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Synthesis and Photocatalytic Activity of One-Dimensional $CdS@TiO_2$ Core-Shell Heterostructures

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Abstract: One-dimensional $CdS@TiO_2$ core-shell heterostructures were fabricated via the hydrolysis of tetrabutyl titanate (TBT) on preformed CdS nanowires. The as-prepared products were characterized by X-ray diffraction, transmission electron microscopy, selected area electron diffraction and diffuse reflectance spectroscopy techniques. Results demonstrated that the hydrolysis of TBT had a great influence on the morphology of the coated TiO_2 shell, resulting in the formation of TiO_2 nanoparticles and nanolayer-modified $CdS@TiO_2$ heterostructures. Degradation of methylene blue using $CdS@TiO_2$ core-shell heterostructures as photocatalysts under visible light irradiation was investigated. Comparative photocatalytic tests showed that the TiO_2 nanoparticles-modified heterostructure exhibited a superior activity due to the passivity of photogenerated charge carriers.

Keywords: One-dimensional $CdS@TiO_2$ heterostructures; Photocatalysis; Methylene blue; Morphology; Mechanism

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Introduction

Photocatalysis using semiconductor has aroused growing interests since the photoinduced splitting of water on TiO_2 electrode was reported in 1972 [1]. For semiconductor, some disadvantages such as limited visible-light absorption, incomplete charge separation and little internal surface area remain to be pivotal problems that hinder practical applications of this highly efficient, "green" technique. The general strategy to solve the above-mentioned problems involves the ion doping [2-6], coupling of two semiconductors [7-12], metal deposition [13], or surface chemical modification etc. [14, 15]. One-dimensional (1D) nanosized heterostructures, such as ZnO/ZnS [9], CdS/MoS_2 [10], ZnO/CdSe [11] heterostructures, are considered as excellent candidates because of their high surface areas, modulated band structures and promoted separation of photogenerated charge carriers.

With a relatively narrow band gap of about 2.4 eV at room temperature, wurtzite CdS is one of the first discovered visible-light driven semiconductors which has promising applications in photochemical catalysis, gas sensor, detector, solar cell, nonlinear optical material, luminescence device, and optoelectronic device [16-18]. On account of this, 1D CdS nanocrystal was obtained through various routes [19-21]. TiO_2 is the most widely investigated photocatalytic material owing to its favorable chemical property, high stability and low cost. With proper band structures, CdS/TiO_2 nanocomposite exhibits good property in photocatalysis [22]. Therefore, it is significant to prepare CdS/TiO_2

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heterostructures and explore their effect of morphology and structure on the photocatalytic activity. To date, CdS sensitized TiO_2@CdS core-shell nanoparticles [23], nanotubes [24-26], nanowires [27, 28], and CdS-embeded TiO_2 heterostructures [29-31] have been successfully fabricated.

Herein, we report the fabrication of 1D CdS@TiO_2 core-shell nanostructures via the hydrolysis of tetrabutyl titanate (TBT) on preformed CdS nanowires. By controlling the hydrolysis of TBT on the surface of CdS nanowires, TiO_2 nanoparticles and nanolayer-coated CdS@TiO_2 heterostructures were obtained. Degradation of methylene blue (MB) using CdS@TiO_2 core-shell heterostructures as photocatalysts under visible light irradiation was investigated. Photocatalytic tests demonstrated that the CdS@TiO_2 heterostructures displayed a strong correlation between their morphology and the photocatalytic activity. The TiO_2 nanoparticles-modified CdS@TiO_2 core-shell heterostructures exhibited enhanced photocatalytic activity due to the promoted separation of charge carriers.

Experimental

All reagents in this study were of analytical grade and used without further purification. TiO_2 nanoparticles and nanolayer-modified 1D CdS@TiO_2 core-shell nanostructures were fabricated via a two-step process. The preparation of CdS nanowires was achieved as described in the literature [32]. In a typical process, the as-prepared CdS nanowires (0.2 mmol) was ultrasonically dispersed in 60 ml absolute ethanol containing 5 ml TBT. Ethanol-water (20 ml, volume ratio =6:1) solution was added dropwise to the above CdS-TBT suspension for TBT hydrolysis, and the dropping rate was controlled at 0.5 ml/min. After being stirred at room temperature for 1 h, TiO_2 nanoparticles-modified CdS@TiO_2 core-shell heterostructure was collected and thoroughly washed with deionized water and absolute ethanol and dried in vacuum for 10 h at 70℃. When the dropping rate adjusted to 2 ml/min and the added ethanol-water solution increased to 50 ml, TiO_2 nanolayer-modified 1D core-shell heterostructure was obtained. The CdS@TiO_2 core-shell products were calcined at 500℃ for 3 h in air atmosphere to eliminate the residual organisms, and cooled to room temperature naturally.

X-ray diffraction (XRD) analysis was measured on an X-ray diffractometer (Bruker D8) with Cu-Kα radiation (λ=1.5418 Å) at the scanning rate of 2°/min for 2θ ranging from 10 to 80°, and the tube voltage and electric current were 40 kV and 20 mA respectively. Transmission electron microscopic (TEM) images were performed with a JEM-100CXII machine at an accelerating voltage of 80 kV. High-resolution TEM images and selected area electron diffraction (SAED) patterns were collected on a JEOl-2000 machine at an accelerating voltage of 200 kV. UV-visible diffuse reflectance spectroscopy was measured on a TU-1901 UV-visible spectrophotometer.

Photocatalytic activity of nanoparticles and nanolayer-modified 1D CdS@TiO_2 core-shell heterostructures was evaluated by the degradation of methylene blue (MB) under visible light irradiation. This study was carried out in an XPA-Photochemical Reactor (XuJiang Electromechanical Plant, Nanjing, China), which contains several jacketed quartz tubes and a 500 W Xe lamp with optical cutoff filters to remove the light at wavelength below 420 nm. For each experiment, CdS@TiO_2 heterostructures (50 mg) were dispersed in 50 ml MB aqueous solution (15 mg/l). The resulting suspensions were stirred for 30 min in the dark to reach the adsorption-desorption equilibrium between MB solution and the solid catalysts. Some solution was taken out from the reaction system before illumination or at 60 min interval during illumination. The obtained solution was centrifuged to collect the supernatant for concentration test.

Results and Discussion

It was found that the dropping rate and volume of ethanol-water solution played important roles in the formation of 1D CdS@TiO_2 core-shell heterostructures. When the ethanol-water solution (20 ml) was added to the CdS-TBT suspension at the rate of 0.5 ml/min, rough product coated with TiO_2 nanoparticles (ca. 3 nm in diameter) was fabricated. When the rate was adjusted to 2 ml/min (50 ml), the coated TiO_2 shell was composed of a dense TiO_2 layer with a thickness of ca. 30 nm. Rapid addition of ethanol-water solution favored the hydrolysis of TBT to a certain extent and accelerated the growth of TiO_2 nanocrystals, finally resulting in the formation of TiO_2 nanoparticles and nanolayer coated 1D CdS@TiO_2 core-shell heterostructures. Therefore, the dropping rate and volume of ethanol-water solution is a key factor in controlling the morphology and microstructure of 1D CdS@TiO_2 heterostructures in this study.

The phase and purity of the as-prepared products were examined by XRD technique. Figure 1 gives XRD patterns of the neat CdS nanowires and nanoparticles-modified 1D CdS@TiO_2 core-shell heterostructure, along with the standard cards of anatase TiO_2 (JCPDS No. 21-1272) and hexagonal CdS (JCPDS No. 41-1049) for comparisons. As shown in Fig. 1(a), all the diffraction peaks could be perfectly indexed to the hexagonal phase of CdS, with lattice constants of a=0.414 nm and c=0.672 nm. No characteristic peaks ascribing to other phases were observed, which indicates high purity of the prepared CdS nanowires. The (002) peak of the CdS nanowires is weak, while the (100) and

(110) peaks are strong compared with the standard card. The reason is that the CdS nanowires trend to grow along [001] direction preferentially, resulting in the fewer exposed (002) crystal planes during the measurement process [33]. The additional diffraction peaks at 2θ of 25.3, 37.8, 48.0, 55.1, and 62.7° in Fig. 1(b) matched well with tetragonal anatase TiO_2, with lattice constants of a=0.378 nm and c=0.951 nm. Figure 1 demonstrated that well-crystallined CdS phase and a CdS@TiO_2 nanocomposite were produced in our study.

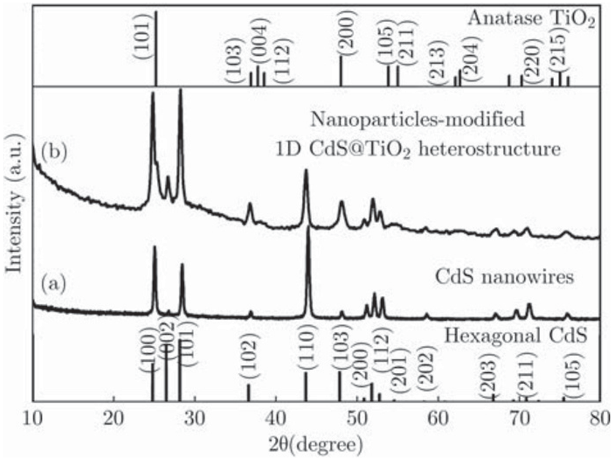


Fig. 1 XRD patterns of (a) neat CdS nanowires and (b) nanoparticles-modified 1D CdS@TiO_2 core-shell heterostructure. The stick spectral represent the standard reflections of anatase TiO_2 and hexagonal CdS.

Further structural analysis of nanoparticles-modified 1D CdS@TiO_2 core-shell heterostructure was carried out by TEM technique. As can be seen in the TEM image (see Fig. 2(a)), the product was several tens of micrometers in length and 20-50 nm in width. The high-resolution TEM image (see Fig. 2(b)) of this material reveals that the heterostructure's surface was rough and the shell was composed of TiO_2 nanoparticles with a diameter of ca. 3 nm. Well-resolved lattice fringes were visible across the entire region, with the interplanar distances of 0.243 nm and 0.335 nm according with (103) d-spacing of anatase TiO_2 and (002) d-spacing of wurtzite CdS respectively. From Fig. 2(b), the CdS nanowires grow along [001] orientation preferentially, which was in good agreement with the XRD results.

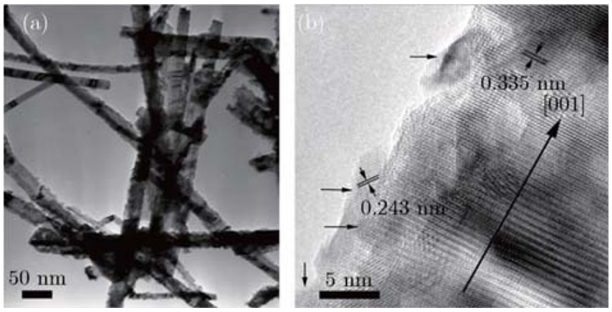


Fig. 2 (a) TEM and (b) high-resolution TEM images of nanoparticles-modified 1D CdS@TiO_2 core-shell heterostructure.

Fig. 3 showed TEM high-resolution images and SAED pattern of the nanolayer-modified 1D CdS@TiO_2 core-shell heterostructure. As shown in the TEM image (see Fig. 3(a)), the heterostructure's surface was smooth and the coated TiO_2 layer was ca. 30 nm thick. Additionally, the product assembled to wiring harness due to the conglutination of the thick TiO_2 shell. High-resolution TEM images given in Fig. 3(b) and 3(c) corresponded to marginal and inner part of the square part in Fig. 3(a) respectively. Well-resolved lattice fringes can be clearly observed in both regions, with the measured d-spacings of 0.351 nm and 0.357 nm ascribed to (101) crystal planes of anatase TiO_2 and (100) crystal planes of hexagonal CdS phase. SAED pattern shown in Fig. 3(e) was mainly composed of two sets of diffraction dots. The dashed parallelogram was indexed as that of hexagonal CdS along the [010] zone axis and diffraction rings as that of TiO_2 shell with polycrystalline nature. TiO_2 nanotubes (see Fig. 3(d)) can be obtained as expected when the core-shell heterostructure was dealt with 5 M HCl solution.

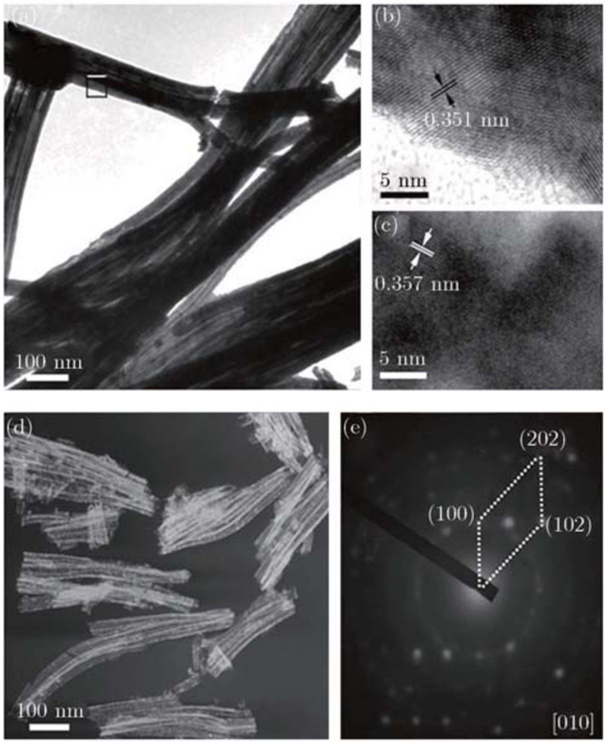


Fig. 3 TEM images of (a) nanolayer-modified 1D CdS@TiO_2 core-shell heterostructure and (d) TiO_2 nanotubes; High-resolution TEM images of (b) TiO_2 shell and (c) CdS core of the rectangular region in (a); (e) SAED pattern of the heterostructure.

To confirm the thermal stability of CdS@TiO_2 core-shell structures, we calcined the pure CdS nanowires at 500 ℃ for 3 h in air atmosphere. It was observed that the yellow CdS nanowires turned to white. Fig. 4 showed XRD pattern of the white product, which was indexed as orthorhombic CdO_2SO_4 (JCPDS No. 32-0140). Thermal stability of pure CdS nanowires was enhanced due to the coated TiO_2 shell.

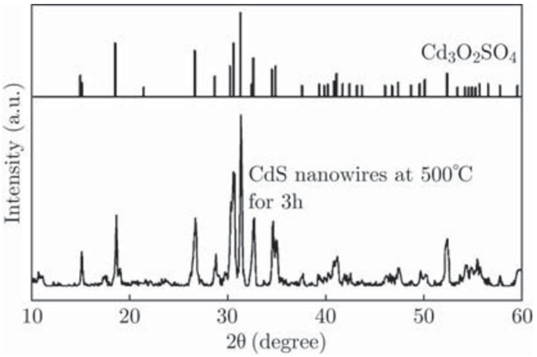


Fig. 4 XRD pattern of pure CdS nanowires annealed at 500 ℃ for 3h in air atmosphere.

Diffuse reflectance spectroscopy was used to measure optical property of nanoparticles-modified 1D $CdS@TiO_2$ core-shell heterostructure, together with the neat CdS nanowires for comparison. As seen from the normalized UV-visible absorption spectral (see Fig. 5), both of the samples had a steep absorption in visible light region, ascribing to the intrinsic absorption of CdS semiconductor. Band gap of 2.38 eV was given for pure CdS phase by the absroption edge (520 nm), which was comparable to the standard bulk CdS (2.4 eV). The heterostructure had strong absorption in the UV light region resulting from the absorption of TiO_2 (Eg=3.2 eV) shell.

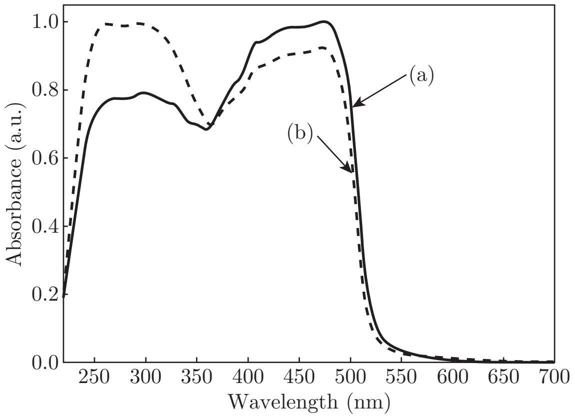
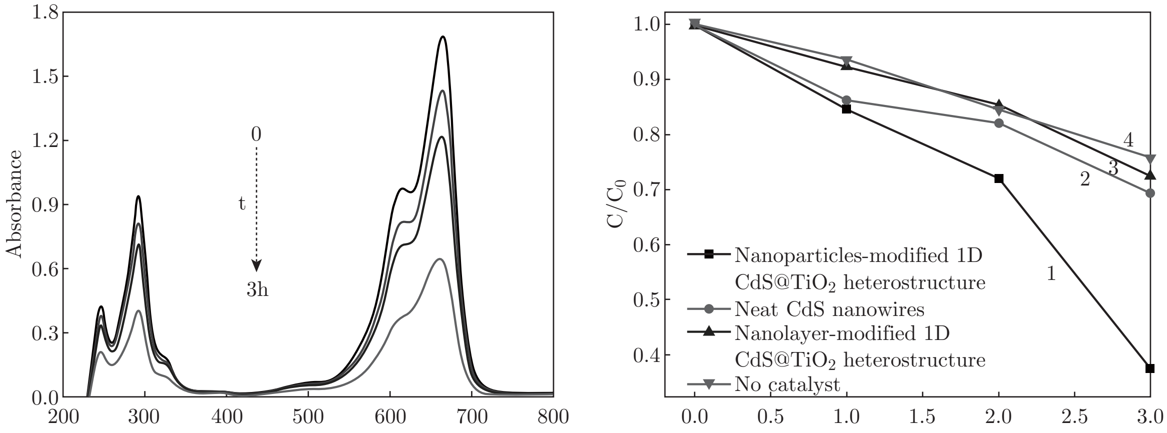


Fig. 5 UV-vis absorption spectral of (a) neat CdS nanowires, and (b) nanoparticles-modified 1D $CdS@TiO_2$ core-shell heterostructure.

To investigate photocatalytic activity of 1D $CdS@TiO_2$ core-shell heterostructure under visible light irradiation ($\lambda > 420$ nm), MB aqueous solution was used as probe contamination [34, 35]. Degradation of MB solution was evaluated by the variety of colors and absorbance at the characteristic wavelength of 664 nm in optical absorption spectrum. The degradation rate was calculated based on the following equation: MB degradation rate (%)=$(A_0\text{-}A_t)/A_0 \times 100\%$, where A_0 and A_t are the initial MB absorbance and residual MB absorbance at t_0 and t time respectively. It was noted that the sample before illumination was treated as the starting point. In the presence of nanoparticles-modified 1D $CdS@TiO_2$ core-shell heterostructure, MB aqueous solution gradually faded under visible-light irradiation as the time of illumination increased. The characteristic absorbance decreased from 1.685 to 0.634 as depicted in the absorption spectrum (see Fig. 6(a)).



(a) Wavelength (nm)

(b) Irradiation time (h)

Fig. 6 (a) Absorption spectrum changes of MB aqueous solution (15 mg/l) degraded by nanoparticles-modified 1D $CdS@TiO_2$ core-shell heterostructure with irradiation time: 0, 1, 2, and 3 h, (b) Visible-light photodegradation of MB under different conditions. Curves: (1) over nanoparticles-modified 1D $CdS@TiO_2$ core-shell heterostructure, (2) over neat CdS nanowires, (3) over nanolayer-modified 1D $CdS@TiO_2$ core-shell heterostructure and (4) no catalyst.

The photodegradation of MB over nanolayer-modified 1D CdS@TiO_2 core-shell heterostructure, as well as neat CdS nanowires were investigated under the same conditions, and the degradation of MB aqueous solution without any photocatalyst was also tested for comparison. As shown in Fig. 6(b), about 63% of the MB was degraded using nanoparticles-modified 1D CdS@TiO_2 heterostructure (curve 1) as catalyst, and the degradation efficiencies were 30%, 28% and 25% under the condition of neat CdS nanowires (curve 2), nanolayer-modified 1D CdS@TiO_2 core-shell heterostructure (curve 3) as catalysts, and without any catalyst (curve 4). About 40% of MB was degraded over TiO_2 photocatalyst after 3 h visible-light irradiation as reported in the article [32]. Clearly, nanoparticles-modified 1D CdS@TiO_2 core-shell heterostructure exhibited greater photocatalytic activity than that of neat CdS nanowires and nanolayer-modified 1D CdS@TiO_2 heterostructure. Based on those results, we propose and discuss a possible mechanism in the following section.

Degradation Mechanism

The photocatalytic degradation can be attributed to the chemical reactions of active groups with contaminant molecules located on photocatalysts' surface. The mechanism mainly involves charge carriers' generation, charge carriers' transfer, and chemical reaction processes. Once the semiconductor is excited by photons, charge carriers, including electron (e^-) and positive hole (h^+), are generated. The e^- and h^+ may move to the surface and react with the adsorbents in the desired process, producing active groups (such as O_2^-, OH·), or undergoing the undesired recombination [36]. A rate increase in the former process or a rate decrease in the latter process will lead to a higher photocatalytic efficiency. Holding high oxidation capacity, the active group OH· and h^+ would decompose MB molecules. As well known, photogenerated charge carriers are produced in CdS phase only when CdS@TiO_2 heterostructure is irradiated by visible light. To react with the adsorbents, the charge carriers should pass the TiO_2 shell and migrate to the surface. The greater activity of nanoparticles-modified 1D CdS@TiO_2 core-shell heterostructure ascribed to the special electronic states on the interface [37], which allows for a semiconductor-semiconductor junction formation. With more negative conduction band potential and less positive valence band potential of CdS nanocrystal, photogenerated electrons prefer to transfer from CdS to TiO_2 phase while the holes remain on the CdS. This shift favors the separation of photogenerated charge carriers [38, 39] and the enhancement of CdS@TiO_2 heterostructures' photocatalytic ativity further. The mechanism diagram is shown in Fig. 7. For the nanolayer-modified 1D CdS@TiO_2 heterostructure, the thick TiO_2 shell hinders the photo absorption of CdS phase or the shift of photogenerated charge carriers, which results in a reduction in active groups and weakens photocatalytic activity finally.

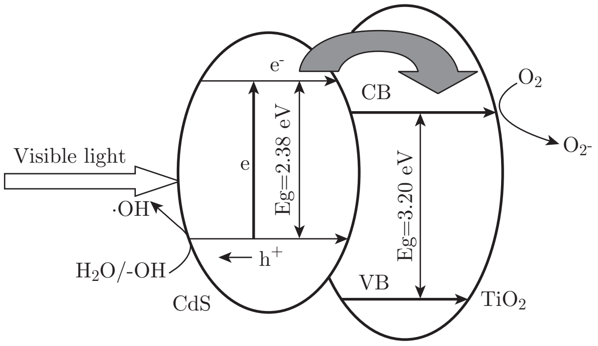


Fig. 7 Diagram of photogenerated charge carriers transmission on nanoparticles-modified 1D CdS@TiO_2 core-shell heterostructure.

Conclusions

In summary, nanoparticles and nanolayer-modified 1D CdS@TiO_2 core-shell heterostructures were prepared successfully via the hydrolysis of TBT on preformed CdS nanowires. By controlling the dropping rate and volume of ethanol-water solution, the anchored TiO_2 shell was composed of nanoparticles with a diameter of ca. 3 nm or a nanolayer of ca. 30 nm thick respectively. The optical property and photocatalytic activity of 1D CdS@TiO_2 core-shell heterostructures were separately investigated. Compared with neat CdS nanowires, the nanoparticles-modified 1D CdS@TiO_2 core-shell heterostructure exhibit enhanced photocatalytic activity, which can be attributed to the promoted separation of charge carriers. However, the coated TiO_2 nanolayer lowers the photocatalytic activity of neat CdS nanowires.

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References

[1] A. Fujishima and K. Honda, Nature 238, 37 (1972). http://dx.doi.org/10.1038/238037a0

[2] W. Y. Choi, A. Termin and M. R. Hoffmann, J. Phys. Chem. 84, 13669 (1994). http://dx.doi.org/10.1021/j100102a038

[3] S. U. M. Khan, M. Al-Shahry and W. B. Ingler Jr, Science 297, 2243 (2002). http://dx.doi.org/10.1126/science.1075035

[4] S. Sakthivel, M. Janczarek and H. Kisch, J. Phys. Chem. B 108, 19384 (2004). http://dx.doi.org/10.1021/jp046857q

[5] X. Du, J. H. He and Y. Q. Zhao, J. Phys. Chem. C 113, 14151 (2009). http://dx.doi.org/10.1021/jp9056175

[6] Y. Matsumoto, M. Murakami, T. Shono, T. Hasegawa and T. Fukumura, Science 291, 854 (2001). http://dx.doi.org/10.1126/science.1056186

[7] H. W. Gu, R. K. Zheng, X. X. Zhang and B. Xu, J. Am. Chem. Soc. 126, 5664 (2004). http://dx.doi.org/10.1021/ja0496423

[8] K. W. Kwon and M. Shim, J. Am. Chem. Soc. 127, 10269 (2005). http://dx.doi.org/10.1021/ja051713q

[9] G. Z. Shen, D. Chen and C. J. Lee, J. Phys. Chem. B 110, 15689 (2006). http://dx.doi.org/10.1021/jp0630119

[10] X. Zong, H. J. Yan, G. P. Wu, G. J. Ma, F. Y. Wen, L. Wang and C. Li, J. Am. Chem. Soc. 130, 7176 (2008). http://dx.doi.org/10.1021/ja8007825

[11] J. Y. Kim and F. E. Osterloh, J. Am. Chem. Soc. 127, 10152 (2005). http://dx.doi.org/10.1021/ja052735f

[12] A. Zaban, O. I. Mićić B. A. Gregg and A. J. Nozik, Langmuir 14, 3153 (1998). http://dx.doi.org/10.1021/la9713863

[13] Y. H. Zheng, L. R. Zheng, Y. Y. Zhan, X. Y. Lin, Q. Zheng and K. M. Wei, Inorg. Chem. 46, 6980 (2007). http://dx.doi.org/10.1021/ic700688f

[14] G. K. Mor, K. Shankar, M. Paulose, O. K. Varghese and C. A. Grimes, Nano. Lett. 6, 215 (2006). http://dx.doi.org/10.1021/nl052099j

[15] G. J. Meyer, Inorg. Chem. 44, 6852 (2005). http://dx.doi.org/10.1021/ic0505908

[16] Z. A. Peng and X. G. Peng, J. Am. Chem. Soc. 123, 183 (2001). http://dx.doi.org/10.1021/ja003633m

[17] L. Wang, L. Y. Wang, C. Q. Zhu, X. W. Wei and X. W. Kan, Anal. Chim. Acta. 468, 35 (2002). http://dx.doi.org/10.1016/S0003-2670(02)00632-3

[18] Y. N. Xia, P. D. Yang, Y. G. Sun, Y. Y. Wu, B. Mayers, B. Gates, Y. D. Yin, F. Kim and H. Q. Yan, Adv. Mater. 15, 353 (2003). http://dx.doi.org/10.1002/adma.200390087

[19] M. Chen, Y. Xie, J. Lu, Y. Xiong, S. Y. Zhang, Y. T. Qian and X. M. Liu, J. Mater. Chem. 12, 748 (2002). http://dx.doi.org/10.1039/b105652m

[20] C. J. Barrelet, Y. Wu, D. C. Bell and C. M. Lieber, J. Am. Chem. Soc. 125, 11498 (2003). http://dx.doi.org/10.1021/ja036990g

[21] C. H. Ye, G. Meng, Y. H. Wang, Z. Jiang and L. D. Zhang, J. Phys. Chem. B 106, 10338 (2002). http://dx.doi.org/10.1021/jp0255785

[22] H. Yin, Y. Wada, T. Kitamura, T. Sakata, H. Mori and S. Yanagida, Chem. Lett. 30, 334 (2001). http://dx.doi.org/10.1246/cl.2001.334

[23] M. G. Kang, H. E. Han and K. J. Kim, J. Photochem. Photobiol. A: Chem. 125, 119 (1999). http://dx.doi.org/10.1016/S1010-6030(99)00092-1

[24] X. F. Gao, W. T. Sun, Z. D. Hu, G. Ai, Y. L. Zhang, S. Feng, F. Li and L. M. Peng, J. Phys. Chem. C 113, 20481 (2009). http://dx.doi.org/10.1021/jp904320d

[25] C. L. Wang, L. Sun, K. P. Xie and C. J. Lin, Sci. China. Ser. B 12, 2148 (2009). http://dx.doi.org/10.1007/s11426-009-0157-1

[26] J. H. Zhu, D. Yang, J. Q. Geng, D. M. Chen and Z. Y. Jiang, J. Nanopart. Res. 10, 729 (2008). http://dx.doi.org/10.1007/s11051-007-9301-z

[27] J. C. Lee, T. G. Kim, W. Lee, S. H. Han and Y. M. Sung, Cryst. Growth Des. 10, 4519 (2009). http://dx.doi.org/10.1021/cg9005373

[28] J. Cao, J. Z. Sun, H. Y. Li, J. Hong and M. Wang, J. Mater. Chem. 14, 1203 (2004). http://dx.doi.org/10.1039/b313541a

[29] J. C. Yu, L. Wu, J. Lin, P. S. Li and Q. Li, Chem. Commun. 13, 1552 (2003). http://dx.doi.org/10.1039/b302418k

[30] H. Fujii, K. Inata, M. Ohtaki, K. Eguchi and H. Arai, J. Mater. Sci. 36, 527 (2001). http://dx.doi.org/10.1023/A:1004857419242

[31] G. S. Li, D. Q. Zhang and J. C. Yu, Environ. Sci. Technol. 43, 7079 (2009). http://dx.doi.org/10.1021/es9011993

[32] L. Wang, H. W. Wei, Y. J. Fan, X. Z. Liu and J. H. Zhan, Nanoscale Res. Lett. 4, 558 (2009). http://dx.doi.org/10.1007/s11671-009-9280-3

[33] J. H. Zhan, X. G. Yang, D. W. Wang, S. D. Li, Y. Xie, Y. N. Xia and Y. T. Qian, Adv. Mater. 12, 1348 (2000). http://dx.doi.org/10.1002/1521-4095(200009)12:18<1348::AID-ADMA1348>3.0.CO;2-X

[34] L. M. Torres-Martínez, A. Cruz-López, I. Juárez-Ramírez and M.E. Meza-de la Rosa, J. Hazard. Mater. 165, 774 (2009). http://dx.doi.org/10.1016/j.jhazmat.2008.10.060

[35] A. Franco, M. C. Neves, M. M. L. Ribeiro Carrott, M. H. Mendonça, M. I. Pereira and O. C. Monteiro, J. Hazard. Mater. 161, 545 (2009). http://dx.doi.org/10.1016/j.jhazmat.2008.03.133

[36] K. Woan, G. Pyrgiotakis and W. Sigmund, Adv. Mater. 21, 1 (2009). http://dx.doi.org/10.1002/adma.200802738

[37] D. C. Hurum and K. A. Gray, J. Phys. Chem. B 109, 977 (2005). http://dx.doi.org/10.1021/jp045395d

[38] X. G. Peng, M. C. Schlamp, A. V. Kadavanich and A. P. Alivisatos, J. Am. Chem. Soc. 119, 7019 (1997). http://dx.doi.org/10.1021/ja970754m

[39] P. A. Sant and P. V. Kamat, Phys. Chem. Chem. Phys. 4, 198 (2002). http://dx.doi.org/10.1039/b107544f