass lining. The vessel was sealed and pressurized with hydrogen to 3 bar, 5 bar and finally 7.6 bar with venting in-between to improve the atmosphere purity. The vessel was placed inside the heating mantle and set to stir at 300 rpm. The temperature was raised to 145°C over an hour and held at 145°C for 4 hours and 40 minutes. The heating mantle was removed and the vessel allowed to cool to room temperature. The reaction mixture evaporated during the experiment and condensed on the room of the vessel, pooling at the base of the vessel outside the glass liner. The reaction product was yellow and soluble in water (furfural is not). The reaction product was centrifuged and filtered to remove the catalyst and stored in the fridge.

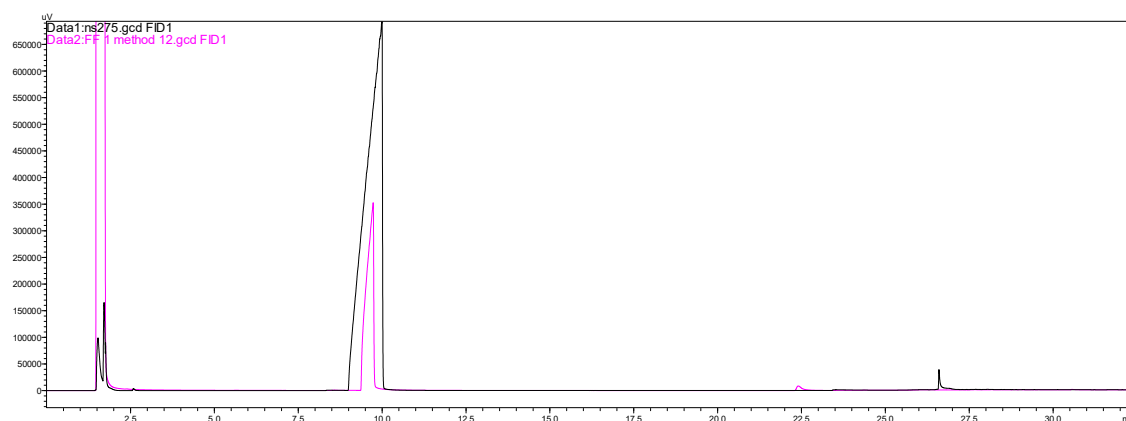


Figure S88 - Gas chromatograph of reaction product (ns275, black) overlaid on top of reactant (furfural, pink). Peaks before 2.5 minutes are solvent peaks.

Quinoline hydrogenation

Gas chromatography method

The temperature was raised from 130°C at a rate of 2.50°C/min to 170°C, then raised further at a rate of 50.00°C/min until 270°C, at which the temperature was held for 5 minutes. The injector was kept at 300°C and the detector at 280°C. Injection volume was 1.0 µL. Carrier gas flow through the column was 50.0 mL/min at a pressure of 100.0 kPa. The carrier gas used was nitrogen.

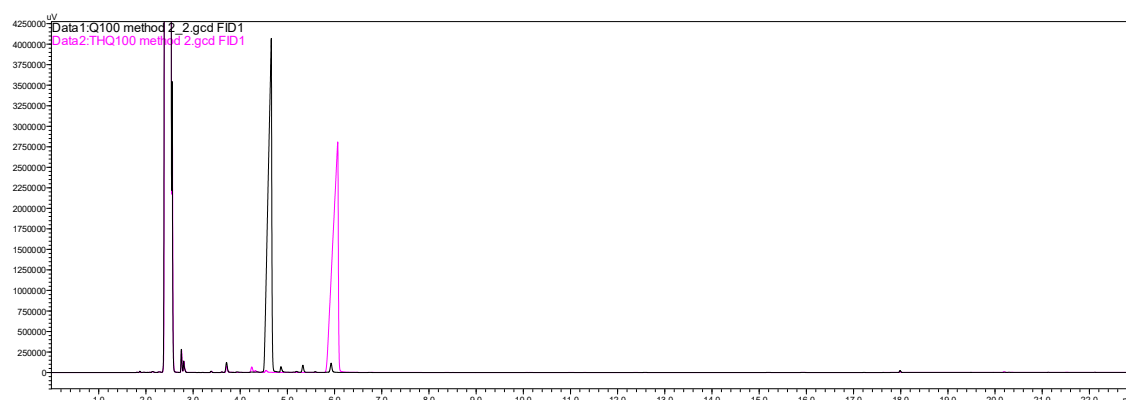


Figure S89 - Gas chromatograph of quinoline (black) compared to tetrahydroquinoline (pink). Peaks before 3 minutes are solvents.

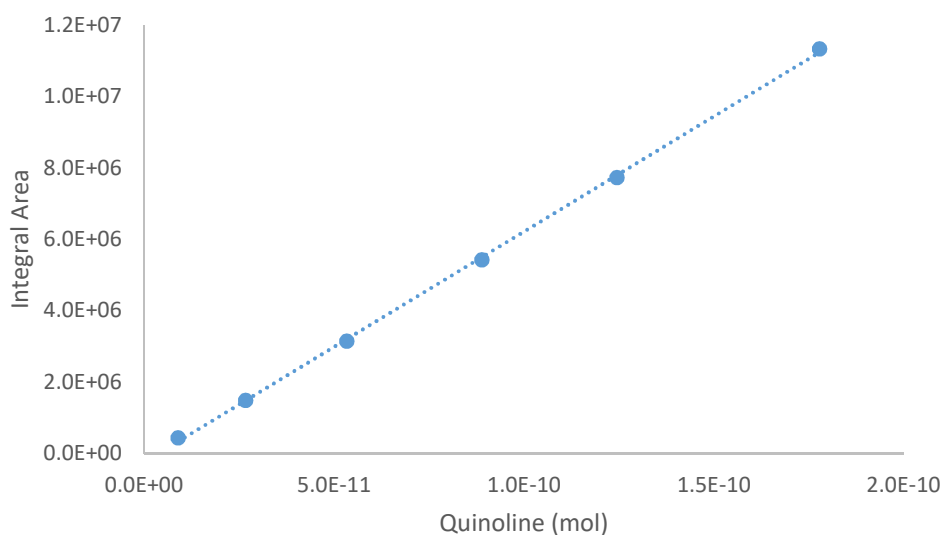


Figure S90 - Quinoline gas chromatography calibration curve.

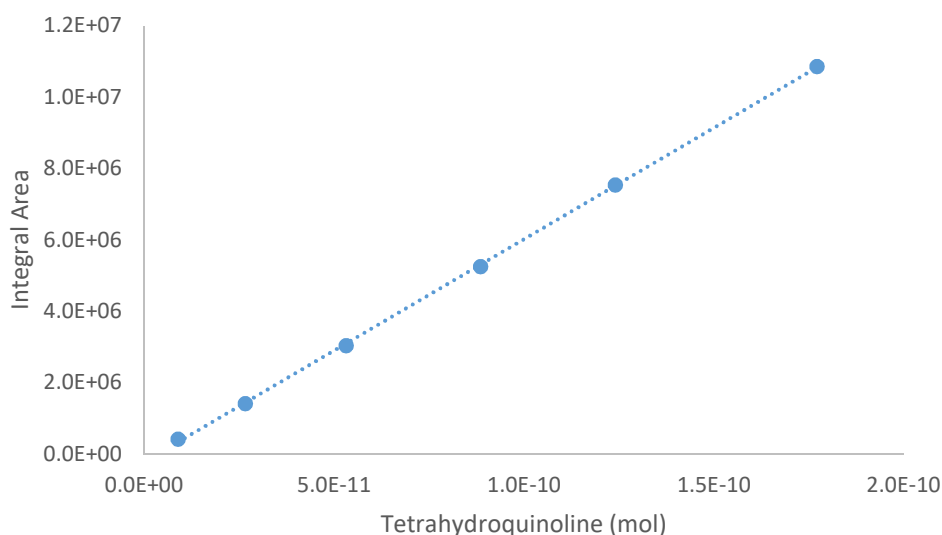


Figure S91 - Tetrahydroquinoline gas chromatography calibration curve.

ns194

6 mL methanol, 120 μ L quinoline, 7.9 mg commercial palladium on carbon (10 wt.%) and a stirrer bar were loaded into the Parr reactor in a Teflon lining. The vessel was sealed and pressurized with hydrogen to 3 bar, 5 bar, and finally 5 bar with venting in-between to improve the atmosphere purity. The vessel was placed in an oil bath preheated to 80°C while stirring at 450 rpm. After 4 hours the internal temperature of the vessel had reached 60°C. The vessel was then removed from the oil bath and allowed to cool. The reaction product was centrifuged and filtered to remove the catalyst and stored in the fridge.

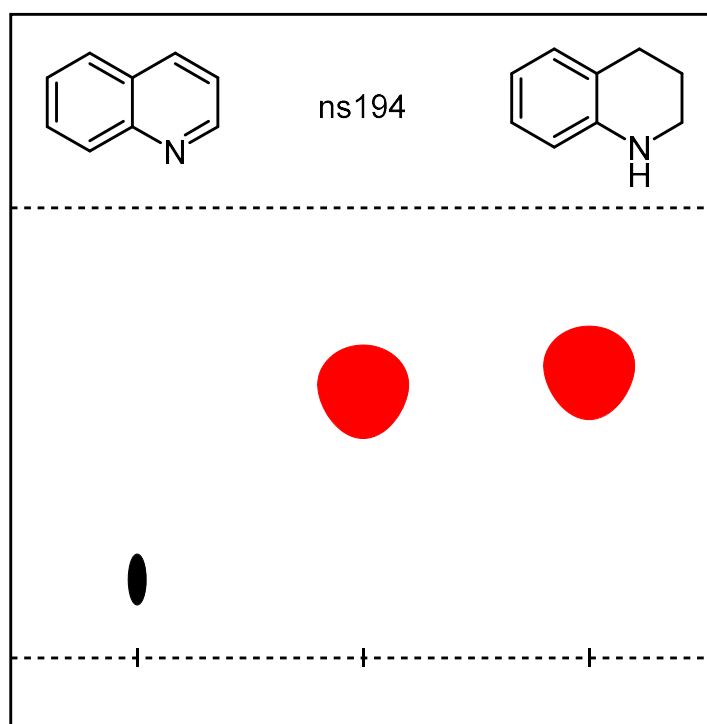


Figure S92 - Thin-layer chromatography of ns194 (middle) compared with quinoline (left) and tetrahydroquinoline (right). The eluent was 1 part hexane to 3 parts dichloromethane.

ns270

6 mL methanol, 120 μ L quinoline, 2 mg ns266pp_washed ($1.04\text{E-}07$ mol Pd) and a stirrer bar were loaded into the Parr reactor in a glass lining. The vessel was sealed and pressurized with hydrogen to 3 bar, 5 bar, 5 bar and finally 5 bar with venting in-between to improve the atmosphere purity. The vessel was placed inside the heating mantle and set to stir at 580 rpm. The temperature was raised to 80°C over 30 minutes and held at 80°C for 7 hours and 20 minutes. The heating mantle was removed and the vessel allowed to cool to room temperature. The solvent evaporated during the experiment and condensed on the room of the vessel, pooling at the base of the vessel outside the glass liner. This left the reaction product remaining in the glass liner. The reaction product was centrifuged and filtered to remove the catalyst and stored in the fridge.

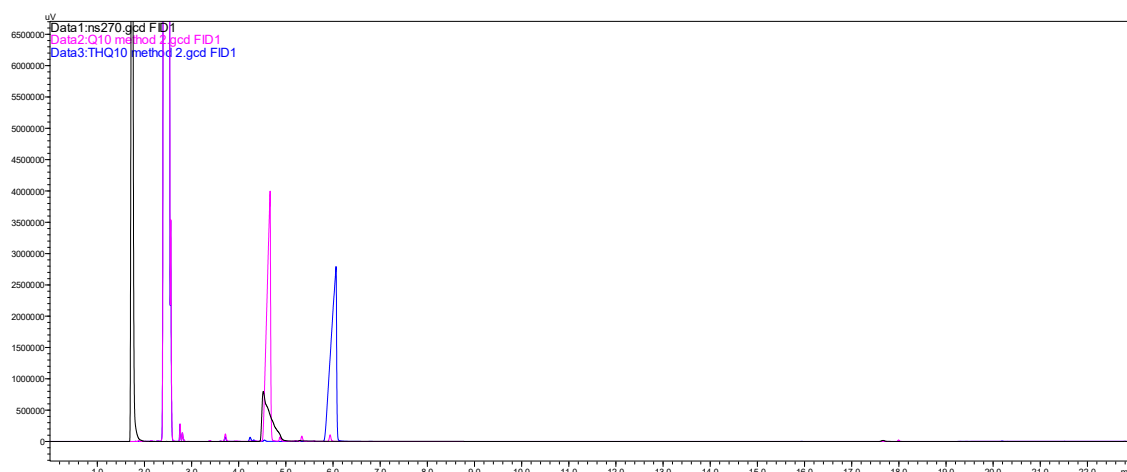
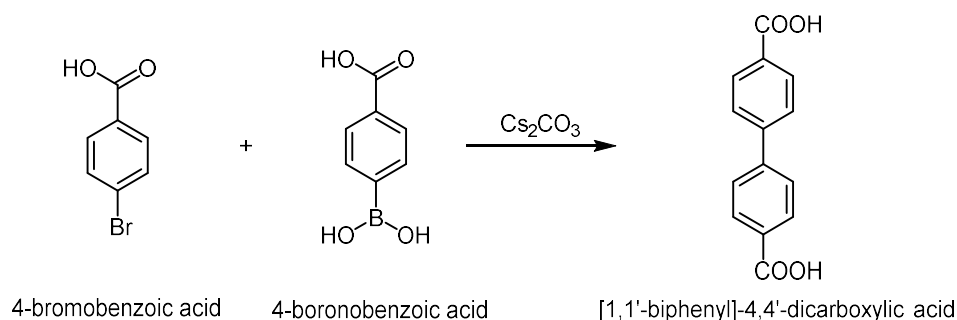


Figure S93 - Gas chromatograph of reaction product (ns270, black) overlaid on top of reactant (quinoline, pink) and expected product (tetrahydroquinoline, blue). Peaks before 3 minutes are solvent peaks.

Suzuki coupling

ns271



Reactants			Products		
Formula	C₇H₅BrO₂	C₇H₇BO₄	CCs₂O₃	Formula	C₁₄H₁₀O₄
MW	201.02	165.94	325.82	MW	242.23
Limiting?	Yes	No	No	Expected Mass	602.51mg
Equivalents	1.00	1.50	1.00	Expected Moles	2.49mmol
Sample Mass	500.00mg	619.12mg	810.42mg	Measured Mass	
Reactant Moles	2.49mmol	3.73mmol	2.49mmol	Product Moles	
Reactant Mass	500.00mg	619.12mg	810.42mg	%Yield	

Figure S94 - Suzuki coupling reaction of 4-bromobenzoic acid and 4-boronobenzoic acid for [1,1'-biphenyl]-4,4'-dicarboxylic acid.

4-bromobenzoic acid (0.50 g, 2.5 mmol), 4-boronobenzoic acid (0.62 g, i.5 eq.), and Cs₂CO₃ (0.81 g, 1 eq.) were placed into a round bottom flask. 3.6 mg of ns266pp_washed (1.87E-07 mol Pd) was added, followed by addition of 7 mL distilled water. The reaction vessel was closed with a glass stopper. The vessel was placed in an oil bath and was magnetically stirred at 80 °C for 20 hours and 40 minutes. After cooling to room temperature, it was diluted with

15 mL water. The solution was filtered while washing with water. The remaining solid was then filtered again while washing with 10% DMSO in THF. The 10% DMSO in THF solution was boiled using a rotary evaporator to remove THF. The remaining solution was then crashed with 200 mL of water. A white precipitate formed. The solution was centrifuged to remove solvent and isolate the white solid. An NMR spectrum of the white solid is shown below in Figure 95 compared to reactants and expected products. The white solid was also found to be soluble in acetone while [1,1'-biphenyl]-4,4'-dicarboxylic acid is not, indicating that the desired product was not formed.

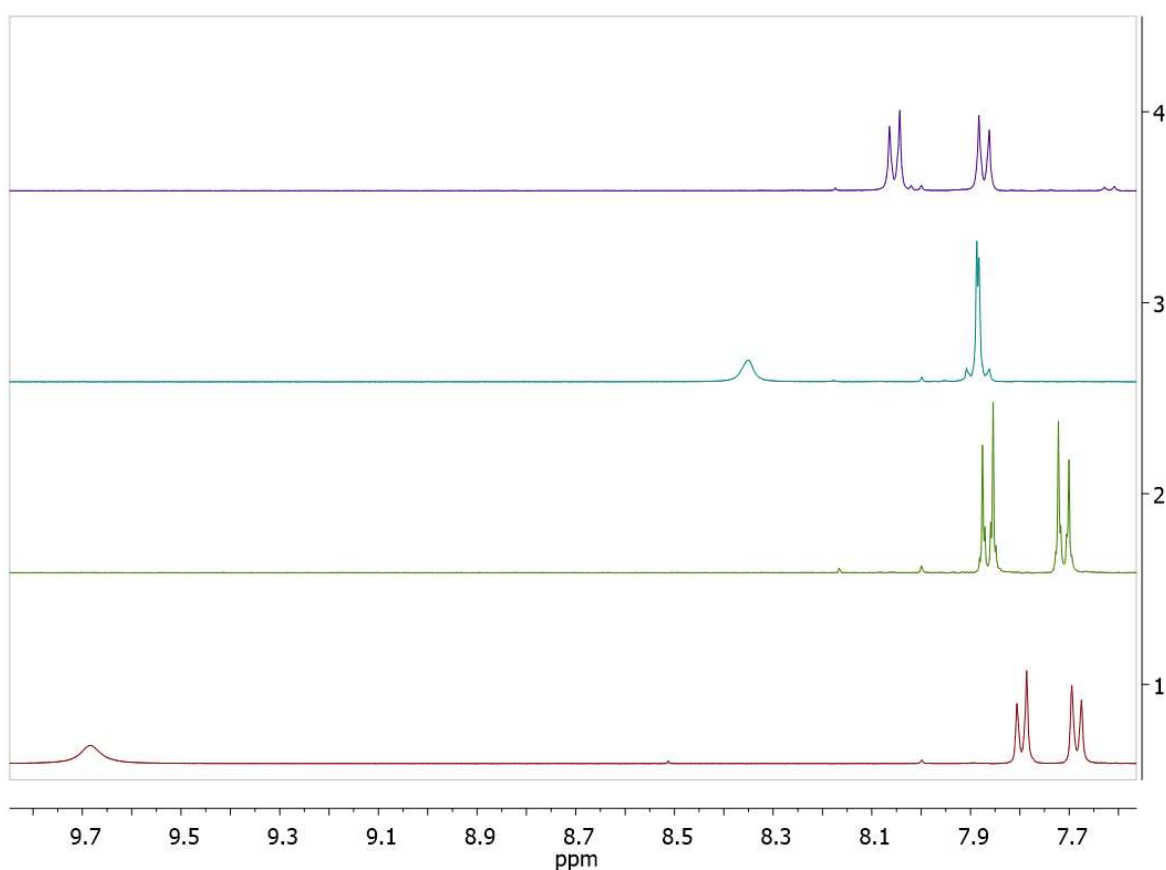
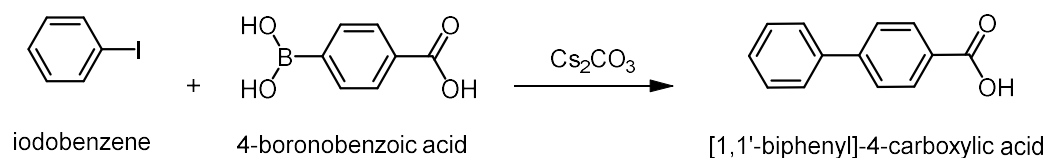


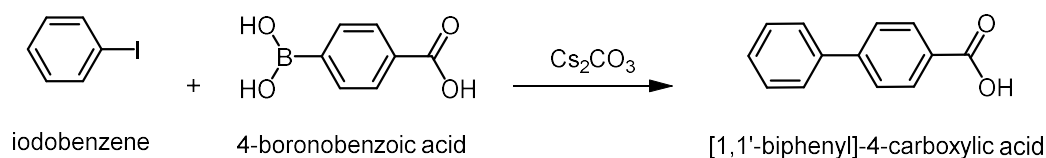
Figure S95 - NMR spectrum of ns271, 4-bromobenzoic acid, 4-boronobenzoic acid and [1,1'-biphenyl]-4,4'-dicarboxylic acid all in d-DMSO in ascending order.



<i>Reactants</i>				<i>Products</i>	
Formula	C₆H₅I	C₇H₇BO₄	CCs₂O₃	Formula	C₁₃H₁₀O₂
MW	204.01	165.94	325.82	MW	198.22
Limiting?	Yes	No	No	Equivalents	
Equivalents	1.00	1.30	1.10	%Completion	
Sample Mass	50.00mg	52.87mg	87.84mg	Expected Mass	48.58mg
%Weight				Expected Moles	245.09μmol
Molarity				Measured Mass	
Density	1.83g/mL			Purity	
Volume	27.32mmL			Product Mass	
Reactant Moles	245.09μmol	318.61μmol	269.59μmol	Product Moles	
Reactant Mass	50.00mg	52.87mg	87.84mg	%Yield	

Figure S96 - Suzuki coupling of iodobenzene and 4-boronobenzoic acid for [1,1'-biphenyl]-4-carboxylic acid.

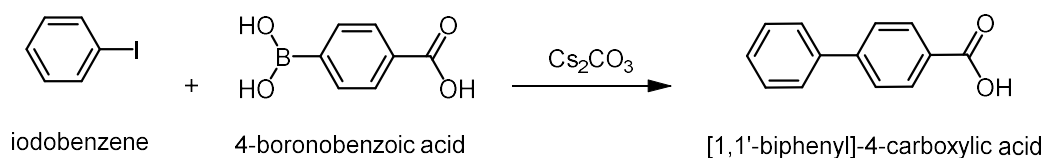
27.3 μL iodobenzene, 53 mg 4-boronobenzoic acid and 91 mg Cs₂CO₃ added to microwave vial. 0.5 mL dioxane and 5.5 mL deionised water added. A stirrer bar and 8.6 mg ns266pp_washed (4.46E-07 mol Pd) added. The microwave vial was closed with a silicon cap and placed in the microwave at 90°C for 24 hours while stirring. After cooling, the catalyst had sunk to the bottom and a white solid was floating above it. The white solid was extracted with a spatula, centrifuged to remove solvent and dried under vacuum overnight. The HNMR of the solid is shown in the main text.



<i>Reactants</i>				<i>Products</i>	
Formula	C₆H₅I	C₇H₇BO₄	CCs₂O₃	Formula	C₁₃H₁₀O₂
MW	204.01	165.94	325.82	MW	198.22
Limiting?	Yes	No	No	Equivalents	
Equivalents	1.00	1.30	1.10	%Completion	
Sample Mass	50.00mg	52.87mg	87.84mg	Expected Mass	48.58mg
%Weight				Expected Moles	245.09μmol
Molarity				Measured Mass	
Density	1.83g/mL			Purity	
Volume	27.32mL			Product Mass	
Reactant Moles	245.09μmol	318.61μmol	269.59μmol	Product Moles	
Reactant Mass	50.00mg	52.87mg	87.84mg	%Yield	

Figure S97 - Suzuki coupling of iodobenzene and 4-boronobenzoic acid for [1,1'-biphenyl]-4-carboxylic acid.

92.5 mg Cs₂CO₃, 10.7 mg ns266pp_washed, 5.5 mL distilled water, 0.5 mL dioxane and a stirrer bar were added to a microwave vial. The vessel was sonicated and then microwaved at 90°C for 24 hours while stirring. The stirrer was removed and the solution was centrifuged at 5 krpm for 15 minutes to separate ns266pp_washed from the solvent. 52.8 mg 4-boronobenzoic acid and 27.3 μL iodobenzene were added to a fresh microwave vial. The solvent mixture was syringe filtered from the vessel containing ns266pp_washed into the fresh vessel containing reactants. A fresh stirrer bar was added to the reaction mixture and the mixture was then microwaved at 90°C for 24 hours while stirring. After cooling, a white precipitate had formed. The stirrer was removed, and the reaction mixture was centrifuged at 5 krpm for 15 minutes to separate the white precipitate from the solvent. The product was then washed two times with water and dried overnight. The NMR spectrum of the precipitate dissolved in DMSO-d₆ is shown in the main text.



<i>Reactants</i>				<i>Products</i>	
Formula	C₆H₅I	C₇H₇BO₄	CCs₂O₃	Formula	C₁₃H₁₀O₂
MW	204.01	165.94	325.82	MW	198.22
Limiting?	Yes	No	No	Equivalents	
Equivalents	1.00	1.30	1.10	%Completion	
Sample Mass		319.28mg	530.46mg	Expected Mass	293.38mg
%Weight				Expected Moles	1.48mmol
Molarity				Measured Mass	
Density	1.83g/mL			Purity	
Volume	165.00mmL			Product Mass	
Reactant Moles	1.48mmol	1.92mmol	1.63mmol	Product Moles	
Reactant Mass	301.95mg	319.28mg	530.46mg	%Yield	

Figure S98 - Suzuki coupling of iodobenzene and 4-boronobenzoic acid for [1,1'-biphenyl]-4-carboxylic acid.

327.5 mg 4-boronobenzoic acid, 541.4 mg Cs₂CO₃, 28.2 mg ns266pp_washed, 165 μL iodobenzene, 3 mL dioxane and 30 mL distilled water were added to a microwave vial. The mixture was sonicated to disperse and a stirrer was added. The vial was heated to ~100°C in an oil bath to dissolve reactants. A small aliquot was taken, filtered and labelled “ns289 1”. The microwave vial was allowed to cool, and then was put in the microwave at 90°C for 2 hours while stirring. A small aliquot was taken, filtered and labelled “ns289 2”. The microwave vial was then put back in the microwave at 90°C for 3 hours while stirring. A small aliquot was taken, filtered and labelled “ns289 3”. The microwave vial was then put back in the microwave at 90°C for 6 hours while stirring. Some white precipitate had formed. The vial was heated to ~100°C in an oil bath to dissolve precipitate. A small aliquot was taken, filtered and labelled “ns289 4”. The microwave vial was allowed to cool, and then was put in the microwave at 90°C for 10 hours while stirring. The vial was heated to ~100°C in an oil bath to dissolve precipitate. A small aliquot was taken, filtered and labelled “ns289 5”. The microwave vial was allowed to cool, and then was put in the microwave at 90°C for 4 hours while stirring. The vial was heated to ~100°C in an oil bath to dissolve precipitate. A small aliquot was taken, filtered and labelled “ns289 6”. The microwave vial was allowed to cool, and then was put in the microwave at 90°C for 6 hours while stirring. The vial was heated to ~100°C in an oil bath to dissolve precipitate. A small aliquot was taken, filtered

and labelled “ns289 7”. The vial was allowed to cool. Later, the vial was again heated to ~100°C in an oil bath to dissolve precipitate. The mixture was filtered twice through a 0.2 μ m pore size syringe filter to remove catalyst. The remaining solvent was measured to have a volume of 18 mL. This solvent was allowed to cool and over one day white precipitate formed. The solution was centrifuged at 5 krpm for 5 minutes to separate the precipitate from the solvent and the precipitate was then washed two times with distilled water and dried under high vacuum. The precipitate was measured to have a mass of 31 mg. A small portion of the precipitate was then dissolved in DMSO- d_6 . The resulting NMR spectrum is shown in the main text.

Samples ns289 1 to 7 were initially dried using a rotary evaporator, and if required subsequent drying was performed under high vacuum. The precipitate formed was then dissolved in DMSO- d_6 . The resulting NMR spectra are shown below.

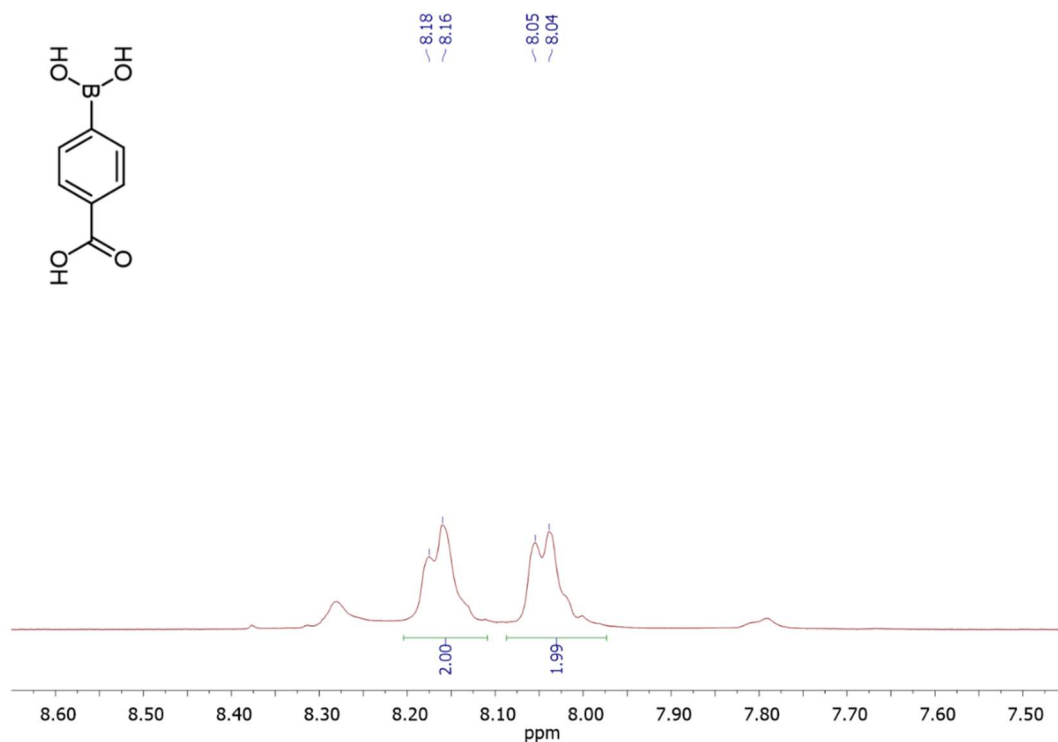


Figure S99 - HNMR spectrum of ns289 1 in DMSO- d_6 . Sample ns289 1 was taken before the reaction began.

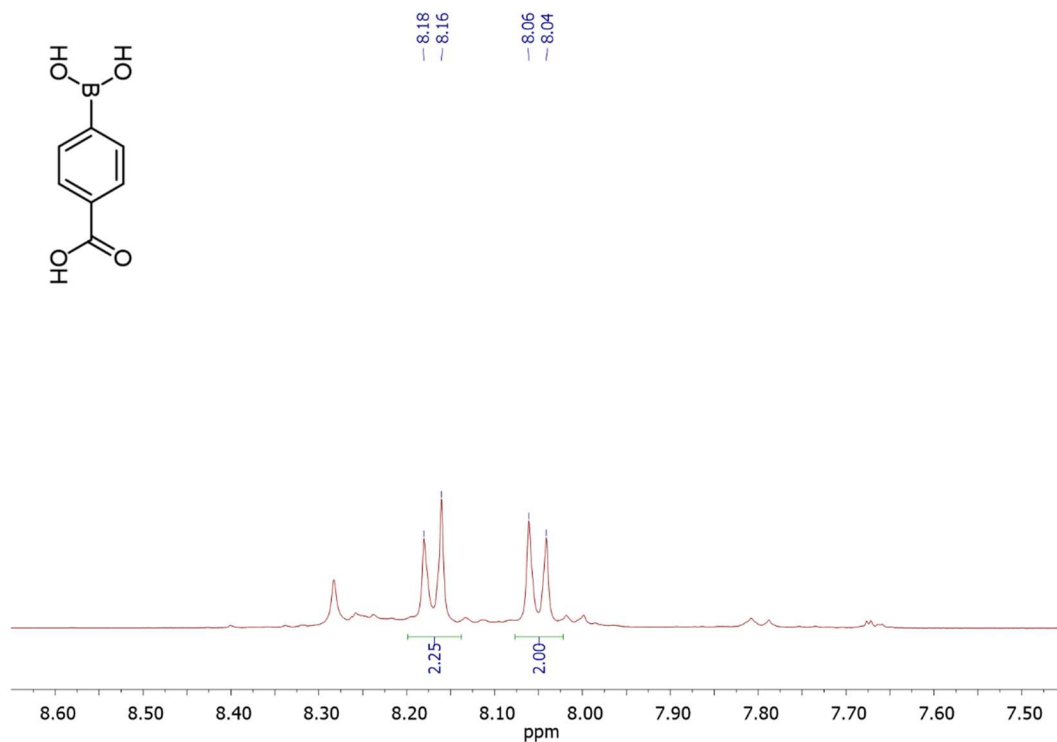


Figure S100 - HNMR spectrum of ns289 2 in DMSO- d_6 . Sample ns289 2 was taken after 2 hours at 90°C.

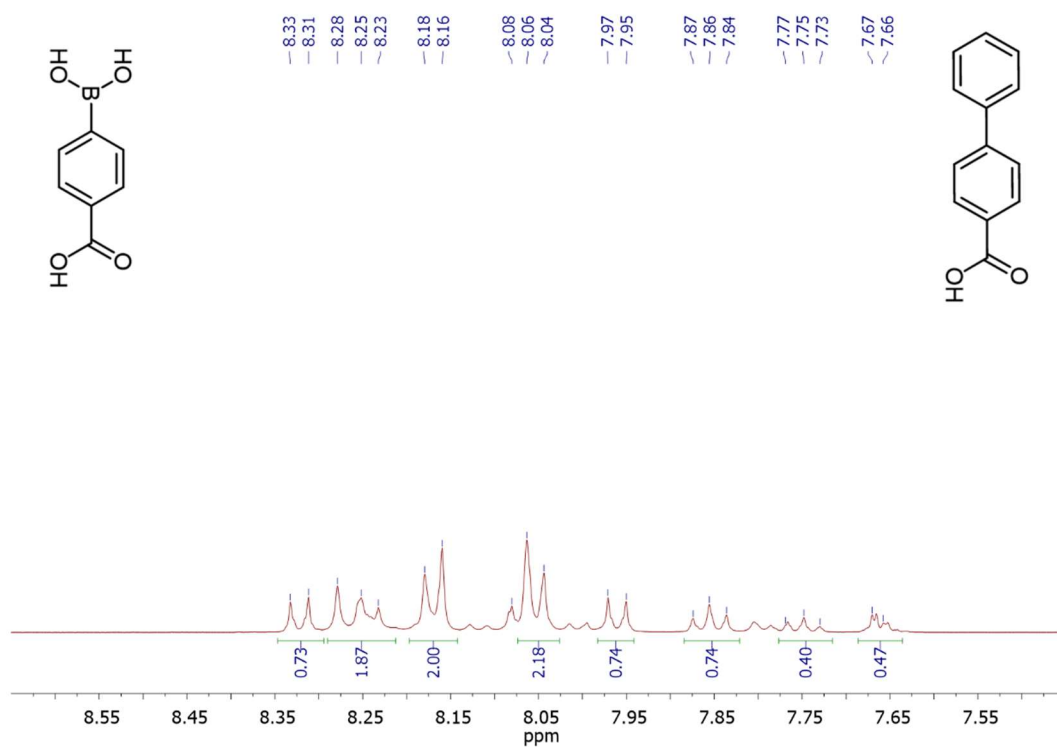


Figure S101 - HNMR spectrum of ns289 3 in DMSO- d_6 . Sample ns289 3 was taken after 5 hours at 90°C.

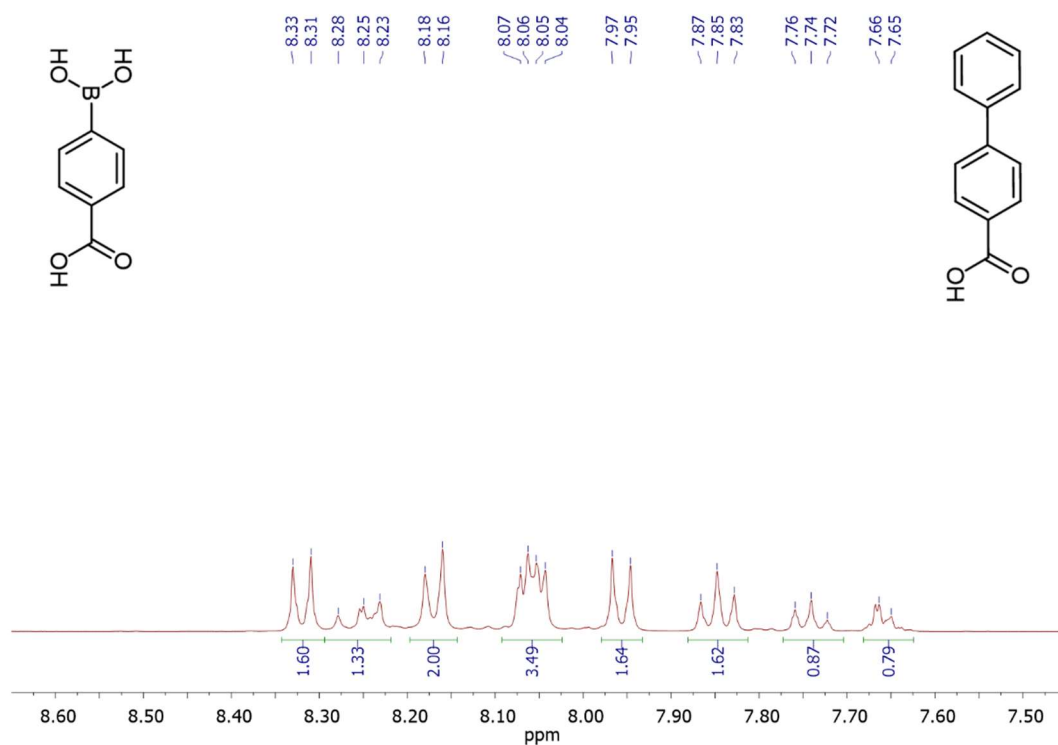


Figure S102 - HNMR spectrum of ns289 4 in DMSO-d₆. Sample ns289 4 was taken after 11 hours at 90°C.

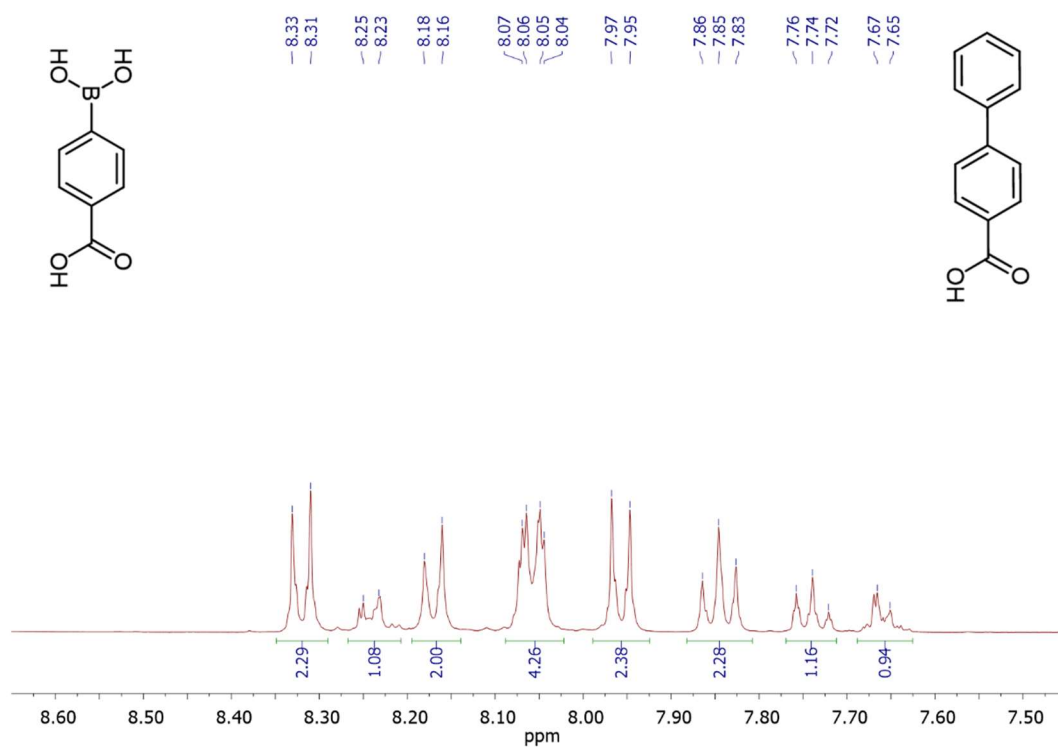


Figure S103 - HNMR spectrum of ns289 5 in DMSO-d₆. Sample ns289 5 was taken after 21 hours at 90°C.

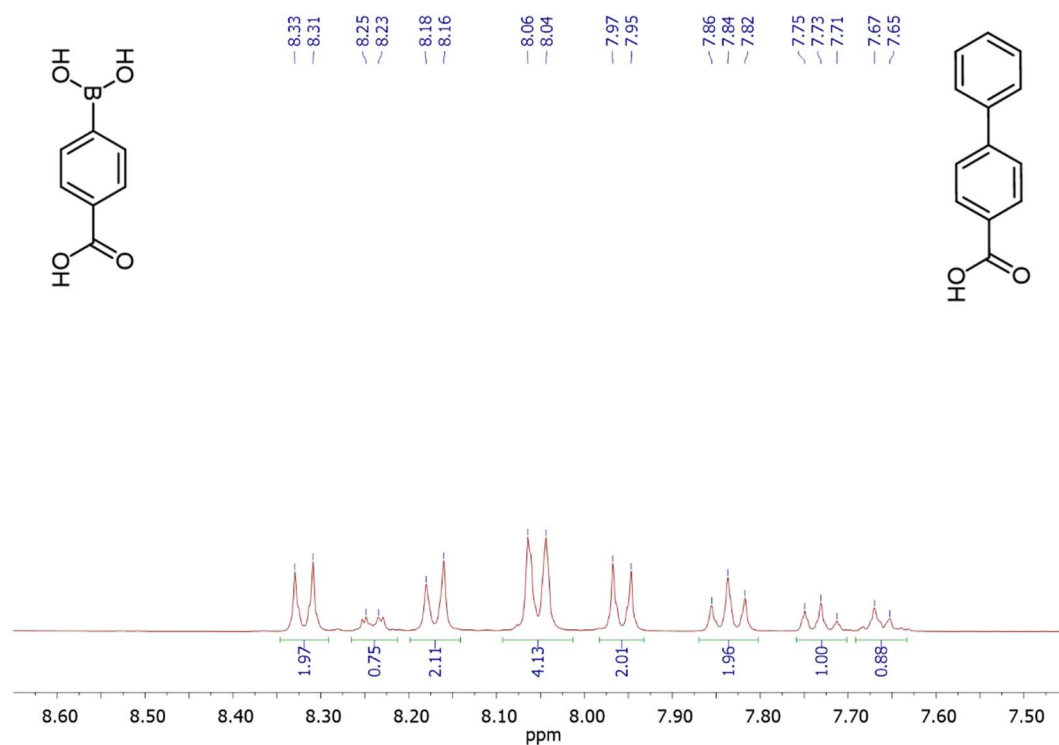


Figure S104 - HNMR spectrum of ns289 6 in DMSO-d₆. Sample ns289 6 was taken after 25 hours at 90°C.

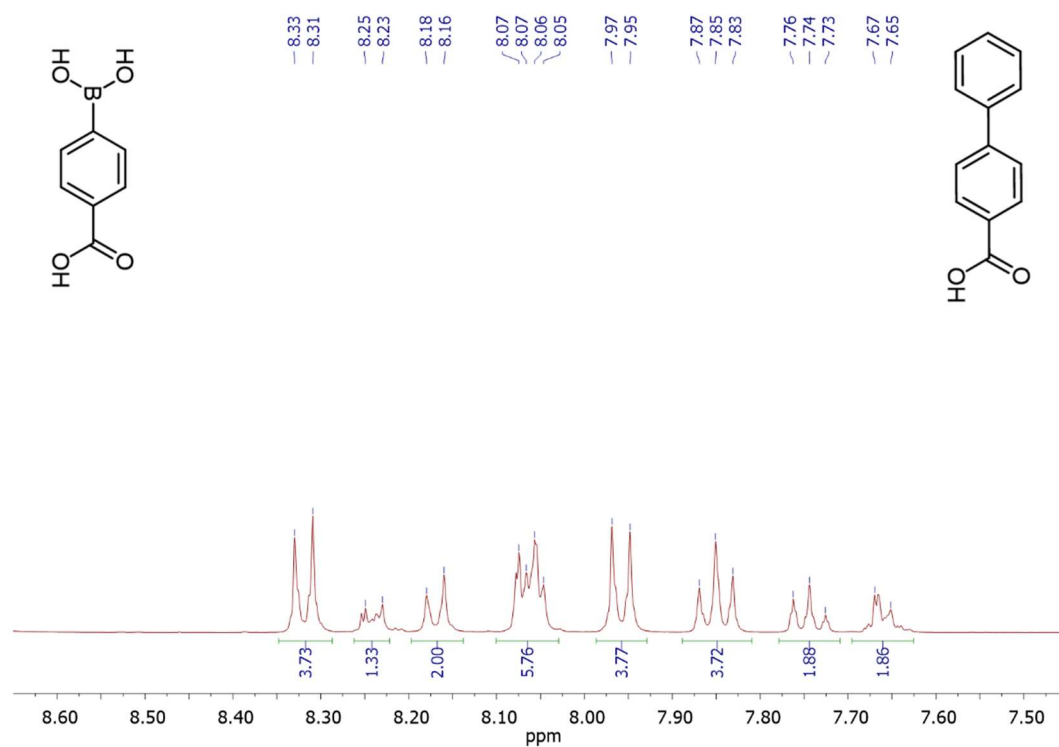
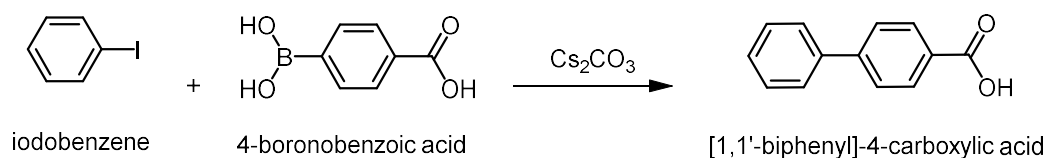


Figure S105 - HNMR spectrum of ns289 7 in DMSO-d₆. Sample ns289 7 was taken after 31 hours at 90°C.



Reactants				Products	
Formula	C₆H₅I	C₇H₇BO₄	CCs₂O₃	Formula	C₁₃H₁₀O₂
MW	204.01	165.94	325.82	MW	198.22
Limiting?	Yes	No	No	Equivalents	
Equivalents	1.00	1.30	1.10	%Completion	
Sample Mass		319.28mg	530.46mg	Expected Mass	293.38mg
%Weight				Expected Moles	1.48mmol
Molarity				Measured Mass	
Density	1.83g/mL			Purity	
Volume	165.00mmL			Product Mass	
Reactant Moles	1.48mmol	1.92mmol	1.63mmol	Product Moles	
Reactant Mass	301.95mg	319.28mg	530.46mg	%Yield	

Figure 106 - Suzuki coupling of iodobenzene and 4-boronobenzoic acid for [1,1'-biphenyl]-4-carboxylic acid.

326.2 mg 4-boronobenzoic acid, 539.3 mg Cs₂CO₃, 165 µL iodobenzene, 3 mL dioxane and 30 mL distilled water were added to a microwave vial. The mixture was sonicated to disperse and a stirrer was added. The vial was heated to ~100°C in an oil bath to dissolve reactants. A small aliquot was taken, filtered and labelled “ns290 1”. The microwave vial was allowed to cool, and then was put in the microwave at 90°C for 2 hours while stirring. A small aliquot was taken, filtered and labelled “ns290 2”. The microwave vial was then put back in the microwave at 90°C for 3 hours while stirring. A small aliquot was taken, filtered and labelled “ns290 3”. The microwave vial was then put back in the microwave at 90°C for 6 hours while stirring. The vial was heated to ~100°C in an oil bath to dissolve an potential precipitate. A small aliquot was taken, filtered and labelled “ns290 4”.

Samples ns290 1 to 4 were initially dried using a rotary evaporator, and if required subsequent drying was performed under high vacuum. The precipitate formed was then dissolved in DMSO-d₆. The resulting NMR spectrums are shown below.

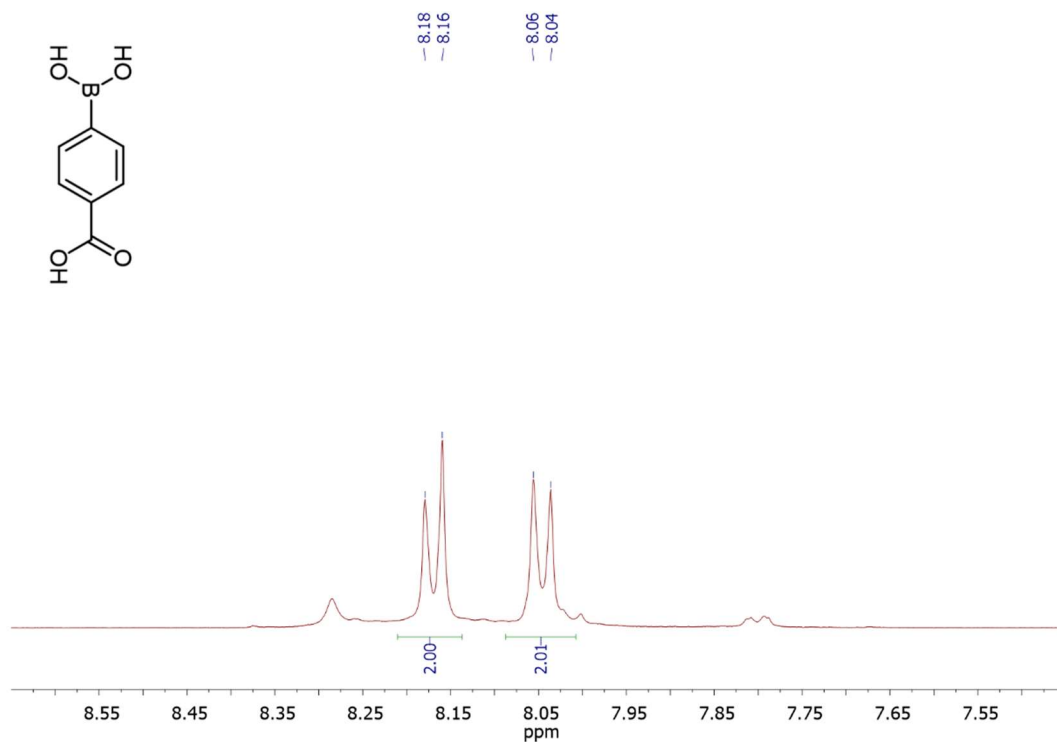


Figure S107 - HNMR spectrum of ns290 1 in DMSO- d_6 . Sample ns290 1 was taken before the reaction began.

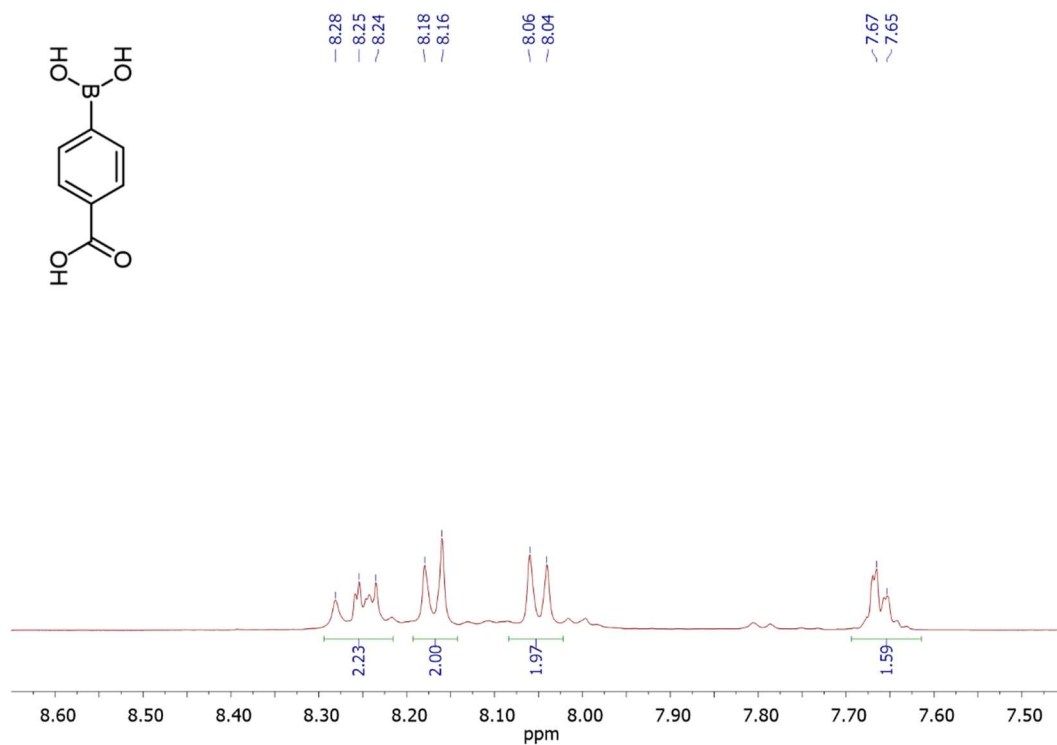


Figure S108 - HNMR spectrum of ns290 2 in DMSO- d_6 . Sample ns290 2 was taken after 2 hours at 90°C.

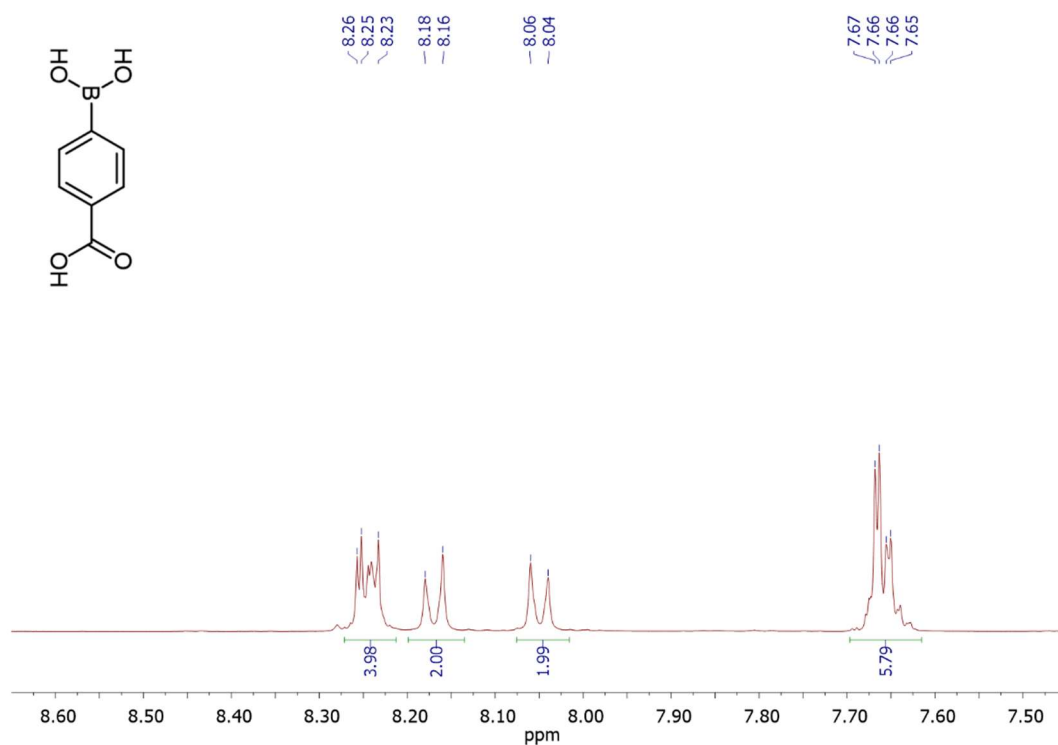


Figure S109 - HNMR spectrum of ns290 3 in DMSO-d₆. Sample ns290 3 was taken after 5 hours at 90°C.

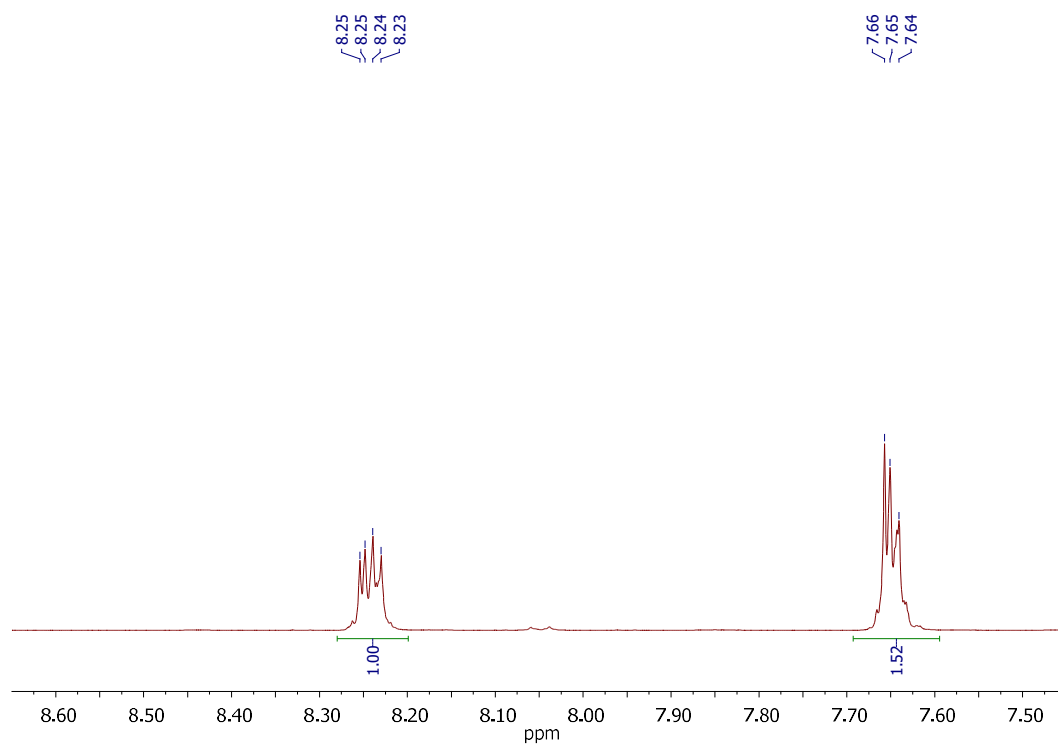


Figure S110 - HNMR spectrum of ns290 4 in DMSO-d₆. Sample ns290 4 was taken after 11 hours at 90°C.

ns292

325.3 mg 4-boronobenzoic acid, 543.3 mg Cs_2CO_3 , 28.7 mg ns264p, 165 μL iodobenzene, 3 mL dioxane and 30 mL distilled water were added to a microwave vial. The mixture was sonicated to disperse and a stirrer was added. The vial was heated to $\sim 100^\circ\text{C}$ in an oil bath to dissolve reactants. A small aliquot was taken, filtered and labelled “ns292 1”. The microwave vial was allowed to cool, and then was put in the microwave at 90°C for 3 hours while stirring. A small aliquot was taken, filtered and labelled “ns292 2”. The microwave vial was allowed to cool, and then was put in the microwave at 90°C for 6 hours while stirring. A small aliquot was taken, filtered and labelled “ns292 3”.

Samples ns292 1 to 3 were initially dried using a rotary evaporator, and if required subsequent drying was performed under high vacuum. The precipitate formed was then dissolved in DMSO-d_6 . The resulting NMR spectrums are shown below.

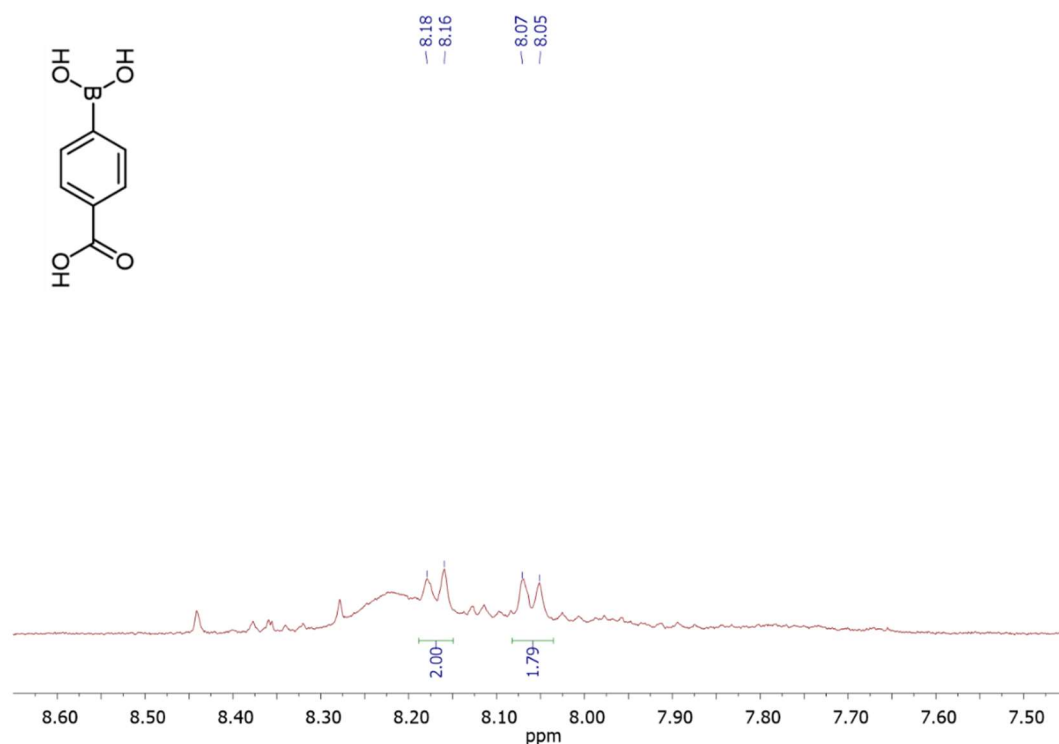


Figure S111 - HNMR spectrum of ns292 1 in DMSO-d_6 . Sample ns292 1 was taken before the reaction began.

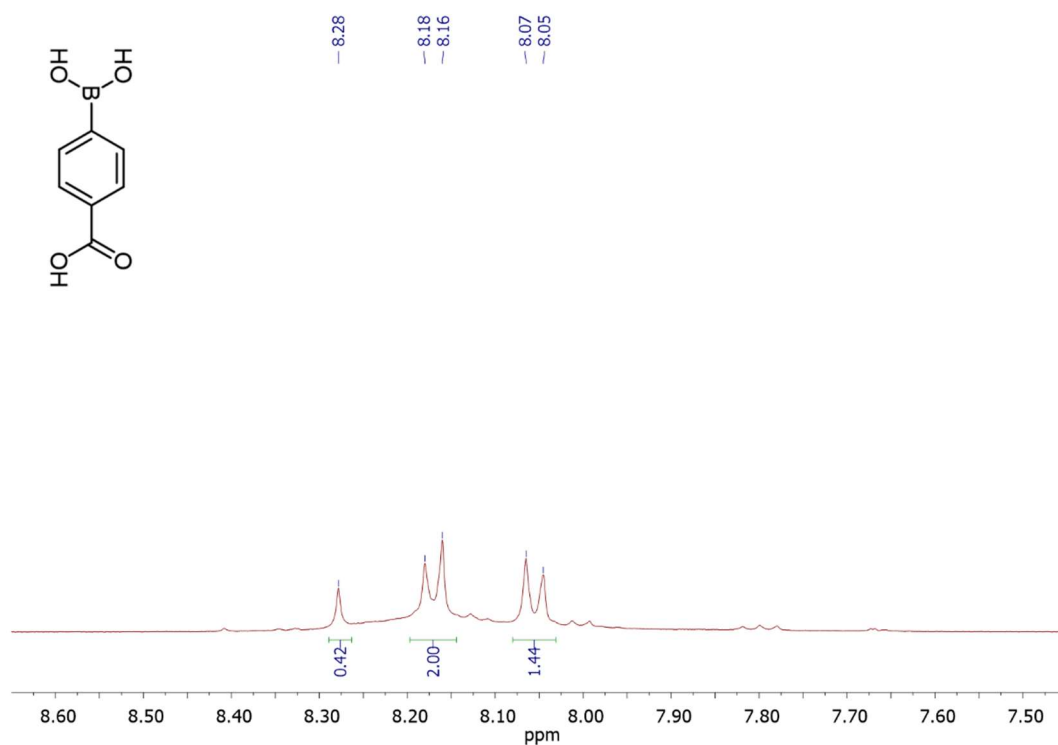


Figure S112 - HNMR spectrum of ns292 2 in DMSO-d₆. Sample ns292 2 was taken after 3 hours at 90°C.

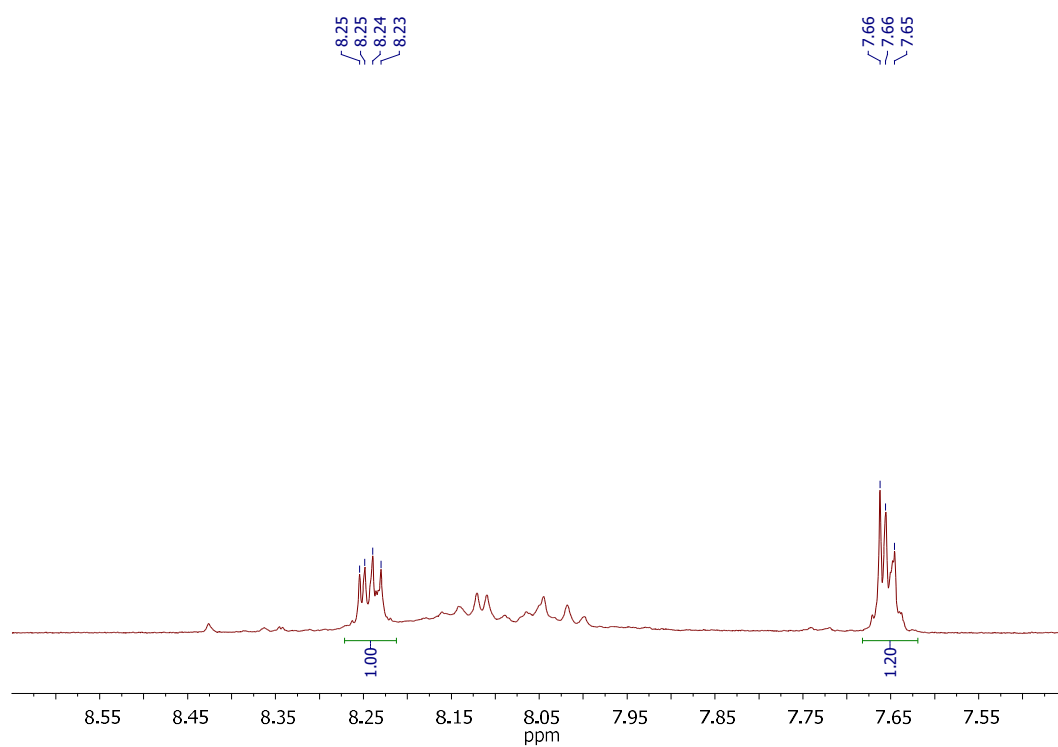


Figure S113 - HNMR spectrum of ns292 3 in DMSO-d₆. Sample ns292 3 was taken after 9 hours at 90°C.

ns295

327.2 mg 4-boronobenzoic acid, 540.6 mg Cs_2CO_3 , 3 mL dioxane and 30 mL distilled water were added to a microwave vial. The mixture was sonicated to disperse and a stirrer was added. The vial was heated to $\sim 100^\circ\text{C}$ in an oil bath to dissolve reactants. The vial was allowed to cool. No precipitate formed and the solution was entirely clear. 29.6 mg ns266pp_washed and 165 μL iodobenzene added. The vial was put in the microwave at 90°C for 2 hours while stirring. The vial was allowed to cool. The solution was slightly cloudy so it was heated to $\sim 100^\circ\text{C}$ in an oil bath to dissolve precipitate. 2 mL was taken and filtered into a beaker. 1.5 mL of this was taken as “ns295 1”. The reaction mixture was then put in the microwave for 3 hours while stirring. The mixture was allowed to cool. The solution was heated to $\sim 100^\circ\text{C}$ in an oil bath to dissolve precipitate. The reaction mixture was then filtered twice with a 0.2 μm pore size filter into a fresh microwave vial. The solution was visibly clear, as shown in Figure 114 below. 0.5 mL of this was taken as “ns295 2”. A fresh stirrer and 165 μL iodobenzene was added. The reaction mixture was then put in the microwave for 2 hours while stirring. 0.5 mL of this was taken as “ns295 3”. The reaction mixture was put in the microwave for 2 hours while stirring. 0.5 mL of this was taken as “ns295 4”.



Figure S114 - Image showing the clarity of the reaction mixture. By eye, no catalyst remains in the solution.

10 μL nitromethane and 990 μL DMSO-d_6 were added to a 2 mL vial to form a 1% nitromethane standard solution.

Samples ns295 1 to 4 were initially dried using a rotary evaporator, and if required subsequent drying was performed under high vacuum. The precipitate formed was then dissolved in DMSO-d₆. 30 μL of the 1% nitromethane solution was added to each sample as a reference. The resulting NMR spectrums are shown below.

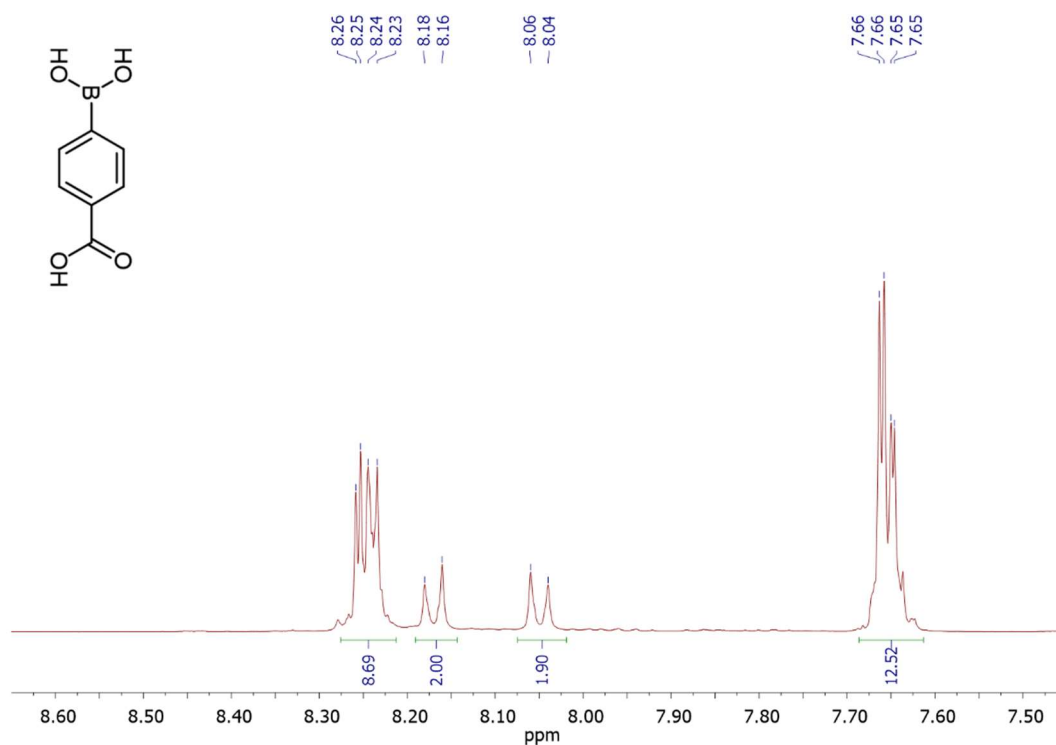


Figure S115 - HNMR spectrum of ns295 1 in DMSO-d₆. Sample ns295 1 taken after 2 hours at 90°C.

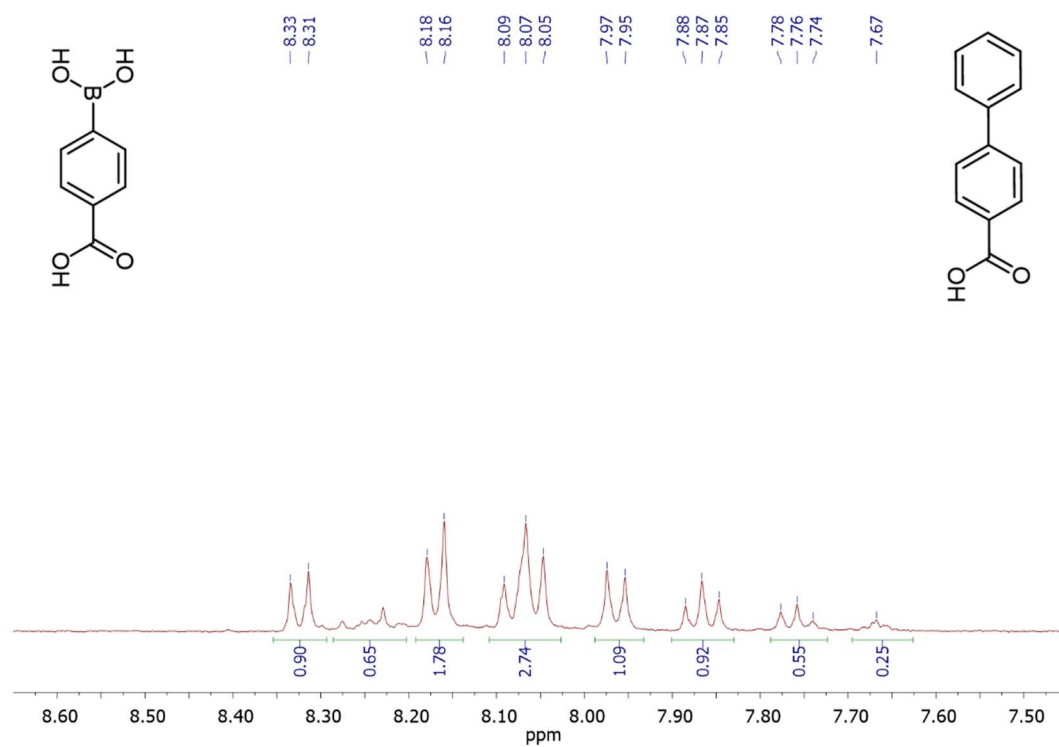


Figure S116 - HNMR spectrum of ns295 2 in DMSO-d₆. Integrals were set to 1 on the nitromethane peak. Sample ns295 2 was taken after 5 hours at 90°C and subsequent filtering of the catalyst.

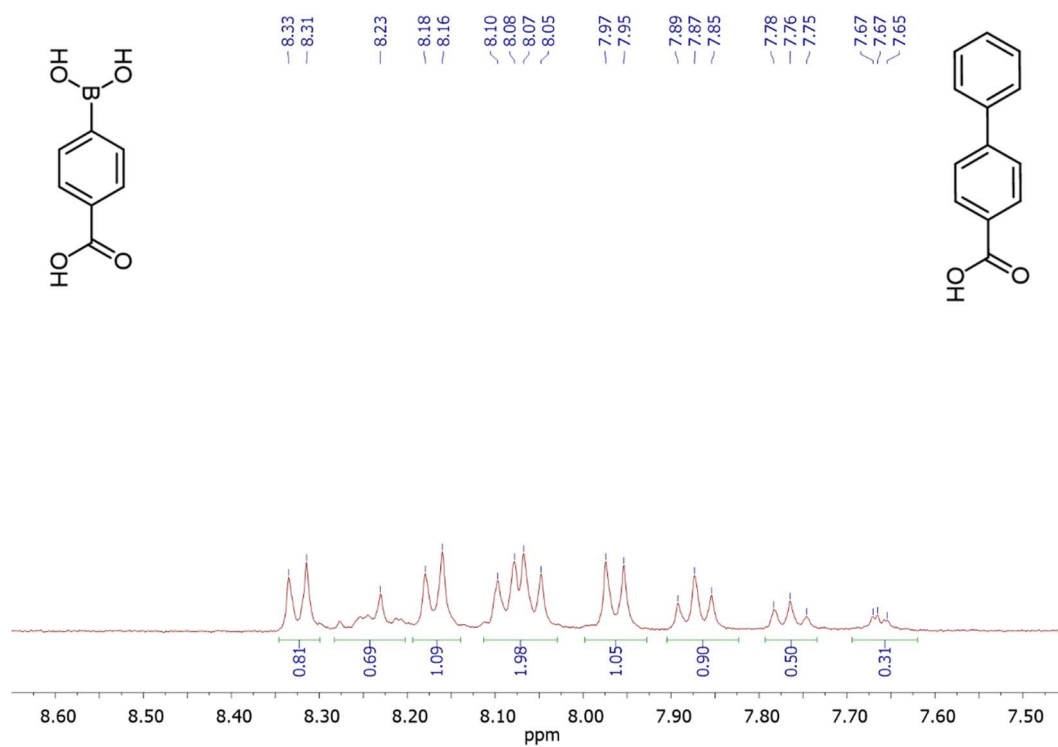


Figure S117 - HNMR spectrum of ns295 3 in DMSO-d₆. Integrals were set to 1 on the nitromethane peak. Sample ns295 3 was taken after 5 hours at 90°C, filtering of catalyst and a further 2 hours at 90°C.

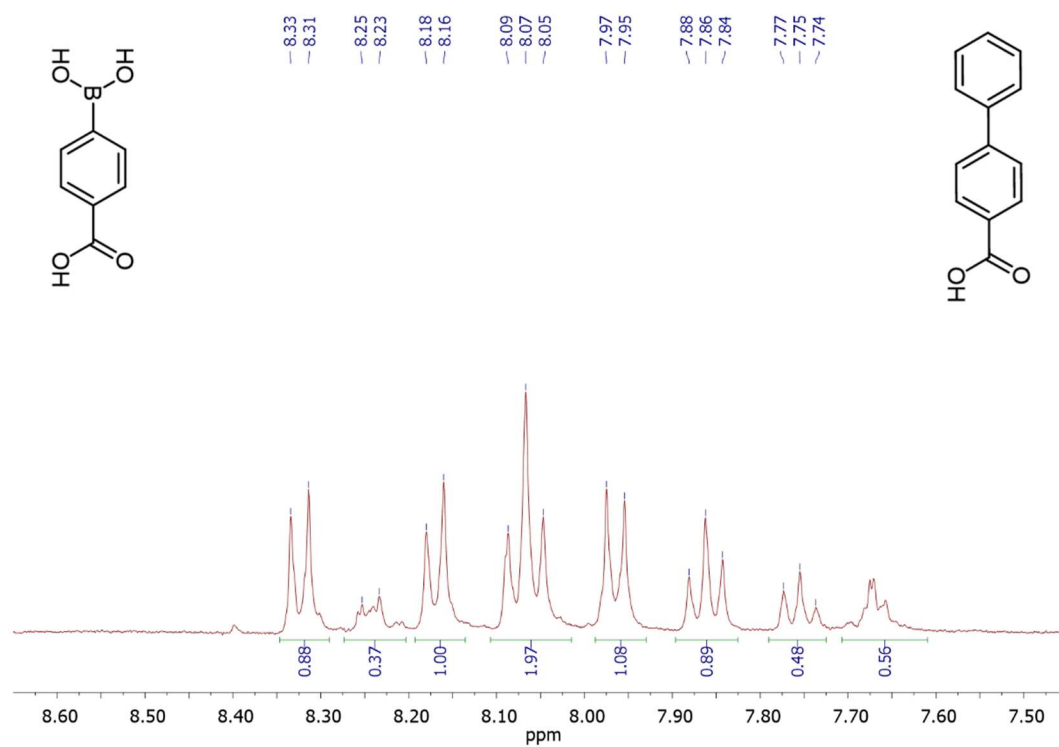


Figure S118 - HNMR spectrum of ns295 4 in DMSO-d₆. Integrals were set to 1 on the nitromethane peak. Sample ns295 4 was taken after 5 hours at 90°C, filtering of catalyst and a further 5 hours at 90°C.

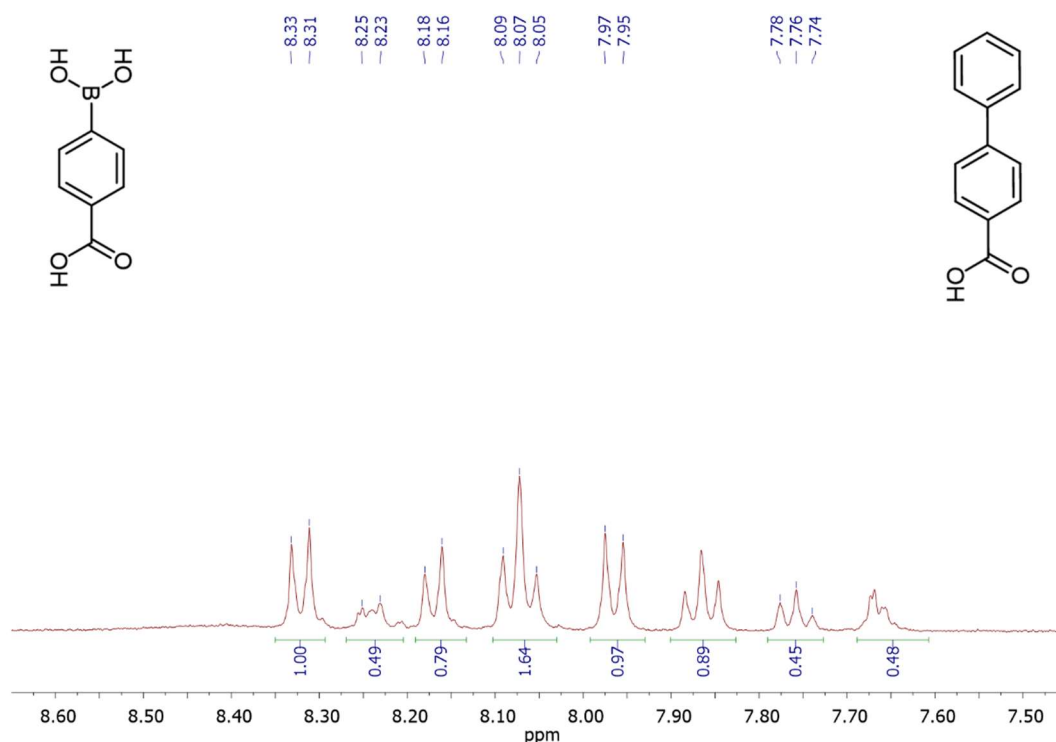


Figure S119 - HNMR spectrum of ns295 5 in DMSO-d₆. Integrals were set to 1 on the nitromethane peak. Sample ns295 5 was taken after 5 hours at 90°C, filtering of catalyst and a further 7 hours at 90°C.

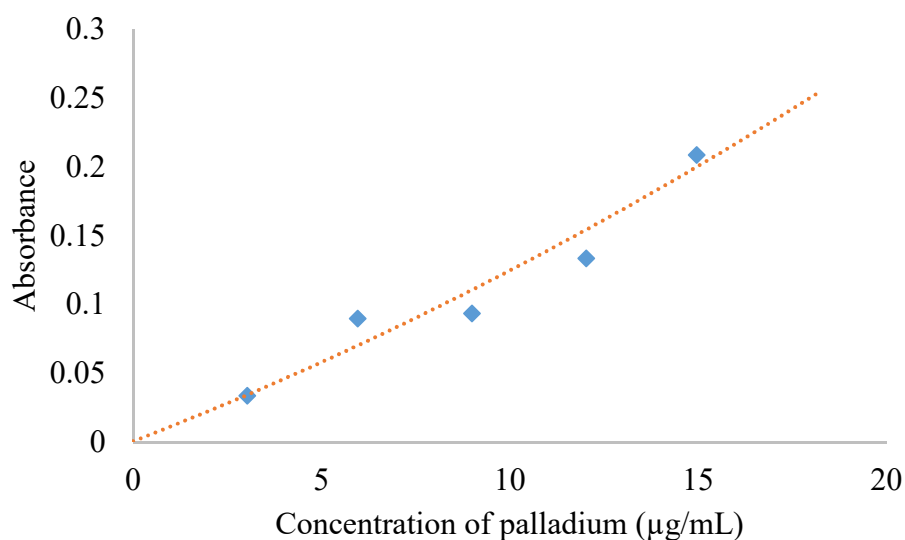
Atomic adsorption data

Standards

Palladium standards for atomic adsorption spectroscopy (AAS) were made from a commercial palladium standard at 1011 ppm of palladium in 5.1 wt.% hydrochloric acid. Aliquots of the standard were distributed into five separate 50 mL volumetric flasks (amounts shown below in column 2 of Table 2). These were made up to the 50 mL mark with 5.1 wt.% hydrochloric acid. The resulting absorbance during AAS is shown below in column 5 of Table 2.

Table S2 - Palladium standards for AAS. Preparation and results.

Standard	Volume of commercial standard	Palladium concentration	%RSD	Mean absorbance
	μL	$\mu\text{g/mL}$		
1	740	14.9628	1.86	0.2088
2	595	12.0309	3.56	0.1336
3	445	8.9979	2.19	0.0935
4	295	5.9649	4.23	0.0898
5	150	3.033	13.16	0.0338

**Figure S120** - Calibration curve for AAS using palladium standards.

Potassium standards for atomic adsorption spectroscopy (AAS) were made from a commercial potassium standard at 1001 ppm of potassium in 5.1 wt.% hydrochloric acid. The standard was allocated into three 50 mL volumetric flasks. 5 to 1.25 mL of these solutions were then allocated into fresh volumetric flasks to make up the final standards. The final concentrations are shown

Table S3 - Potassium standards for AAS. Concentrations and results.

Standard	Concentration $\mu\text{g/mL}$	%RSD	Mean absorbance
1	4.20	2.91	0.3745
2	2.10	4.52	0.1799
3	1.35	6.00	0.1275
4	0.68	3.33	0.0624
5	0.53	6.72	0.0639

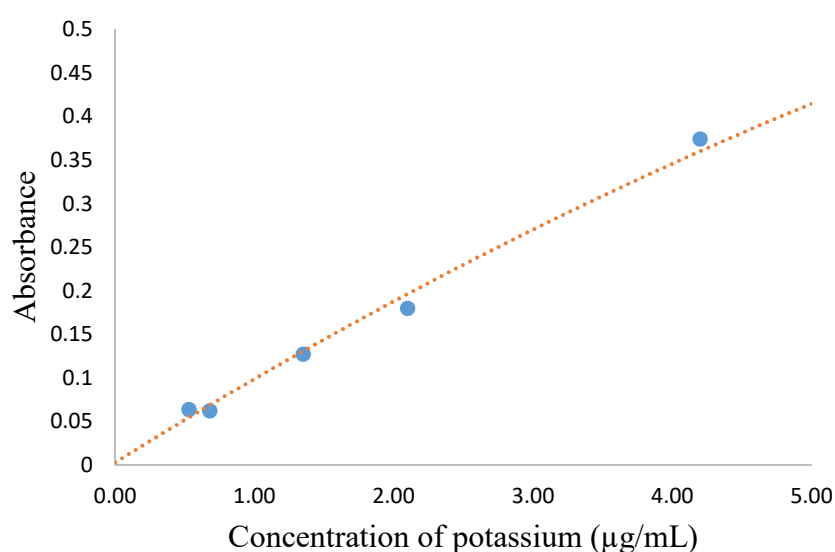


Figure S121 - Calibration curve for AAS using potassium standards.

Samples

AAS data was obtained for ZIF-8@Pd-TA precursors ns264, ns269, ns274b and ns274c. Sample ns266 was omitted as there was not enough material to provide satisfactory data. Each sample was weighed into a 10 mL volumetric flask. Each sample was digested in 1.6 mL hydrochloric acid (37%) for 15 minutes at 70°C. The volume of the flask was then made up to the mark with deionised water to make up a 5.1 wt.% hydrochloric acid solution, due to the previously added acid. The digested samples were then used to obtain AAS data for each sample. Results are shown in main text.

AAS data was obtained for samples ns264p, ns266pp_washed, ns269p, ns274pb and ns274pc. A portion of each sample was weighed carefully and washed into a 10 mL volumetric flask. Each sample was digested in ~2 mL of equal parts nitric acid (97%) and hydrochloric acid (37%) for 3 days. The volume of the flask was then made up to the mark with 5.1 wt.% hydrochloric acid. Although not all of the sample in each flask had digested, it was assumed that all the palladium contained in the samples had digested. The remaining carbon material was filtered off. The digested samples were then used to obtain AAS data for each sample. Results are shown in main text.

Formulas for growth of square lattice of hexagons

$$C = \frac{\left(\left((2(2N + 1)) * \frac{N}{2} \right) + (2(N - 1) + 1) - 4 \right)}{4}$$

Equation S1 - Formula for the number of carbon atoms (C) present in a square lattice N hexagons across, with four palladium atoms imbedded in the corners of the lattice, if N is an even number.

$$C = \frac{\left(\left((2(2N + 1)) * \frac{N + 1}{2} \right) - 4 \right)}{4}$$

Equation S2 - Formula for the number of carbon atoms (C) present in a square lattice N hexagons across, with four palladium atoms imbedded in the corners of the lattice, if N is an odd number.

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