ELSEVIER

Journal of Photochemistry and Photobiology A: Chemistry 90 (1995) 167–170

Journal of
PHOTOCHEMISTRY
AND
PHOTOBIOLOGY
A: CHEMISTRY

Modification and photosensitization of size-quantized particulate CdS film photoelectrodes with bacteriorhodopsin (BR)

Baohui Wang [a,*], Dejun Wang [a], Xueqi Fu [b], Yi Cui [a], Tiejin Li [a]

[a] Department of Chemistry, Jilin University, Changchun 130023, People's Republic of China
[b] Department of Molecular Biology, Jilin University, Changchun 130023, People's Republic of China

Received 2 November 1994; accepted 26 January 1995

Abstract

Bacteriorhodopsin (BR) was used to modify the surface of a novel size-quantized particulate CdS photoelectrode fabricated by electrodeposition. The photovoltaic features and interfacial electron transfer of the electrodes were studied by surface photovoltaic spectroscopy and a photoelectrochemical method. The results show that BR-modified CdS film photoelectrodes achieve a higher photocurrent yield due to the incorporation of the proton pump BR. On the basis of the observations, the mechanisms of photosensitization and interfacial electron transfer are proposed.

Keywords: Photosensitization; Particulate CdS film photoelectrodes; Bacteriorhodopsin

1. Introduction

During the past decade, scientists from different disciplines have demonstrated a keen interest in the physical and chemical properties of size-quantized particulate semiconductors [1–3]. Although investigations of particulate semiconductors encompass a wide range of topics, two aspects have attracted both the academic (present) and technological (future) interest of many researchers: optical properties and interfacial electron transfer. The former relates to the potential application of such materials in electronic devices, and the latter to the photocatalysis and photosensitization of particulate semiconductors as electrodes. Photosensitization of wide gap semiconductor electrodes was extensively researched during the 1960s and 1970s [4]. In most cases, organic dyes were adsorbed on the surface of semiconductors. There have been two important current developments in this field: (1) the use of particulate semiconductors instead of bulk electrodes [5]; (2) the photosensitization of particulate semiconductors with dyes [6,7] and narrow band gap semiconductors [8]. A few investigations have been performed on the photoelectrochemical properties of thin layer electrodes of particulate semiconductors. These electrodes were prepared either via chemical deposition on substrates [9] or by spin coating from concentrated colloidal solutions [10]. High photocurrent quantum yields were observed for these electrodes after excitation with light.

Bacteriorhodopsin (BR), which is found in *Halobacterium halobium*, functions as a light-driven proton pump [11], i.e. the protein converts light energy into chemical energy. BR is extremely stable as a visual pigment analogue in vitro against light. The photochemical behaviour of BR has recently stimulated extensive investigations of its potential applications in molecular electronic devices [12] and optical computers and memories [13,14]. A photovoltage has been demonstrated and the mechanism has been well elucidated from the investigation of thin films of BR [15]. This photovoltage results from the displacement of charge in the BR molecule initiated by rapid photoisomerization of the chromophore retinal [13]. In view of its special functions and remarkable stability, BR has been used as a photosensitizer to modify particulate semiconductors.

In this paper, recent results on the modification and photosensitization of photoelectrodes of size-quantized particulate CdS film with BR are reported. The CdS film photoelectrodes were obtained by electrodeposition on indium-tin oxide (ITO) and BR was incorporated into the CdS film by the modification of the surface. The photovoltaic behaviour of the modified CdS films and the processes of interfacial electron transfer were systematically investigated by surface photovoltaic spectroscopy (SPS) and photoelec-

---

* Corresponding author.

SSDI 1010-6030(95)04053-6

trochemical methods. The results show that the BR-modified CdS film electrodes yield stable photocurrents which are much larger in magnitude than those of the unmodified electrodes and possess strong photosensitizing character and stability. On the basis of these measurements, the mechanisms of photosensitization and interfacial electron transfer are proposed and discussed.

2. Experimental details

2.1. Preparation and characterization of Q-CdS film

According to the method of Baranski et al. [16] and Hodes et al. [17], size-quantized CdS films (Q-CdS) were electrodeposited onto ITO (conduction glass coated with indium-tin oxide) substrates from a dimethylsulphoxide (DMSO) solution of 0.1 M $CdCl_2$ and 0.1 M S under a constant current density of 1 mA cm^{-2}. The electrolysis was carried out at a constant current density and temperature using a three-electrode system. The thicknesses of the films were measured separately from scanning electron microscopy (SEM) views of the cleaved cross- sections. The absorption spectra of the photoelectrodes were recorded using a Shimadzu UV-365 spectrophotometer. The size of the particles in the films was evaluated from the optical absorption spectra of the films [18]. The thickness of the films was about 1 μm.

2.2. BR modification on Q-CdS/ITO

BR was isolated from strain R1S9 of *H. halobium* using a technique described by Oesterhelt and Stoeckenius [19]. BR was suspended in pure water and emulsified by mixing with *N*-(2-hydroxyethyl)-piperazine-*N*′-2-ethane sulphonic acid (HEPES) to yield a violet HEPES solution of BR. The monomer was prepared by the method of Dencher and Heyn [20]. A drop of this solution was placed on the Q-CdS/ITO electrode. A thin layer of BR was deposited and built up on the surface of the electrode by spin coating. The coating process resulted in a BR-modified photoelectrode BR/Q-CdS/ITO with a BR layer thickness of about 0.1–0.2 μm.

2.3. Surface photovoltaic spectroscopy (SPS)

The surface photovoltage effect, which consists of a change in the surface potential barrier caused by illumination, has successfully been applied to the investigation of electron processes in semiconductors. Measurements of the surface photovoltage vs. the light wavelength (i.e. SPS) yield information about the surface parameters, band gap and photosensitization in semiconductors. Because the photovoltage arises from the creation of electron–hole pairs by photoexcitation, SPS probes excitation and charge transfer. It is a simple and precise method for understanding interfacial electron transfer in semiconductors, especially in thin particulate semiconductor films. The principles and apparatus for SPS measurements have been described in detail elsewhere [21]. In our experiments, SPS measurements were carried out with a solid junction photovoltaic cell ITO/BR/Q-CdS/ITO (or ITO/Q-CdS/ITO) using a light source–monochromator–lock-in detection technique. Monochromatic light was obtained by passing light from a 500 W xenon lamp through a double-prism monochromator (Hilger and Watts, D300). A lock-in amplifier (Brookdeal, 9503-SC), synchronized with a light chopper, was employed to amplify the photovoltage signal. The spectra were normalized to unity at their maxima and the characteristic bands of the xenon lamp were subtracted by a computer.

2.4. Photoelectrochemical measurements

Photoelectrochemical investigations (i.e. photocurrent action spectra) were performed in potentiostatic configuration with a conventional three-electrode system consisting of BR/Q-CdS/ITO as the working electrode, platinized Pt as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode. An aqueous solution of 0.1 M S^{2-}/0.1 M Sn^{2-} (polysulphide ion) was used as electrolyte. The photocurrent spectra were recorded using the light source–monochromator–lock-in detection technique described above. The spectra were normalized by considering the correction arising from the spectral intensity distribution of the light source.

3. Results and discussion

The size-quantized particulate semiconductors exhibit very different chemical and physical properties from the bulk solid and individual molecules. One of the most pronounced features of particulate semiconductors is the size quantization effect, manifested by a large shift in the wavelength of the absorption threshold in the absorption spectrum. Fig. 1 shows the absorption spectra of a Q-CdS film electrodeposited on ITO and a bulk CdS film. It should be noted that the onset of absorption of the Q-CdS film is shifted to shorter wavelengths (475 nm) in comparison with that of the bulk material, i.e. the film displays a large blue shift (about 40 nm). According to the absorption threshold, the particulate size in Q-CdS is estimated to be about 5 nm. Therefore the electrodeposited CdS films obviously possess size quantization effects.

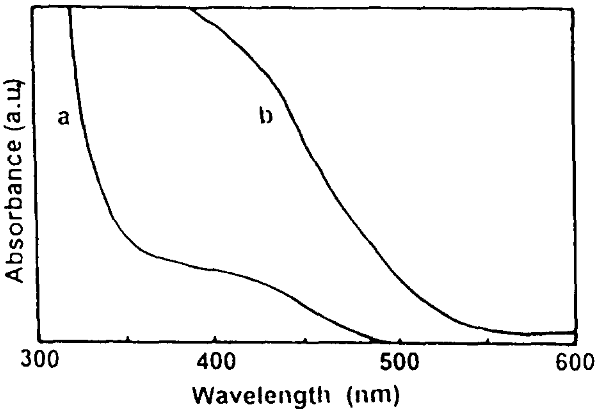

Fig. 1. Absorption spectra of CdS films: (a) Q-CdS film; (b) bulk CdS film.

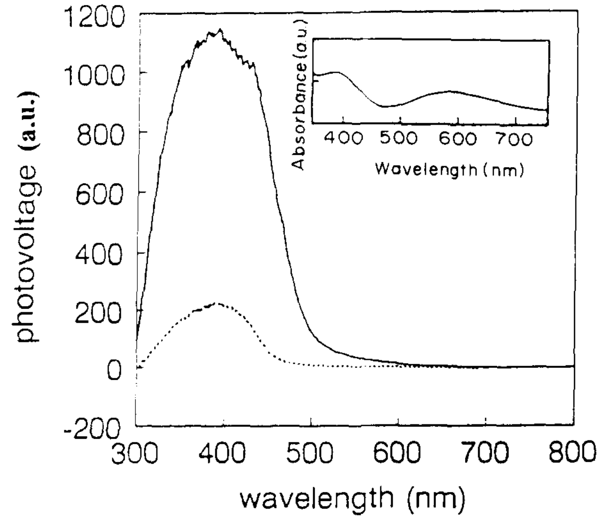

Fig. 2. Surface photovoltaic spectrum of BR-modified Q-CdS/ITO film (ITO/BR/Q-CdS/ITO system). The inset shows the absorption spectrum of BR/Q-CdS/ITO. Full line, BR monomer on Q-CdS/ITO; broken line, Q-CdS/ITO.

When size-quantized particulate films are used as photoelectrodes instead of bulk materials, they display a particular quantum efficiency in photoelectric conversion and are therefore promising materials for photovoltaic applications. Fig. 2 shows the surface photovoltaic spectra of the unmodified Q-CdS film (Q-CdS/ITO) and the BR-modified Q-CdS film (BR/Q-CdS/ITO) photoelectrodes. Firstly, it can be observed that the BR/Q-CdS/ITO photoelectrode yields a much higher stable photovoltage than that of unmodified Q-CdS/ITO (approximately five times higher in the present case). The experimental increase in the photovoltage indicates that BR functions as a photosensitizer in the Q-CdS/ITO electrode. Secondly, the spectral distribution of the BR-modified electrode is quite different from that of the unmodified electrode. It is evident from this figure that BR modification causes a distinct broadening of the spectral features of Q-CdS, characterized by the emergence of very fine structure. In comparison, the broadened band consists of two peaks. The main peak dominating the spectrum originates from Q-CdS, and the position of the clear shoulder peak at 412 nm is the same as that of the absorption band of intermediate M(412) in BR (see Fig. 4, later). It is obvious that the shoulder peak is a sensitizing band caused by M(412). This result suggests that interfacial electron transfer occurs between Q-CdS and BR. In order to prove these observations, a photoelectrochemical method was employed to measure the photocurrent action spectra of the unmodified and modified Q-CdS film electrodes, which are illustrated in Fig. 3. The same features are also observed in these spectra. The results strongly support the above conclusions. In addition to the features mentioned above, it is found that the peak due to intermediate M(412) is stronger than that due to Q-CdS. This implies that interfacial electron transfer takes place more easily in the liquid phase than in the solid phase. These observations suggest that the modification of BR involves two effects: (1) an enhancement of the photovoltaic response; (2) the emergence of a sensitizing band. With regard to the mechanism of generation of photovoltage in semiconductors and the photocycle of BR, some explanations are given in the discussion below.

The generation of photovoltage depends on the creation of charge (electron–hole formation by photoabsorption), followed by the separation in space by a built-in electronic field (the space-charge layer). The former requires semiconductors with a suitable band gap. The latter requires that the electron and/or hole can be separated and transported a certain distance using a reasonable built-in electric field. The higher the built-in electric field, the more extensive the photovoltage. In each photocycle, a high potential proton is pumped out of the BR membrane and an electrochemical potential gradient is formed across the membrane, reaching 300 mV. The gradient is used as a proton motive force for the cycle. When the BR membrane comes into contact with the Q-CdS film, it corresponds to the increase in the built-in electric field. The change speeds up the separation of electrons and holes, resulting in an increase in the photovoltage caused by the BR-modified Q-CdS film. In this case, the modification of BR on Q-CdS alters the kinetics of charge transfer on illumination so that a higher photocurrent yield is obtained.

On absorption of light, BR undergoes a photocycle which involves a reversible conversion in energy and structure. The process consists of a cyclic sequence of intermediates with lifetimes varying from 5 ps to several milliseconds

$$\mathrm{BR(570)} \xrightarrow{5\ \mathrm{ps}} \mathrm{K(620)} \xrightarrow{2\ \mu\mathrm{s}} \mathrm{L(550)} \xrightarrow{50\ \mu\mathrm{s}}$$
$$\mathrm{M(412)} \xrightarrow{1\ \mathrm{ms}} \mathrm{O(640)} \xrightarrow{10\ \mathrm{ms}} \mathrm{BR(570)}$$

The intermediates formed during the cycle are abbreviated by a single letter. The numbers in parentheses represent the absorption maxima of the intermediates in nanometres. The

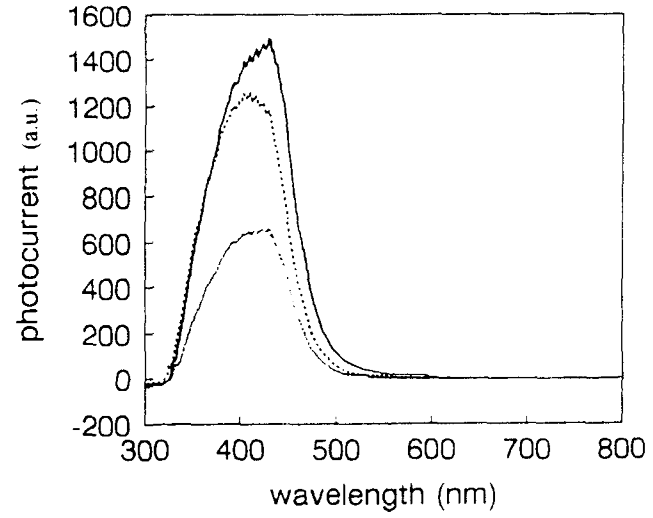

Fig. 3. Photocurrent action spectra of BR-modified Q-CdS/ITO films (ITO/Q-CdS/BR/S^{2-}/Sn^{2-}/Pt system): full line, BR monomer on Q-CdS/ITO; broken line, BR trimer on Q-CdS/ITO; dotted line, Q-CdS/ITO.

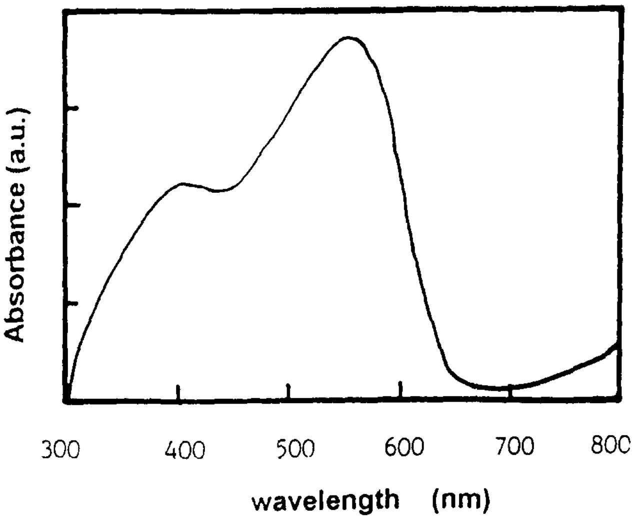

Fig. 4. Diffuse reflectance absorption spectrum of dry BR fragment.

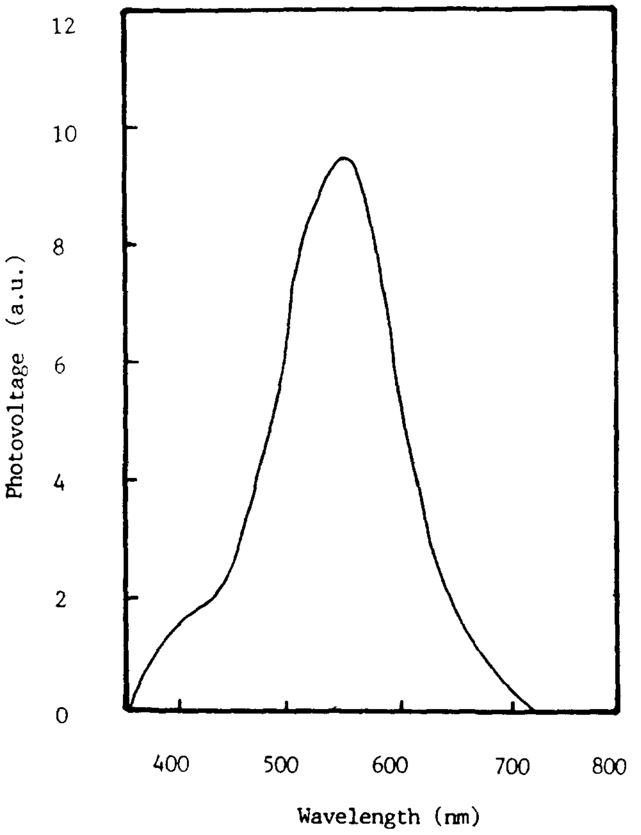

Fig. 5. Surface photovoltaic spectrum of dry BR film fabricated from dry BR fragment.

numbers above the arrow indicate the lifetimes of the intermediates. These data clearly indicate that M(412) and O(640) are the most stable intermediates. M(412) plays an important role in the photocycle. From the intermediate, protons are pumped into or out of the membrane, resulting in an electrochemical potential gradient. The half-time of M(412) decay is about 1–2 ms in aqueous suspension, but 45–50 ms or longer in dried BR or modified BR [22]. Figs. 4 and 5 show the diffuse reflectance absorption spectrum of a dry BR fragment and the surface photovoltaic spectrum of a dry BR film fabricated from a dry BR fragment. From the surface photovoltaic spectrum of dry BR, two bands of photovoltaic response are observed at 570 nm and 412 nm. The locations of the response are in good agreement with the absorption spectrum (Fig. 4), which means that the two bands originate from the absorption of BR(570) and intermediate M(412). Reviewing the surface photovoltaic spectrum of the BR-modified Q-CdS film (Fig. 2), we should note that only the sensitizing band from M(412) appears at 412 nm, while the band due to BR(570) is absent. This suggests that only the energy levels of M(412) are matched with those of Q-CdS and thus interfacial electron transfer can occur. Due to the effect of quantum confinement, the band gap of Q-CdS is broadened and the conduction band of Q-CdS becomes higher than that of bulk CdS. M(412), as a photoisomer of BR, is characterized by higher excited states which meet the specific requirements of the incorporation of energy. Therefore the electrons in the excited states of M(412) are injected into the conduction band of Q-CdS to achieve photosensitization. The above illustrations only provide a tentative mechanism for the modification and photosensitization of Q-CdS with BR. To gain insight into the mechanism, more experiments are needed.

References

[1] A. Henglein, *Top. Curr. Chem.*, *143* (1988) 113.

[2] A.J. Bard, H.D. Abruna, C.E. Chidsey, L.R. Faulkner, S.W. Feldberg, K. Itaya, M. Majda, O. Melroy, R.W. Murray, M.D. Porter, M.P. Soriaga and H.S. White, *J. Phys. Chem.*, *97* (1993) 7147.

[3] D. Liu and P.V. Kamat, *J. Phys. Chem.*, *97* (1993) 10 769.

[4] H. Gerischer and F. Willig, *Top. Curr. Chem.*, *61* (1976) 31.

[5] S. Hotchandani and P.V. Kamat, *J. Electrochem. Soc.*, *139* (1992) 1630.

[6] B. O'Regan and M. Grätzel, *Nature*, *353* (1991) 737.

[7] W.E. Ford and M.A.J. Rodgers, *J. Phys. Chem.*, *98* (1994) 3822.

[8] R. Vogel, K. Pohl and H. Weller, *Chem. Phys. Lett.*, *174* (1990) 241.

[9] B. O'Regan, J. Moser, M. Anderson and M. Grätzel, *J. Phys. Chem.*, *94* (1990) 8720.

[10] L. Spanhel and M. Anderson, *J. Am. Chem. Soc.*, *113* (1991) 2826.

[11] W.W. Stoeckenius and R.A. Bogomolni, *Annu. Rev. Biochem.*, *52* (1982) 587.

[12] H. Takei, A. Lewis, Z. Chen and I. Nabenzahl, *Appl. Opt.*, *30* (1991) 500.

[13] R.R. Brirge, *Annu. Rev. Phys. Chem.*, *41* (1990) 683.

[14] K. Ogawa, S. Kinoshita, H. Kawahara and K. Fukada, *Chem. Lett.*, *1990* (1990) 2025.

[15] R. Simmeth and G.W. Rayfield, *Biophys. J.*, *57* (1990) 1099.

[16] A.S. Baranski, W. Fawcett, A.C. McDonald, R.M. Nobriga and J.R. MacDonald, *J. Electrochem. Soc.*, *963* (1981) 128.

[17] G. Hodes, I.D.J. Howell and L.M. Peter, *J. Electrochem. Soc.*, *139* (1992) 3136.

[18] H. Weller, *Angew. Chem. Int. Ed. Engl.*, *32* (1993) 41.

[19] D. Oesterhelt and W. Stoeckenius, *Methods Enzymol.*, *31* (1974) 667.

[20] N.A. Dencher and M.P. Heyn, *Methods Enzymol.*, *88* (1982) 5.

[21] D. Wang, W. Lu, T. He, Z. Zhu, G. Hong and T. Li, in T.N. Veziroglu, Y. Zhu and D. Bao (eds.), *Hydrogen Systems*, Vol. 1, Pergamon, Oxford, 1985, p. 225.

[22] R. Korenstein and B. Hess, *Nature*, *270* (1977) 184.