The Investigation of The Surface Properties and Conductivity Distribution of TiO_2 Nanocrystalline Film Using Scanning Tunneling Microscopy

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Abstract

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The use of solid-state materials for efficient conversion of sunlight into electricity has long been a goal of inorganic photochemistry. A molecular approach has been to sensitize wide-bandgap oxide semiconductors to visible light with organic and inorganic compounds exhibiting charge-transfer excited states

Atomic force microscopy (AFM) and scanning tunneling microscopy (STM) have been demonstrated in this research as powerful tools for surface studies of nanocrystalline TiO_2 films, and has been used to characterize the surface properties of TiO_2 film used as semiconducting material in dye-sensitized solar cells. The characterization of both the surface morphology and surface electronic properties of the film have been carried out In addition to the usual qualitative analysis of the sample surface based on the topography images, fractal dimension analysis as a measure of surface roughness and fractality has also been applied during the characterization

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Chapter 1

Introduction

The use of solid-state materials for efficient conversion of sunlight into electricity has long been a goal of inorganic photochemistry (Meyer 1997). A molecular approach has been to sensitize wide-bandgap oxide semiconductors to visible light with organic and inorganic compounds exhibiting charge-transfer excited states. There has been a considerable interest in the study of dye-sensitized electrochemical system for direct conversion of light energy into electrical current during the last decade, especially after the development of highly efficient TiO_2 nanocrystalline dye-sensitized solar cell by Grätzel and collaborators in 1991 (O'Regan and Grätzel 1991). They used TiO_2 in the form of carefully prepared nanocrystalline layers, in combination with organic electrolytes, and ruthenium complexes as sensitizers. High-energy efficiency in the range of at least 7–10% has been confirmed by another research group (Grünwald and Tributsch 1997).

Dye-sensitized cells differ from the conventional semiconductor devices in that they separate the function of light absorption and charge carrier transport (O'Regan and Grätzel 1991). In these devices, a photocurrent is generated when visible light absorption by the dye sensitizer leads to electron injection into the conduction band of the semiconductor. The injected electrons are subsequently transported through the interconnecting network of semiconductor nanoparticles and are collected at the back electrode where they are withdrawn as a current. Electrochemical reactions, which subsequently take place at the interfaces and in the electrolyte solution, complete the cycle. In the ideal situation, when these reactions alone take place, the solar cell will be stable, delivering photocurrents indefinitely (Kalyanasundaram and Grätzel 1998).

Despite the early success of this new type of solar cell, shown by its relatively high efficiency, attempts to improve its performance (e.g. white light conversion efficiency, stability, etc.) are still under way. Efficient sensitization

requires that the rate of interfacial electron transfer be much greater than the rate decay of the dye excited state to ground (Tachibana et al. 1996). The kinetics of these processes is therefore a critical factor controlling device efficiency (Hagfeldt and Grätzel 1995). Various electrochemical techniques have been employed to determine the kinetics parameters of these processes in order to obtain a better understanding of the cell operation. Zaban (Zaban, Ferrere, and Gregg 1998) has made it clear that the relative position of energies at semiconductor/dye/electrolyte interface is the most fundamental property in the design of dye-sensitized solar cells.

The dye sensitization process is concerned primarily with the surface and interfacial processes. Measurements of interfacial structure and properties, including electrode topography, the crystallographic orientation of the electrode, the double-layer structure, reactant concentration, and the presence and concentration of adsorbates and contaminants, are therefore crucial in understanding the factors controlling interfacial electron-transfer reactions (Ward and White 1996). Early studies of chemical photoprocesses at TiO_2 have made it clear that surface energetics and surface states play an important role in the efficiency and range of applicability of this semiconductor material (Frank and Bard 1975). Thus, the importance of surface properties cannot be underestimated. It is the high surface area of the film, in combination with dye sensitizer of ideal spectral characteristics, which is responsible for the high light harvesting efficiency (LHE) of the new type of solar cells (O'Regan and Grätzel 1991).

In the dye-sensitized solar cell, the semiconductor (e.g. TiO_2) serves primarily as an electron transport medium. The electrons themselves are generated by the photoexcitation of the dye sensitizer. The overall efficiency and performance of the cell depends very much on the electron transfer efficiency, i.e. how many injected electrons can be transported through the bulk of the semiconductor and reach the counter electrode. This transfer efficiency is suggested to depend on the electronic properties of the semiconductor thin film.

An *ideal* description of semiconductor film used in dye-sensitized solar cells would be as a collection of large number of interconnected particles with large pores in between so that electrons injected onto any of the constituent particle can traverse through the network and reach the collector/back electrode without being lost (trapped) (Kalyanasundaram and Grätzel 1998). However, this is an idealization. In porous nanocrystalline electrodes, a large number of electron traps are expected to be present. The strongly enhanced internal surface area and the numerous interconnected nanocrystallites give rise to a large number of electron traps at the semiconductor/electrolyte interface and at grain boundaries, respectively (Boschloo and Goossens 1996). The existence of these traps has been proven by O'Regan et al. (O'Regan et al. 1990) as early as 1990 using photocurrent transient response. Thus, it is evidently clear that some of the injected electrons will not be able to reach the back contact electrode due to electron trapping by the surface traps. The film can therefore be looked upon as having a non-uniform conductivity across its surface. If that is the case, it would be desirable to be able to produce a map of conductivity distribution that can be used as a tool for the identification of regions (or sites) of different level of activity so that characterization of surface electronic properties can be undertaken on a more localized scale.

By using an appropriate technique it should be possible to produce a map of conductivity distribution from the surface analysis of the film. Such a technique is available from the scanning probe microscopy (SPM) technology, which allows one to perform analysis of surface on a microscopically localized scale.

The advent of scanning tunneling microscopy (STM) in 1982 (Binnig et al. 1993) has initiated a new approach in the analysis of surface properties of electrodes, as well as brought a new horizon in the investigation of electrochemical processes such as those taking place in dye-sensitized solar cells. Some of the most obvious advantages of STM over other earlier established surface analysis techniques are its capability to provide direct true atomic- and molecular-level characterization of electrode interfaces in real space *ex situ* and *in*

situ, the more localized nature of its measurements, and the ease with which the measurements are performed (it does not require a high vacuum environment) (Bonnel 1993; Fan and Bard 1990; Ward and White 1996).

Early STM study of TiO_2 surfaces relevant to the optical energy conversion and photocatalysis can be traced back to the work of Itaya and Tomita (Itaya and Tomita 1989), in which TiO_2/aqueous solution interface and the effect of substrate potential on the STM behaviour were studied. STM and its related spectroscopic technique (STS) were also used by Bard and Fan (Fan and Bard 1990) in their work to study the surface of single crystal TiO_2 and to determine its surface electronic structure. Most recently, Lin *et al.* (Lin et al. 1999) extended the work of Bard and Fan and reported the application of STM and STS for the characterization of TiO_2 nanocrystalline thin film.

Scanning tunneling microscopy and atomic force microscopy (AFM) were used as the primary tools in this research for the characterization of the surface properties of TiO_2 nanocrystalline thin film. The work was focused on the imaging of conductivity distribution across the surface of TiO_2 film. The purpose of this research is to establish techniques of using STM in the investigation of conductivity distribution in TiO_2 nanocrystalline thin film as well as to provide a firm background for further study in the identification and characterization of regions of good charge transfer. A better understanding in this area will certainly pave the way to the improvement of electron transfer efficiency in dye-sensitized solar cell system.