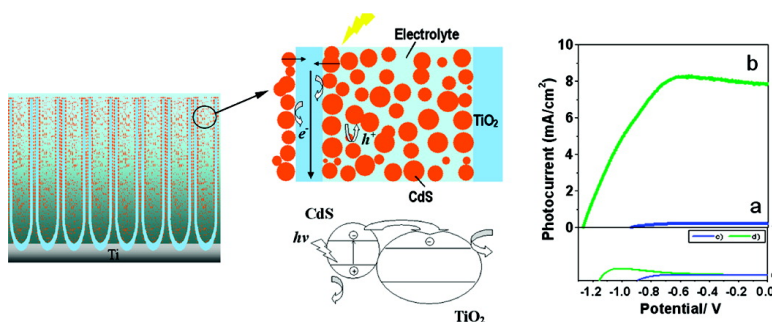


CdS Quantum Dots Sensitized TiO Nanotube-Array Photoelectrodes

Wen-Tao Sun, Yuan Yu, Hua-Yong Pan, Xian-Feng Gao, Qing Chen, and Lian-Mao Peng

J. Am. Chem. Soc., **2008**, 130 (4), 1124-1125 • DOI: 10.1021/ja0777741

Downloaded from <http://pubs.acs.org> on February 8, 2009



More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Links to the 7 articles that cite this article, as of the time of this article download
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

[View the Full Text HTML](#)



CdS Quantum Dots Sensitized TiO₂ Nanotube-Array Photoelectrodes

Wen-Tao Sun, Yuan Yu, Hua-Yong Pan, Xian-Feng Gao, Qing Chen, and Lian-Mao Peng*

Key Laboratory for the Physics and Chemistry of Nanodevices and Department of Electronics,
Peking University, Beijing 100871, China

Received October 9, 2007; E-mail: lmpeng@pku.edu.cn

Titanium dioxide (TiO₂) is one of the most important wide gap semiconductors and is widely investigated for use in water photoelectrolysis, photocatalysis, heterojunction solar cells, environmental purification and gas sensing.¹ Very recently highly ordered TiO₂ nanotube arrays were synthesized by anodic oxidation of titanium and had generated considerable scientific interest.^{2,3} Various methods have been developed to reduce the band gap of TiO₂ via, for example, substitutional doping (C, N, etc.)⁴ and combining TiO₂ with organic dyes or narrow-gap semiconductor quantum dots (QDs),^{5,6} such as CdS, CdSe, InP, and PbS QDs. Niitsoo et al.^{6h} fabricated a CdS/CdSe/TiO₂ electrode showing an efficiency of 2.8%. Grimes and co-workers^{2f,7} reported the use of highly ordered transparent TiO₂ nanotube arrays in dye-sensitized solar cells (DSCs). However, little work has been done on the TiO₂ nanotube-arrays and semiconductor QDs-based composite structures.⁸

In this paper we report an investigation on the CdS QDs sensitized TiO₂ nanotube array photoelectrodes and their performance in photoelectrochemical (PEC) solar cells. These materials resulted in a significant PEC cell efficiency of 4.15% under AM 1.5 G illuminations, a large open-circuit photovoltage of 1.27 V, a generated photocurrent of 7.82 mA/cm², and a fill factor of 0.578. These results clearly demonstrate that significant improvement on the PEC cell efficiency can be obtained via incorporating inorganic semiconductor QDs into the TiO₂ nanotube array films.

The highly ordered TiO₂ nanotube films were synthesized by anodic oxidation in a NH₄F organic electrolyte, similarly to that described by Paulose et al.^{3a} CdS QDs were deposited into the crystallized TiO₂ nanotubes by sequential chemical bath deposition (S-CBD) method.⁹ The morphologies of the TiO₂ nanotube films were examined using a field-emission gun scanning electron microscope (SEM). Figure 1a is a typical SEM image of the as-synthesized TiO₂ nanotube film, which reveals a regularly arranged pore structure of the film. These pores have a uniform size distribution around 120 nm. Shown in Figure 1b is a cross-sectional view of the film showing that the film is composed of well-aligned nanotubes of about 12.3 μm in length which grow vertically from a Ti substrate. Shown in Figure 1c is a low magnification SEM image of the CdS deposited nanotube film showing that well-ordered pores structure still exists, suggesting that the CdS deposition process does not damage the ordered TiO₂ nanotube array structure. Closer observation (Figure 1d) reveals that the surface of the CdS deposited TiO₂ nanotube array film is very clean, and some QDs (marked with arrows) have been deposited into TiO₂ nanotubes. Even at the cracks no visible particle aggregates are found on the outside walls of TiO₂ nanotubes after CdS deposition.

CdS QDs deposited TiO₂ nanotubes were further investigated using transmission electron microscope (TEM). Figure 1e is a low magnification TEM image of the film sample, showing clearly that the sample has an ordered array tubular structure. Figure 1f is a higher-magnification TEM image of a single nanotube, showing

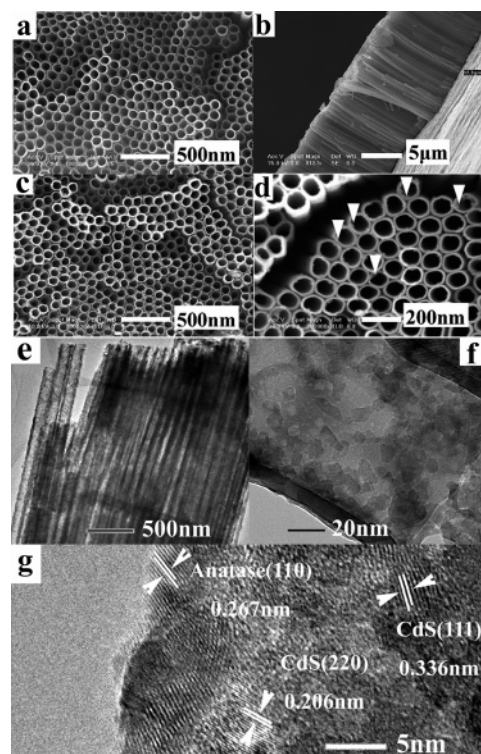


Figure 1. Morphologies of TiO₂ nanotube-array film: (a) a typical top view SEM image of the TiO₂ nanotube array film; (b) a cross-sectional view of the well aligned TiO₂ nanotubes film. SEM images showing CdS-deposited TiO₂ nanotube-array film at (c) low and (d) high magnifications; (e, f) TEM images of the TiO₂ nanotube film after CdS QDs were deposited into the film; (g) a HRTEM image of a CdS deposited nanotube.

that many QDs have been deposited into the pore of the TiO₂ nanotube. The size of the QDs ranges from 2 to 10 nm. Figure 1g is a high-resolution TEM (HRTEM) image of the sample. The observed lattice spacing of 0.267 nm in the left part of the image corresponds to the (110) plane of anatase (JPCDS 21-1272), showing that the wall of the nanotubes is TiO₂. The observed 0.206 and 0.336 nm fringes of the QDs in the nanotube correspond to the (111) and (220) planes, respectively, of the cubic phase of CdS (JPCDS 80-0019). The composition and structure of the TiO₂ nanotube and deposited QDs were also characterized by energy dispersive X-ray spectroscopy (EDX) and X-ray diffraction (XRD) (Supporting Information), which further confirms that the nanotube composites are composed of TiO₂ nanotubes and CdS QDs.

Shown in Figure 2 are experimental current–voltage (*I*–*V*) characteristics measured from an as-synthesized nanotube array photoelectrode (with a tube length of about 19.2 μm). For the plain TiO₂ nanotube film electrode the open-circuit photovoltage (*V*_{oc}) is 0.94 V versus Ag/AgCl electrode, while for the as-prepared CdS-deposited TiO₂ nanotube film electrode *V*_{oc} is about 1.27 V. The

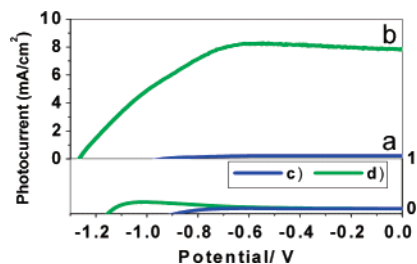


Figure 2. Photocurrent versus voltage in 1 M Na₂S under AM 1.5 G at 138.4 mW/cm² illumination for (a) plain and (b) CdS-modified TiO₂ nanotube film electrode. (c, d) Corresponding currents in the dark for curves a,b.

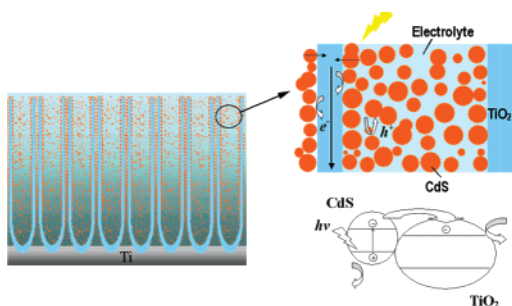


Figure 3. Sketch showing the nanostructure of CdS modified TiO₂ nanotube film electrode and charge-transfer processes between CdS and TiO₂.

generated photocurrent (J_{sc}) increased from 0.22 (for the plain TiO₂ nanotubes) to 7.82 mA/cm² (CdS modified). The J_{sc} response of the CdS-modified electrodes is 35 times higher than that of the plain TiO₂ nanotube film electrode. The fill factor FF = 0.578, and cell efficiency is 4.15% for the as-modified CdS–TiO₂ nanotube film.

Although many other solar cell performance related factors have not been optimized in this work, the photocurrent and cell efficiency achieved here are already exciting. To the best of our knowledge, the film electrodes considered here have the highest performance among all CdS–TiO₂ systems reported. To summarize the main features of our cells, we depicted in Figure 3 the basic structure of the CdS modified TiO₂ nanotube-array electrode and the main charge-transfer processes between TiO₂ and CdS after being activated by the light. The achieved high efficiency may be attributed to two major improvements. First, the QDs afford multiple excitons from the absorption of a single photon. Second, the crystalline nature of the nanotubes and the film geometry allow a fast and efficient transfer of the photogenerated electrons from CdS QDs to the Ti substrate, which compares favorably with the traditional mesoporous film electrodes leading to a much reduced electron–hole recombination and much improved photocurrent and efficiency.

Our results show that CdS QDs can be used to sensitize TiO₂ nanotube-array films making them more responsive to the visible spectrum of the sunlight. The significant photocurrent and efficiency achieved here confirm that the unique nanotube structures can facilitate the propagation and kinetic separation of photogenerated

charges, suggesting important applications of the inorganic QDs sensitized TiO₂ nanotube-array films in solar cell applications.

Acknowledgment. This work was supported by the Ministry of Science and Technology (Grant Nos. 2006CB932401 and 2006AA03Z350), and National Science Foundation of China (Grant Nos. 10434010 and 90606026).

Supporting Information Available: Synthesis of TiO₂ nanotube arrays and CdS QDs, EDX and XRD, PEC performance measurements, photocurrent spectra, and IPCE results. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) (a) Hoffmann, M. R.; Martin, S. T.; Choi, W.; Bahnemann, D. W. *Chem. Rev.* **1995**, *95*, 69. (b) Kim, K. J.; Benksten, K. D.; Lagemaat, J. V.; Frank, A. J. *Chem. Mater.* **2002**, *14*, 1042. (c) Wang, R.; Hashimoto, K.; Fujishima, A. *Nature* **1997**, *388*, 431. (d) Gratzel, M. J. *Photochem. Photobiol. A* **2004**, *168*, 235. (e) Gratzel, M.; *Prog. Photovolt: Res. Appl.* **2006**, *14*, 429.
- (2) (a) Gong, D.; Grimes, C. A.; Varghese, O. K.; Hu, W.; Singh, R. S.; Chen, Z.; Dickey, E. C. *J. Mater. Res.* **2001**, *16*, 3331. (b) Ruan, C.; Paulose, M.; Varghese, O. K.; Mor, G. K.; Grimes, C. A. *J. Phys. Chem. B* **2005**, *109*, 15754. (c) Macak, J. M.; Tsuchiaki, H.; Schmuki, P. *Angew. Chem., Int. Ed.* **2005**, *44*, 2100. (d) Macak, J. M.; Tsuchiaki, H.; Taveira, L.; Aldabergerova, S.; Schmuki, P. *Angew. Chem., Int. Ed.* **2005**, *44*, 7463. (e) Paulose, M.; Varghese, O. K.; Mor, G. K.; Grimes, C. A.; Ong, K. G. *Nanotechnology* **2006**, *17*, 398. (f) Mor, G. K.; Shankar, K.; Paulose, M.; Varghese, O. K.; Grimes, C. A. *Nano Lett.* **2006**, *6*, 215. (g) Paulose, M.; Shankar, K.; Varghese, O. K.; Mor, G. K.; Hardin, B.; Grimes, C. A. *Nanotechnology* **2006**, *17*, 1446.
- (3) (a) Paulose, M.; Shankar, K.; Yoriya, S.; Prakasham, H. E.; Varghese, O. K.; Mor, G. K.; Latempa, T. A.; Fitzgerald, A.; Grimes, C. A. *J. Phys. Chem. B* **2006**, *110*, 16179. (b) Zhu, K.; Neale, N. R.; Miedaner, A.; Frank, A. J. *Nano Lett.* **2007**, *7*, 69. (c) Funk, S.; Hokkanen, B.; Burghaus, U.; Ghicov, A.; Schmuki, P. *Nano Lett.* **2007**, *7*, 1091. (d) Albu, S. P.; Ghicov, A.; Macak, J. M.; Hahn, R.; Schmuki, P. *Nano Lett.* **2007**, *7*, 1286. (e) Prakasham, H. E.; Shankar, K.; Paulose, M.; Varghese, O. K.; Grimes, C. A. *J. Phys. Chem. C* **2007**, *111*, 7235. (f) Park, J.; Bauer, S.; Mark, K. V.; Schmuki, P. *Nano Lett.* **2007**, *7*, 1686. (g) Macak, J. M.; Tsuchiaki, H.; Ghicov, A.; Schmuki, P. *Electrochem. Commun.* **2005**, *7*, 1133. (h) Gratzel, M. *Prog. Photovoltaics: Res. Appl.* **2000**, *8*, 171.
- (4) Ghicov, A.; Macak, J. M.; Tsuchiaki, H.; Kunze, J.; Haeublein, V.; Frey, L.; Schmuki, P. *Nano Lett.* **2006**, *6*, 1080.
- (5) (a) Linsebigler, A. L.; Lu, G. Q.; Yates, J. T. *Chem. Rev.* **1995**, *95*, 735. (b) Plass, R.; Pelet, S.; Krueger, J.; Gratzel, M.; Bach, U. *J. Phys. Chem. B* **2002**, *106*, 7578. (c) Sasaki, T.; Watanabe, M. *J. Phys. Chem. B* **1997**, *101*, 10159. (d) Hickey, S. G.; Riley, D. J.; Tull, E. J. *J. Phys. Chem. B* **2000**, *104*, 7623. (e) Peter, L. M.; Riley, D. J.; Tull, E. J.; Wijayantha, K. G. U. *Chem. Commun.* **2002**, 1030. (f) Kim, J. C.; Choi, J.; Lee, Y. B.; Hong, J. H.; Lee, J. I.; Yang, J. W.; Lee, W. I. *Chem. Commun.* **2006**, 5024.
- (6) (a) Robel, I.; Kuno, M.; Kamat, P. V. *J. Am. Chem. Soc.* **2007**, *129*, 4136. (b) Robel, I.; Subramanian, V.; Kuno, M.; Kamat, P. V. *J. Am. Chem. Soc.* **2006**, *128*, 2385. (c) Sun, Y.; Hao, E.; Zhang, X.; Yang, B.; Shen, J.; Chi, L.; Fuchs, H. *Langmuir* **1997**, *13*, 5168. (d) Wang, P.; Wang, L.; Ma, B.; Li, B.; Qiu, Y. *J. Phys. Chem. B* **2006**, *110*, 14406. (e) Zaban, A.; Micic, O. I.; Gregg, B. A.; Nozik, A. J. *Langmuir* **1998**, *14*, 3153. (f) Ho, W.; Yu, J. C.; Lin, J.; Yu, J.; Li, P. *Langmuir* **2004**, *20*, 5865. (g) Robel, I.; Kuno, M.; Kamat, P. V. *J. Am. Chem. Soc.* **2007**, *129*, 4136. (h) Niitsoo, O.; Sarkar, S. K.; Pejoux, C.; Rühle, S.; Cahen D.; Hodes, G. *J. Photochem. Photobiol. A: Chem.* **2006**, *181*, 306.
- (7) Shankar, K.; Mor, G. K.; Prakasham, E. H.; Yoriya, S.; Paulose, M.; Varghese, O. K.; Grimes, C. A. *Nanotechnology* **2007**, *18*, 1. (b) Mor, G. K.; Shankar, K.; Paulose, M.; Varghese, O. K.; Grimes, C. A. *Appl. Phys. Lett.* **2007**, *91*, 152111. (c) Paulose, M.; Shankar, K.; Varghese, O. K.; Mor, G. K.; Grimes, C. A. *J. Phys. D: Appl. Phys.* **2006**, *39*, 2498.
- (8) Chen, S.; Paulose, M.; Ruan, C.; Mor, G. K.; Varghese, O. K.; Kouzoudis, D.; Grimes, C. A. *J. Photochem. Photobiol. A: Chem.* **2006**, *181*, 177.
- (9) Larramona, G.; Chone, C.; Jacob, A.; Sakakura, D.; Delatouche, B.; Pere, D.; Cieren, X.; Nagino, M.; Bayon, R. *Chem. Mater.* **2006**, *18*, 1688.

JA0777741