Photosensitization of nanocrystalline TiO_2 by photosynthetic protein

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New alternative sensitizers play important roles in the further development of the biomimic solar cell. Herein we reported the sensitization of nanocrystalline TiO_2 (nano-TiO_2) by photosynthetic protein for the first time. As reported previously [1], the dye (porphyrin and its ramification) could effectively sensitize the nano-TiO_2. The photosynthetic reaction center (RC) isolated from purple bacteria is a transmembrane pigment-protein complex that contains bacteriochlorophylls[2]. In addition, the RC itself was a very highly efficient material for the conversion of light energy into electric energy. For the nano-TiO_2 composite film sensitized by RC, its photocurrent was enhanced by 2-3 times in comparison with the protein-free nano-TiO_2 film. The prepared films also expanded the light-harvesting range to near-infrared zone. Our results showed the promising usage of nano-TiO_2 sensitized by photosynthetic protein for the development of photoelectric energy converters.

The nano-TiO_2 was prepared by electrochemical deposition in aqueous 50 mM $TiCl_3$, pH 2–2.5. The film was electronically conducting. The SEM image showed that the electrodeposited TiO_2 particles were uniform and their sizes were about 50–70 nm. The coating thickness increased continuously with deposition time. However, the mechanical defects increased when the thickness exceeded ~0.5 μm. The thickness used in experiments was about 400 nm. The XRD results showed that this material was amorphous in the hydrated form, and became anatase after firing at 450 ºC for 1h.

The immobilization for RC in nano-TiO_2 was characterized by a CCD Spectral-photometer and a electrochemical work station. Absorbance spectrum of nano-TiO_2 sensitized by protein was shown in Figure 1. The cyclic voltammetry was carried in a Tris-HCl buffer (pH 8.0). For the RC-sensitized film, the base line current increased and a small reduction peak at potential of about –0.05 V (vs. SHE) was observed, which owed to the photo-initiated or electric-driven redox couple in RC. As a comparison, no redox peak was observed for RC-free nano-TiO_2 film. It suggested that RC enhances the light-to-electron efficiency in nano-TiO_2 film[3]. It could be explained that the protein has a lot of interlocking groups (–COOH, –OH, $–NH_2$, etc.), actually, which serve as an electronic bridge, and significantly enhanced the contact between the protein molecule and the semiconductor surface.

Photosensitization of nano-TiO_2 by photo-synthetic protein could increase the photocurrent at magnitude of 2–3 folds than that of non-sensitized one in the wavelength range of 300–950 nm (Figure 2). It could be concluded that the photocurrent was enhanced by the interaction between the protein and the nano-TiO_2. Under white light illumination (1×10^{-2} W cm^{-2}), a short-circuit photocurrent of 2–3 μA cm^{-2} was obtained. The electrochemical and the photoelectrochemical investigations indicated that the structure and activity of the protein were well maintained.

The absorbance band for the protein was mainly in the range of 600-900 nm, while the main absorption band for TiO_2 was in the range of 300−500 nm (see Figure 1). Thus, the composite films sensitized by RC protein prepared in this work expanded the light-harvesting range to near-infrared zone and enhance the conversion efficiency in the whole visible to NIR region.

Acknowledgements

This work is supported by NSFC (Projects 39970195 & 2990500), by Shanghai Photo-S&T Special Fund and by the EYTP and TRAPORT of MOE. P. R. C.

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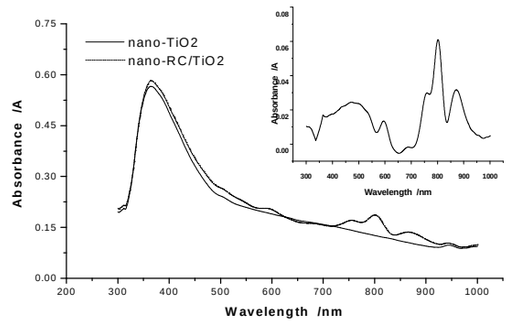

Figure 1 Absorbance spectra for nano-TiO2 and RC/nano-TiO_2 film. The insert showed the difference spectrum of the two films.

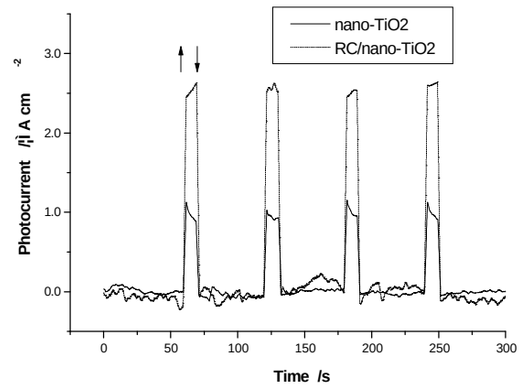

Figure 2 Short-circuit photocurrent changes induced by switching on (↑) and off (↓) the illumination for the RC/nano-TiO_2 and nano-TiO_2 film.