Fabrication, characterization and photovoltaic study of a TiO$_2$ microporous electrode

Yao-chun Shen[a]*, Lin Wang[a], Zuhong Lu[a], Yu Wei[a], Qingfu Zhou[b], Haifang Mao[b], Huijun Xu[b]

[a]National Laboratory of Molecular and Biomolecular Electronics, Southeast University, Nanjing 210018, China
[b]Institute of Photographic Chemistry, Academic Sinica, Beijing 100101, China

Abstract

A transparent titanium dioxide (TiO$_2$) film of thickness 1 μm has been prepared by speading colloidal particles on a conducting glass support. Atomic force microscope analysis reveals that the film is composed of interconnected particles and pores. The roughness factor of the TiO$_2$ microporous electrode is determined to be 50 by an absorption spectroscopy study. Sensitization of electrode with phthalocyanine molecules extends the absorbance of the electrode into the visible region. At 690 nm, the incident-photon-to-current-conversion efficiency is about 4%, one of the highest ever reported for phthalocyanine photovoltaic cells.

1. Introduction

Organic photovoltaic solar cells have been intensively investigated. These devices usually have a sandwich structure in which the organic dye layer used to absorb incident light is interposed between metal and semiconductor (or metal) electrodes [1–4]. The major advantages of the organic cells are the ease of fabrication and low cost. Thus far, however, power conversion efficiency is poor. The low efficiency of organic photovoltaic cells is due to the high resistivity if the dye layer is thick [3, 4] or due to the low absorbance if the dye layer is thin [5]. Two approaches have been developed to improve the energy conversion efficiency. One is to increase the conductivity of the dye layer by doping with an appropriate sensititzer such as iodine and AgI [3, 6]. The other is to increase the roughness of the electrode surface so that a large number of dye molecules can be adsorbed directly to the surface [7]. If the roughness factor of an electrode is sufficiently large, even a monolayer of dye molecules could absorb most

of the incident photons [8]. Consequently the study of a microporous electrode with a large roughness factor is of general interest.

In this paper, we report the fabrication and characterization of the titanium dioxide (TiO$_2$) microporous electrode. In addition, a photovoltaic study of phthalocyanine-coated TiO$_2$ electrode is also presented.

2. Experiment

TiO$_2$ colloidal solutions were prepared by hydrolysis of tetrabutyl titanate ((C$_4$H$_9$O)$_4$Ti) by a similar procedure to that described in [7]. The colloidal solution was then concentrated to a desired density through vacuum rotation evaporation. The concentrated solution was spread on a conducting glass (SnO$_2$) support. This was heated in air in a Lindberg tube furnace in which the temperature was increased gradually to 700 K and then kept at 700 K for $\frac{1}{2}$ h. The conductivity of the film can be achieved by final heating at 800 K under argon flow for another $\frac{1}{2}$ h.

The zinc phthalocyanine (ZnPc) dye used was synthesized in our institute and its molecular formula is
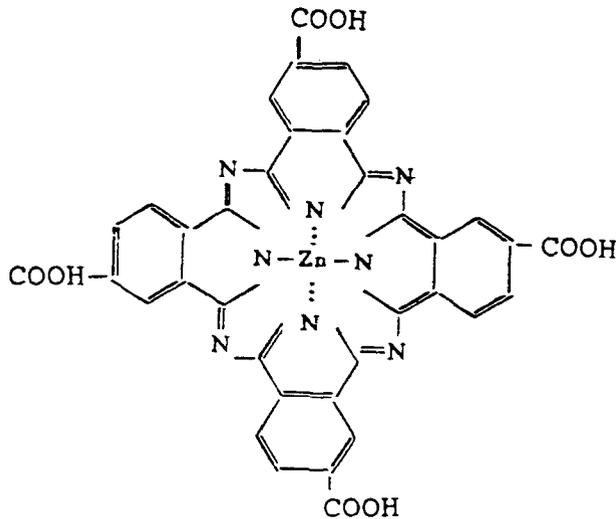
* Corresponding author.

COOH

Fig. 1. The structure of the ZnPc molecule.

shown in Fig. 1. The ZnPc/TiO₂ electrode was prepared by immersing the TiO₂ electrode for 2 or 3 h in ZnPc solution (10^{-3} M, in ammonia). The electrode became green after coating with dye molecules. A two-electrode photoelectrochemical (PEC) cell was used in the photovoltaic study which is composed of a ZnPc/TiO₂ electrode and a platinum electrode separated by an electrolyte containing 0.1 M Na₂SO₄ and 0.05 M hydroquinone.

The morphology of the TiO₂ electrode was examined with an atomic force microscope (DI Co., NanoScope III). The absorption spectra were recorded with a Shimadzu UV-2201 UV–visible spectrometer. The photocurrent and photovoltage were measured with a potentiostat model CMBP-1. Monochromatic illumination was obtained using a 500 W xenon arc lamp in combination with a grating monochromator model WPG3D. The intensity of the light was calibrated using a model FP-3 radiometer–photometer.

3. Results and discussion

3.1. Morphology of TiO₂ film

The atomic force microscopy (AFM) picture in Fig. 2 shows the morphology of the TiO₂ film on a conducting glass support. The TiO₂ film is microporous since it is composed of interconnected particles and pores. These pores have two important functions: (i) the dye molecules can penetrate into the microporous electrode through these pores when the electrode is immersed in the dye solution so that more molecules could be adsorbed directly onto the surface of the electrode; (ii) the electrolyte can contact directly the dye molecules through these pores so that the dye molecules could obtain electrons from the electrolyte in order to fulfil
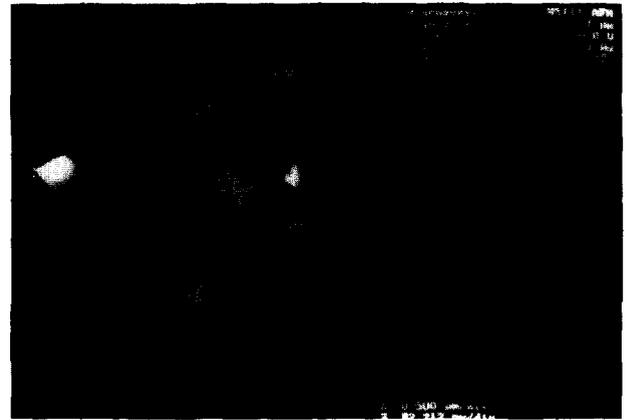

Fig. 2. The morphology of the TiO₂ microporous electrode.

the photovoltaic conversion process. It can also be seen that the TiO₂ particles in the film are uniform with an average width of about 10 nm and length of 250 nm, which are much larger than the size of TiO₂ particles in colloidal solution (about 4 nm as determined by transmission electron microscopy). Further experimental results show that the initial heating process is crucial to the morphology of the TiO₂ electrode. The size of the particle in the TiO₂ film may range from about 10 nm to a few hundred nanometers corresponding to different heating processes.

3.2. Roughness factor of the TiO₂ microporous electrode

The absorption spectra of the TiO₂ electrode with and without a coating of ZnPc have been measured and are shown in Fig. 3. The bare TiO₂ film exhibits the fundamental absorption edge of anatase (band gap energy, 3.2 eV) in the UV region. The ZnPc/TiO₂ electrode displaces the characteristic absorption of ZnPc with a maximum in the visible region at around
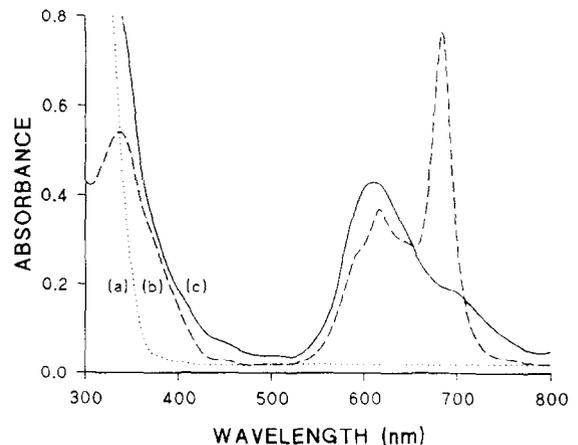

Fig. 3. Absorption spectra of the bare TiO₂ electrode (curve (a)), ZnPc in ammonia solution (curve (b)) and the ZnPc/TiO₂ electrode (curve (c)). Both curve (a) and curve (c) use a conducting glass support as reference.
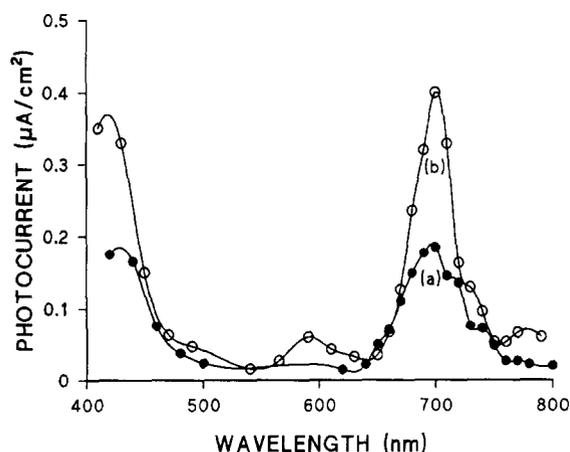
Fig. 4. Photocurrent action spectra of the ZnPc/TiO$_2$ electrode using 0.1 M Na$_2$SO$_4$ (curve (a)) and 0.1 M Na$_2$SO$_4$ + 0.05 M hydroquinone (curve (b)) as electrolyte.

610 nm, indicating that the sensitization of TiO$_2$ electrode with dye molecules could extend the absorbance of the electrode into the visible region. The difference between the absorbance of ZnPc in ammonia solution (curve (b)) and that of ZnPc on the TiO$_2$ electrode (curve (c)) can be attributed to the aggregation and interaction of dye molecules on the TiO$_2$ electrode [9]. At 610 nm, the absorbance of the ZnPc/TiO$_2$ electrode and the extinction coefficient of the ZnPc dye are about 0.42 and 10^8 cm^2 mol^{-1} respectively. Using a similar procedure to that described in Ref. [8], a roughness factor of 50 can be derived for the TiO$_2$ microporous electrode by assuming complete monolayer coverage and a 2 nm^2 area for each molecule.

3.3. Photovoltaic study

Fig. 4 shows the measured short-circuit photocurrent of the ZnPc/TiO$_2$ electrode as a function of wavelength. The spectra have been corrected for the intensity of the incident light. Adding hydroquinone to the electrolyte not only improves the stability of the PEC cell but also doubles the photovoltaic response, indicating that hydroquinone is a good electron donator for ZnPc molecules in this devices. At $\lambda = 690$ nm, the incident light power P and the short-circuit current density I_{sc} are 18 μW cm^{-2} and 0.4 μA cm^{-2} respectively. The incident-photon-to-current-conversion efficiency (IPCE) is 4% as calculated from

$$IPCE = \frac{1240}{\lambda} \frac{I_{sc}}{P} 100\% \qquad (1)$$

Considering that only about 20% of the incident light is absorbed by the dye molecules at 690 nm, the quantum efficiency, defined as the ratio of electrons flowing at a short circuit divided by the number of photons absorbed in the organic dye layer at a given wavelength [4], attains about 20%, which is larger than previous

results [1–4]. The improvement in the IPCE of the PEC cell based on the TiO$_2$ microporous electrode can be explained as follows. The ZnPc dye is adsorbed on the surface of the TiO$_2$ electrode so that nearly all ZnPc molecules are in direct contact with the TiO$_2$ electrode. The photogenerated carriers resulted from absorption of incident photons by dye molecules can be easily transported into the conduction band of the TiO$_2$ semiconductor. In conventional structures a large fraction of ZnPc molecules have no direct contact with the TiO$_2$ substrate; therefore electron transfer from these molecules into the conduction band of TiO$_2$ can occur only with difficulty or not at all. Thus the increase in IPCE is understood to be the result of the direct contact of ZnPc molecules with the TiO$_2$ electrode.

4. Conclusion

We can draw the following conclusions from the above.

(i) A TiO$_2$ microporous electrode has been prepared by depositing TiO$_2$ colloidal particles on a conducting glass support. An AFM study shows that the film is composed of TiO$_2$ particles and pores. The particle size can be controlled by the heating process.

(ii) Sensitization of the TiO$_2$ microporous electrode with phthalocyanine molecules extends the absorbance of the electrode into the visible region. The IPCE is 4%. The improvement in IPCE is attributed to the fact that almost all the ZnPc molecules are in direct contact with the TiO$_2$ surface in the ZnPc/TiO$_2$ electrode. The fabrication of a thicker TiO$_2$ electrode and the use of an appropriate sensitizer including low band gap semiconductor materials are two approaches currently being studied to improve the energy conversion efficiency.

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