

TiO₂ Surface Modification and Characterization with Nanosized PbS in Dye-Sensitized Solar Cells

Peng Wang, Liduo Wang,* Beibei Ma, Bin Li, and Yong Qiu*

Key Lab of Organic Optoelectronics & Molecular Engineering of Ministry of Education, Department of Chemistry, Tsinghua University, Beijing 100084, China

Received: January 19, 2006; In Final Form: May 10, 2006

The nanoporous TiO₂ films utilized in dye-sensitized solar cells (DSSCs) possess a large surface-to-volume ratio, which facilitates the adsorption of sensitizing dye and the recombination due to the high density of surface traps. In this paper, nanosized PbS was fabricated on the TiO₂ films. The components of the modified TiO₂ film were studied by X-ray diffraction (XRD) and electron probe microanalysis (EPMA), while the structure of the film was characterized with BET physisorption and high-resolution scanning electron microscopy (HRSEM). The results showed that the PbS particles were 2–3 nm and discrete on the surface of TiO₂. Diffusion photovoltage (PV) spectroscopy was employed to study the charge separation and diffusion processes inside modified and unmodified TiO₂ films. The diffusion PV signals revealed that the traps on the surface of TiO₂ were extremely reduced due to the presence of PbS. The results of transient photovoltage and back *I*–*V* characteristics showed that the back reaction, that is, the recombination due to the reaction between an electron on TiO₂ and the hole-transporting media, was retarded significantly.

Introduction

Nanocrystalline porous TiO₂ films have been employed in dye-sensitized solar cells (DSSCs) because the high surface area of these films facilitates efficient light absorption for a monolayer of adsorbed sensitizing dyes.¹ However, the polycrystalline and porous nature of TiO₂ results in a large number of trap sites (surface states) at grain boundaries. These surface-state sites, mainly the Ti³⁺ states,² which have been assigned to oxygen deficiencies or adsorbed species,³ are energetically located below the TiO₂ conduction band with a distribution of energy levels that is usually assumed to be an exponential distribution.^{4,5} Such surface states are normally considered to be deleterious to the function of semiconductors since they can trap carriers and promote their recombination.^{5–7} It is noteworthy that the charge recombination between the injected electrons that are trapped in surface states and the oxidized species in the hole-conducting media remains one of the major limiting factors for the efficiency of the DSSCs. Many studies to reduce such surface states have been tried to improve the conversion efficiency, such as passivating the recombination centers at the interface of a nanoporous TiO₂ film with TiCl₄,^{8,9} by diminishing the density of trapping sites,¹⁰ utilization of composite or bilayer semiconductor electrodes such as MgO–Al₂O₃,¹¹ SnO₂–ZnO,¹² Al₂O₃–TiO₂,¹³ and so forth. It was concluded by Ramakrishna et al.¹⁴ that the use of suitable organic or organometallic molecules for surface treatment holds great promise for tuning the desired surface electronic properties.

In this paper, nanosized PbS was used as a surface-modification material to reduce the surface states. Nanosized PbS has been used as a sensitizer in DSSCs in previous works. The photoelectric properties of porous TiO₂ films sensitized by PbS were reported by Hoyer et al.¹⁵ in 1995. Further study of

this type of film indicated the sensitization effect of PbS on the TiO₂ film.^{16–19} The conversion characterization of the solar cells based on TiO₂ films by using PbS as a sensitizer was also studied.^{20–23} An overall conversion efficiency of 0.49% was achieved in all solid-state DSSCs with spiro-OMeTAD as the hole-transfer material.²¹ In the works above, PbS is a replacement for the dye molecules, while it serves as a surface-state depressor in our work. To our best knowledge, this is the first time for such a study on a dye-sensitized solar cell by using PbS as a surface-state depressor to be reported.

In this article, the components of the PbS-modified TiO₂ film were studied by X-ray diffraction (XRD) and electron probe microanalysis (EPMA), while the structure of the film was characterized with BET physisorption and high-resolution scanning electron microscopy (HRSEM). Diffusion photovoltage (PV) spectra of modified and unmodified TiO₂ films were investigated in order to explore the change of surface states of TiO₂. The back-current–voltage characteristics and transient photovoltage spectroscopy of cells were used to study the recombination process in the modified cells, which is highly related to the performance of the solar cells.

Experimental Methods

A TiO₂ colloid dispersion was prepared by addition of 17.8 mL of deionized water to 2.2 g of P25 TiO₂ powder (Degussa product, a mixture of ca. 30% rutile and 70% anatase, BET surface area 50 ± 10 m²/g, mean particle size 21 nm) in a conical flask. After a 15-min sonication process, 0.2 mL of acetylacetone was added to prevent reaggregation of the TiO₂ particles and 0.1 mL of detergent (Triton X-100) was introduced to facilitate the spreading of the colloid on the substrate. After that, an additional 0.66 g of poly(ethylene glycol) (PEG, *M_w* = 20 000) was added to increase the porosity of the film.

To prepare the nanoporous TiO₂ film, transparent conductive ITO glass (15 Ω per square) was completely cleaned and a thin

* Authors to whom correspondence should be addressed. Tel: (008610) 62788802. Fax: (008610) 62795137. E-mail: Chldwang@mail.tsinghua.edu.cn (Wang), Qiuy@mail.tsinghua.edu.cn (Qiu).

compact TiO₂ film (about 8 nm in thickness) was first deposited on ITO by dip-coating²⁴ in order to improve ohmic contact and adhesion between the following porous TiO₂ layer and the conductive ITO glass. The above colloidal TiO₂ dispersion was spread on the surface of a compact TiO₂ film with a glass rod. The thickness of the porous layer was controlled by an adhesive tape. Afterward, the film was thermo-treated at 450 °C for 30 min. The thickness of the resulting porous TiO₂ film was about 4.5 μm. The TiO₂ surface modification by PbS was performed in-situ as previously reported.^{20,25} The nanoporous TiO₂ electrode was dipped for 1 min into a saturated solution of Pb(NO₃)₂, then rinsed with water and dipped into a 0.1 M Na₂S solution for 1 min, and finally rinsed with water again. This procedure was repeated three times.

To prepare a sample of diffusion PV test, the unmodified and PbS-modified TiO₂ films were formed on the surface of the indium–tin oxide (ITO) substrate (covered with a 10-nm-thick Ag film) according to the same method as above. Then, a layer of 200-nm-thick Ag was formed by evaporation on the surface of TiO₂ and served as a back electrode.

The diffusion PV measurements were carried out with a solid-junction photovoltaic cell: glass/ITO/Ag/TiO₂/Ag. The setup of the measurement of PV is similar to the previous work²⁶ except that no spacer was applied here. A 500-W xenon lamp with a double-prism monochromator (CVI DK242) was utilized to excite the spectrally dependent PV in the range of 300–800 nm. A lock-in amplifier (Stanford Research SR830) synchronized with a light chopper was employed to amplify the photovoltage signal.

For the transient photovoltage studies of the DSSCs, the cells were probed with a weak laser pulse at 532 nm, which was generated by a frequency-doubled Nd:YAG laser (pulse duration 15 ns). The 532-nm probe light was strongly absorbed by the dye and was incident from the front (ITO) side of the DSSCs in an effort to make the measurement under real operating conditions. The DSSCs under test were kept in the environment for more than 5 min to reach their steady states, which gave out an open-circuit voltage of around 250 mV before being illuminated with the laser pulse. The intensity of the laser pulse was modulated to keep the transient peak voltage of cells ≤ 20 mV, which was less than 10% of the steady-state photovoltage. The transient photovoltage signal was tested under an open-circuit condition and recorded by a TDS220 oscilloscope (Tektronix).

Results and Discussion

Figure 1 shows the X-ray diffraction (XRD) patterns of unmodified or PbS-modified TiO₂ films. It shows that the PbS particles were formed on the surface of the porous TiO₂ film. According to the Scherrer formula, the average size of PbS was calculated to be 2.6 nm.

BET physisorption was employed to characterize the BET surface area and pore volume of the TiO₂ powder (Degussa P25) and the unmodified and PbS-modified TiO₂ films. BJH pore-size distributions derived from desorption data are presented in Figure 2, and the corresponding parameters are listed in Table 1. The comparison shows that after modification with nanosized PbS, the surface area and pore volume of the TiO₂ film decreased 11% and 5.8%, respectively.

From Figure 2, we know that, as the basis of the TiO₂ colloid, the P25 powder has a mass distribution of pore diameter at 2–3 nm. In the TiO₂ porous films, additional pores mainly around 20–33 nm were formed. It can be ascribed to poly(ethylene glycol) (PEG, *M_w* = 20 000) added in the TiO₂ colloid, which

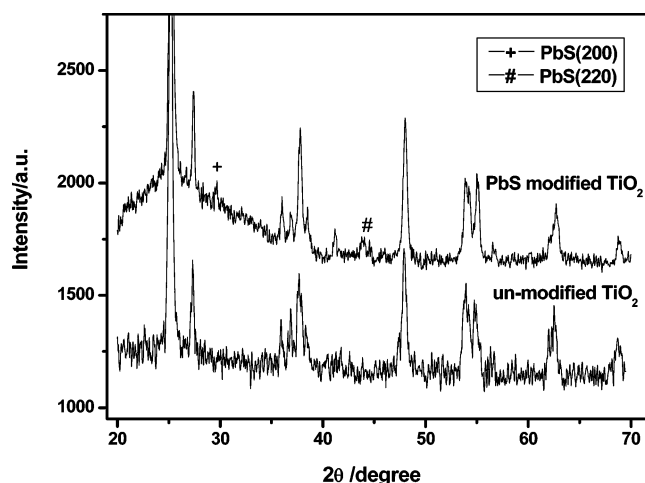


Figure 1. XRD patterns of unmodified and PbS-modified TiO₂ films.

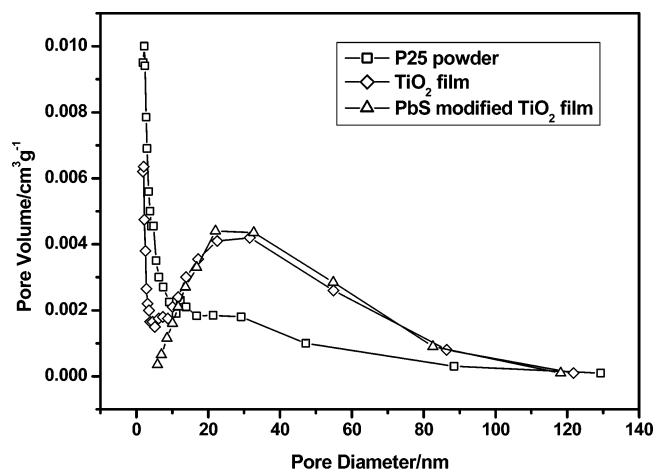


Figure 2. Pore size distribution of P25 powder, unmodified and PbS-modified TiO₂.

TABLE 1: Physicochemical Property of the P25 Powder, Unmodified and PbS-Modified TiO₂ Films

	<i>A_{BET}</i> (m ² /g) ^a	<i>V</i> (cm ³ /g) ^b
P25 powder	51.25	0.146
unmodified TiO ₂ film	51.26	0.276
PbS-modified TiO ₂ film	45.38	0.260

^a *A_{BET}*: BET surface area. ^b *V*: pore volume.

was burned out during the thermo-treatment process. After modification with PbS, the pores around 20–33 nm remained, while the smaller-diameter pores decreased evidently, especially for the pores about 2–3 nm in diameter, which almost disappeared. These changes are due to the PbS filling in the pores, which is consistent with the PbS size of 2.6 nm in XRD analysis above.

HRSEM images, which are shown in Figure 3, also confirmed the surface-area and pore-volume analysis results. The PbS-modified and unmodified TiO₂ films have a similar surface appearance with the pore size of about 20–35 nm. The pores around 2 nm were not observed since the size is out of the limit of the equipment.

Element component analysis by EPMA is listed in Table 2. It shows that the amount of PbS on the surface of TiO₂ film is 4.6% with respect to the TiO₂.

Assuming that PbS is present on the TiO₂ surface as a thin film, the surface area covered by PbS can be described by eq 1, and the total surface area of TiO₂ can be described by eq 2. In these equations, *S_{PbS}* and *S_{TiO2}* are the surface area covered

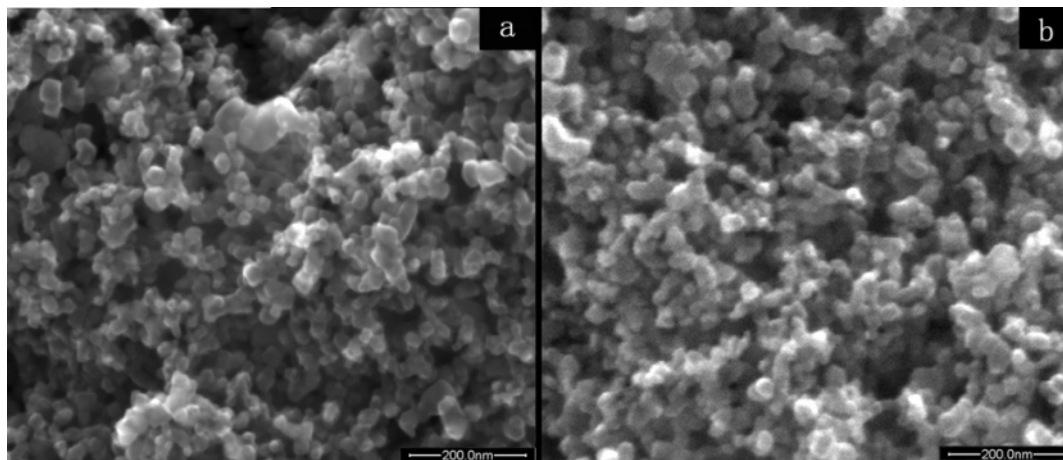


Figure 3. HRSEM images of (a) unmodified and (b) PbS-modified TiO₂ films.

TABLE 2: Element Microanalysis of PbS-Modified TiO₂ Film

element	wt (%)	at (%)
O	36.78	64.53
S	0.54	0.47
Pb	3.84	0.52
Ti	58.84	34.48

by PbS and the total surface area of TiO₂, m_{PbS} and m_{TiO_2} are the PbS mass on the TiO₂ film and the TiO₂ mass, ρ_{PbS} and d_{PbS} are the density and thickness of PbS on the TiO₂, and A_{BET} is the BET surface area of the TiO₂ porous film.

$$S_{\text{PbS}} = \frac{m_{\text{PbS}}}{\rho_{\text{PbS}} d_{\text{PbS}}} \quad (1)$$

$$S_{\text{TiO}_2} = A_{\text{BET}} m_{\text{TiO}_2} \quad (2)$$

If eq 1 is divided by eq 2, we get eq 3 as below:

$$\frac{S_{\text{PbS}}}{S_{\text{TiO}_2}} = \frac{m_{\text{PbS}}}{m_{\text{TiO}_2}} \frac{1}{\rho_{\text{PbS}} d_{\text{PbS}} A_{\text{BET}}} \quad (3)$$

Since the values of $m_{\text{PbS}}/m_{\text{TiO}_2}$ and A_{BET} are all measured by the EPMA and BET physisorption above, the values of ρ_{PbS} can refer to the handbook and the value of d_{PbS} is considered as 2 nm according to the XRD result, and the value of $S_{\text{PbS}}/S_{\text{TiO}_2}$ can be calculated out, which is 6.0%. The result indicates that about 6% of the TiO₂ surface is covered with PbS under our assumed conditions and the PbS particles are discrete on the surface of TiO₂.

Diffusion photovoltage spectra were investigated in order to explore the change of surface states of TiO₂. Figure 4 shows the comparison of unmodified and PbS-modified nanoporous TiO₂ films. It can be seen from Figure 4 that a strong PV signal appeared when TiO₂ was illuminated, that is to say that a different charge diffusion process occurred. It also shows that the PV signal occurs toward a different direction in zones (a) and (b). The PV signal at zone (a) corresponds to the wavelength from 310 to 400 nm, which is consistent with the band gap of TiO₂ absorption. A negative PV signal means that negative charges are injected into the ITO electrode while positive charges remain inside the TiO₂ film.²⁷ As for the region from 400 to about 750 nm (zone (b)), the PV signal is totally reverse to that of zone (a). In this instance, holes, instead of electrons, diffuse to the collection electrode. It is well-known that in both anatase and rutile nanosized TiO₂ (both phases exist in P25 TiO₂

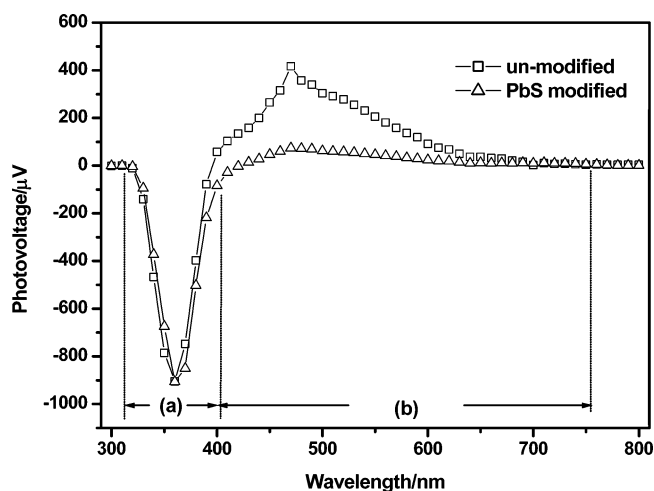


Figure 4. Photovoltage spectra for unmodified and PbS-modified TiO₂ films.

powder) there are quite a number of surface states involving Ti³⁺ states beneath the conduction band. Such trap states are observed to lie 2–3 eV above the valence band and act as electron traps.^{2,3,28} When excited at $h\nu < E_g$, electrons are captured in the surface states so that holes are easier to diffuse to the collection electrode, and thus a positive photovoltage signal is observed. It is also shown in Figure 4 that the modification by PbS had no effect on the TiO₂ absorption and thus no effect on the photovoltage in zone (a) either. However, PbS did have a great influence on the trap states of TiO₂ from 400 to around 750 nm. As PbS was introduced, the voltage in zone (b) decreased to a dramatically low level. We can see from this result that the surface states of PbS-modified TiO₂ were greatly suppressed, which is supposed to be helpful for obtaining high-performance DSSCs.

It is well-known that a decrease in surface states of TiO₂ will definitely suppress the electron–hole recombination. Figure 5 compares the transient photovoltage responses of quasi-solid-state DSSCs employing unmodified or PbS-modified TiO₂ films, which have been normalized to the same peak height at time zero. The decay curve of the photovoltage gives a representation of the recombination rate.^{29,30} Figure 5 shows that the decay time remarkably increased when TiO₂ was modified with PbS, which means the electron–hole recombination was hindered efficiently. This result is consistent with the diffusion PV spectra that the number of surface states decreased due to PbS modification.

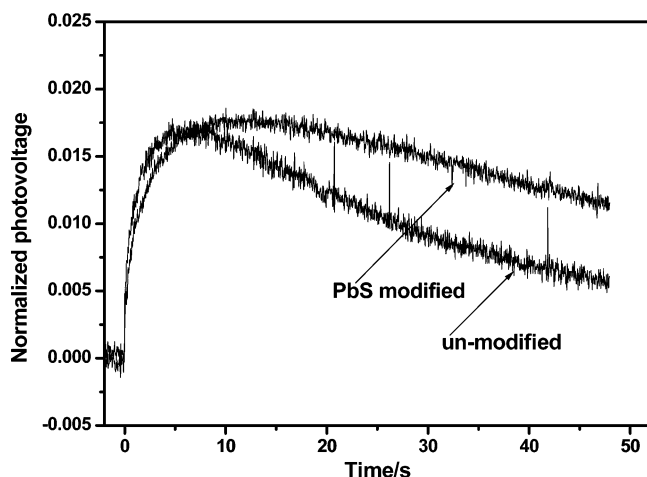


Figure 5. Normalized transient open-circuit photovoltages for DSSCs employing unmodified or PbS-modified TiO₂ films.

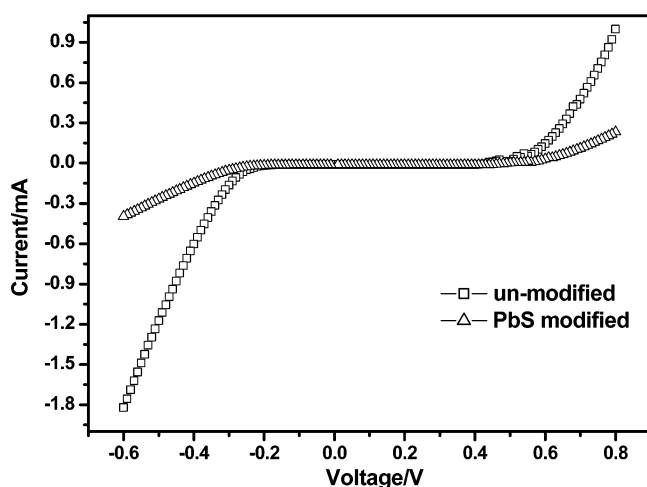


Figure 6. Dark I - V characteristics of DSSCs with unmodified or PbS-modified TiO₂ films.

At the same time, the retardation of recombination is also confirmed by the back-reaction characteristics of DSSCs with PbS-modified TiO₂ films. It can be seen in Figure 6 that the back reaction was suppressed due to the PbS modification. With a smaller dark current present, a bigger open-circuit voltage was obtained and a performance improvement of DSSCs was achieved.

Conclusion

In summary, we have demonstrated the nanosized PbS modification on the TiO₂ porous films. BET physisorption indicated that the pore sizes of unmodified TiO₂ films are mainly about 2–3 and 20–33 nm, while those of PbS-modified TiO₂ are mainly about 20–33 nm. The PbS particles are discrete on the surface of TiO₂. The addition of PbS did not change the surface area and pore volume of the film evidently, but increased the open-circuit voltages of devices by suppressing the surface states on TiO₂ and possibly also blocking the direct contact

between the hole-transporting material and TiO₂. On the basis of the results above, we know that the surface modification with optimum nanosized PbS on TiO₂ can lead to a performance improvement effectively.

Acknowledgment. This work was supported by the National Natural Science Foundation of China No. 90101029, No. 50473009, and the National Key Basic Research and Development Program of China under Grant No. 2002CB613405.

Supporting Information Available: Current–voltage characterization of DSSCs utilizing unmodified and PbS-modified TiO₂ films. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References and Notes

- O'Regan, B.; Gratzel, M. *Nature* **1991**, *353*, 737.
- Hagfeldt, A.; Gratzel, M. *Chem. Dev.* **1995**, *95*, 49.
- Nelson, J.; Haque, S. A.; Klug, D. R.; Durrant, J. R. *Phys. Rev. B* **2001**, *63*, 5321.
- Kroeze, J. E.; Savenije, T. J.; Warman, J. M. *J. Am. Chem. Soc.* **2004**, *126*, 7608.
- Haque, S. A.; Tachibana, Y.; Willis, R. L.; Moser, J. E.; Gratzel, M.; Klug, D. R.; Durrant, J. R. *J. Phys. Chem. B* **2000**, *104*, 538.
- Gregg, B. A.; Chen, S. G.; Ferrere, S. *J. Phys. Chem. B* **2003**, *107*, 3019.
- Mora-Sero, I.; Bisquert, J. *Nano Lett.* **2003**, *3*, 945.
- Barbe, C. J.; Arendse, F.; Comte, P.; Jirousek, M.; Lenzmann, F.; Shklover, V.; Gratzel, M. *J. Am. Ceram. Soc.* **1997**, *80*, 3157.
- Park, N. G.; Schlichthorl, G.; van de Lagemaat, J.; Cheong, H. M.; Mascarenhas, A.; Frank, A. J. *J. Phys. Chem. B* **1999**, *103*, 3308.
- Gratzel, M.; Kalyanasundaram, K. *Curr. Sci.* **1994**, *66*, 706.
- Taguchi, T.; Zhang, X. T.; Sutanto, I.; Tokuhito, K.; Rao, T. N.; Watanabe, H.; Nakamori, T.; Uragami, M.; Fujishima, A. *Chem. Commun.* **2003**, *19*, 2480.
- Tennakone, K.; Kumara, G.; Kottegoda, I. R. M.; Perera, V. P. S. *Chem. Commun.* **1999**, 15.
- Palomares, E.; Clifford, J. N.; Haque, S. A.; Lutz, T.; Durrant, J. R. *J. Am. Chem. Soc.* **2003**, *125*, 475.
- Ramakrishna, G.; Singh, A. K.; Palit, D. K.; Ghosh, H. N. *J. Phys. Chem. B* **2004**, *108*, 1701.
- Hoyer, P.; Konenkamp, R. *Appl. Phys. Lett.* **1995**, *66*, 349.
- Sun, Y. P.; Hao, E. C.; Zhang, X.; Yang, B.; Gao, M. Y.; Shen, J. C. *Chem. Commun.* **1996**, 2381.
- Hao, E. C.; Yang, B.; Yu, S.; Gao, M. Y.; Shen, J. C. *Chem. Mater.* **1997**, *9*, 1598.
- Sun, Y. P.; Hao, E.; Zhang, X.; Yang, B.; Shen, J. C.; Chi, L. F.; Fuchs, H. *Langmuir* **1997**, *13*, 5168.
- Yang, S. M.; Wang, Z. S.; Huang, C. H. *Synth. Met.* **2001**, *123*, 267.
- Vogel, R.; Hoyer, P.; Weller, H. *J. Phys. Chem.* **1994**, *98*, 3183.
- Plass, R.; Pelet, S.; Krueger, J.; Gratzel, M.; Bach, U. *J. Phys. Chem. B* **2002**, *106*, 7578.
- Hong, J. S.; Choi, D. S.; Kang, M. G.; Kim, D.; Kim, K. J. *J. Photochem. Photobiol., A-Chem.* **2001**, *143*, 87.
- Yang, S. M.; Huang, C. H.; Zhai, J.; Wang, Z. S.; Jiang, J. J. *Mater. Chem.* **2002**, *12*, 1459.
- Li, B.; Wang, L. D.; Zhang, D. Q.; Qiu, Y. *Chin. Sci. Bull.* **2004**, *49*, 123.
- Li, B.; Wang, L. D.; Li, J. W.; Qiu, Y. *Chin. Phys. Lett.* **2004**, *21*, 1391.
- Duzhko, V.; Timoshenko, V. Y.; Koch, F.; Dittrich, T. *Phys. Rev. B* **2001**, *64*, 075204.
- Mahrov, B.; Boschloo, G.; Hagfeldt, A.; Dloczik, L.; Dittrich, T. *Appl. Phys. Lett.* **2004**, *84*, 5455.
- Redmond, G.; Fitzmaurice, D.; Graetzel, M. *J. Phys. Chem.* **1993**, *97*, 6951.
- Kopidakis, N.; Benkstein, K. D.; van de Lagemaat, J.; Frank, A. J. *J. Phys. Chem. B* **2003**, *107*, 11307.
- O'Regan, B.; Lenzmann, F. *J. Phys. Chem. B* **2004**, *108*, 4342.