Enhanced photocatalytic activity in composites of TiO$_2$ nanotubes and CdS nanoparticles

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A new composite consisting of TiO$_2$ nanotubes and CdS nanoparticles, where CdS particles bind covalently to the titania surface through a bifunctional organic linker, was successfully fabricated; this titania nanotube-based composite shows enhanced photocatalytic activity under visible-light irradiation.

Titania (TiO$_2$) is an important semiconductor with many technological applications in a wide variety of fields such as photocatalysts, optical coatings, gas sensors, etc.[1] Particularly, recent research has been focused on the fabrication of titanias on a nanometer scale due to their unique properties and superior performance over bulk materials.[2] A critical drawback of titania, however, is that it has a large band gap (3.2 eV), which is too large to allow efficient absorption of most sunlight. Accordingly, there have been significant efforts to modify the band gap of titania by doping with other elements, sensitizing with dyes, and coating the surface with Au or Pd, so that it can be made responsive to the solar spectrum.[3] It would thus be desirable to combine titania with a narrow band gap semiconductor that can efficiently absorb sunlight.
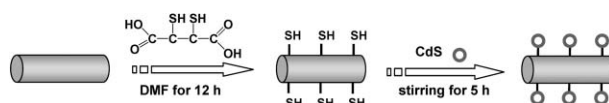
In this communication, we describe a new composite composed of CdS naoparticles (NPs) and TiO$_2$ nanotubes in which a bi-functional organic molecule was employed to strongly bind cadmium sulfide to the titania surface. For TiO$_2$ nanotubes, it has been shown that their catalytic activity is superior compared to the corresponding titania NPs.[4] CdS was selected as an active absorbing material because it has a narrow band gap (2.4 eV) and its conduction band level is slightly higher than that of TiO$_2$.[5] The resulting composite based on TiO$_2$ nanotubes allowed us to carry out a systematic study of the reduction of methyl viologen (MV) aimed at understanding the catalytic activity of the hybrid materials under visible light. An important advantage of this nanotube-based composite is that CdS NPs are evenly-dispersed on the oxide surface with strong covalent bonding, which can improve the efficiency of electron transfer from sensitized CdS NPs to a host titania matrix. As anticipated, our TiO$_2$–CdS composite exhibits enhanced photocatalytic activity under visible-light irradiation compared to the TiO$_2$–CdS composite based on titania NPs.

For the fabrication of TiO$_2$ nanotubes, a mixed solution of titanium ethoxide and ethanol was allowed to permeate into a porous anodic aluminium oxide membrane (diameter 200 nm, length 60 μm) under vacuum filtration. The filled membrane was dried under a N$_2$ atmosphere for 1 h, followed by sintering at 500 °C in air. The titania nanotubes were obtained after etching the alumina template with a 2 M NaOH solution. The X-ray powder diffraction (XRD) of the tubes showed exclusively the anatase phase. No rutile phase was identified in the XRD pattern. The synthesis of CdS NPs with an average diameter of 5 nm was achieved using a slight modification of a published procedure.[6]

As illustrated in Fig. 1, the covalent attachment of CdS NPs to the surface of TiO$_2$ nanotubes was achieved by using a linker molecule, 2,3-dimercapto-succinic acid (DMSA), with bi-functional groups at each terminus. Ultrasonicating a mixture of the nanotubes and DMSA in an acidified DMF solution yielded thiolated-TiO$_2$ nanotubes, in which strong Ti–O–C bonds are formed as a result of the reaction of the hydroxy groups of the titania surface with the carboxylic acid groups of DMSA. In a subsequent reaction, intact thiol groups of DMSA on the titania surface reacted with tributylphosphine-capped CdS NPs in THF, leading to the formation of TiO$_2$–CdS nanocomposites strongly bonded through DMSA. The TiO$_2$–CdS composites were washed several times with methanol and finally sonicated for 10 min to prevent aggregation of the CdS-attached tubes.

The hybrid structure of the resulting composites of TiO$_2$ nanotubes–CdS NPs was characterized by transmission electron microscopy (TEM) and UV-visible spectroscopy. Fig. 2 displays TEM images of the pristine and CdS-attached TiO$_2$ nanotubes, distinctively showing that CdS NPs are uniformly coated on the titania surfaces. TEM in various regions of the sample reveals that nearly monodisperse CdS particles with an average diameter of 5 nm are composed of a pure cubic phase without any indication of hexagonal CdS impurity, which was also confirmed by their XRD data. The inset is a representative high resolution TEM image of CdS in which the lattice fringes match well with the cubic symmetry.

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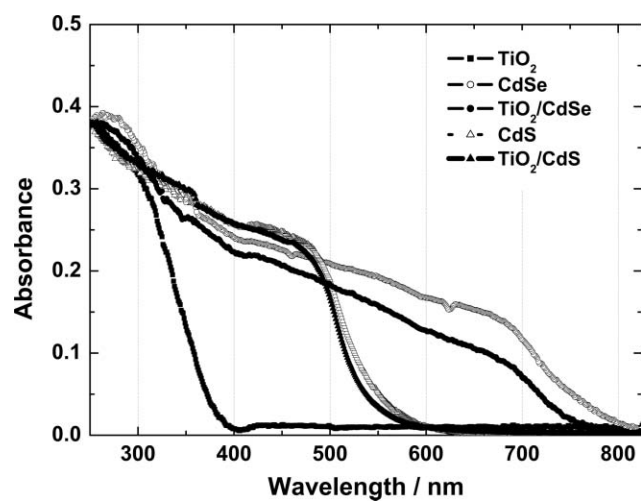[e]Department of Chemistry, Inha University, Incheon, 402-751, Korea

Fig. 1 Schematic representation of binding of CdS NPs to the surface of a TiO$_2$ nanotube via 2,3-dimercapto-succinic acid.
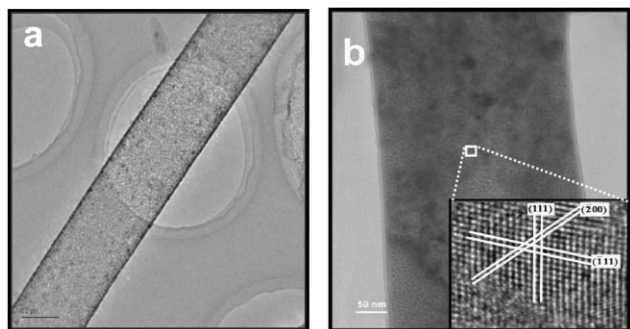
Fig. 2 TEM micrographs of typical pristine TiO$_2$ and CdS-anchored TiO$_2$ nanotubes. The inset shows a high resolution image of CdS in which the lattice fringes coincide well with the cubic symmetry of CdS.

The UV-visible diffuse reflectance spectra of TiO$_2$–CdS composites, TiO$_2$ nanotubes, and CdS NPs are shown in Fig. 3. For comparison, CdSe analogues fabricated in a similar way were also included. Unlike the TiO$_2$ spectra, the nanocomposite samples show absorption peaks in the visible region, which are attributed to the CdQ (Q = S, Se) NPs attached to the TiO$_2$ nanotubes. A notable feature is that absorption peaks of the composites are blue-shifted compared to those of the corresponding CdQ NPs. The observed shifts might be ascribed to the attachment of CdQ onto the titania surface *via* the linker molecules. A similar blue shift was observed in a composite sample of CdS–SiO$_2$, in which the shift originates from an electronic interaction between CdS and SiO$_2$ induced by formation of a Si–O–Cd covalent linkage.[7] This suggests that an electronic interaction between TiO$_2$ nanotubes and CdQ NPs can also be operative.

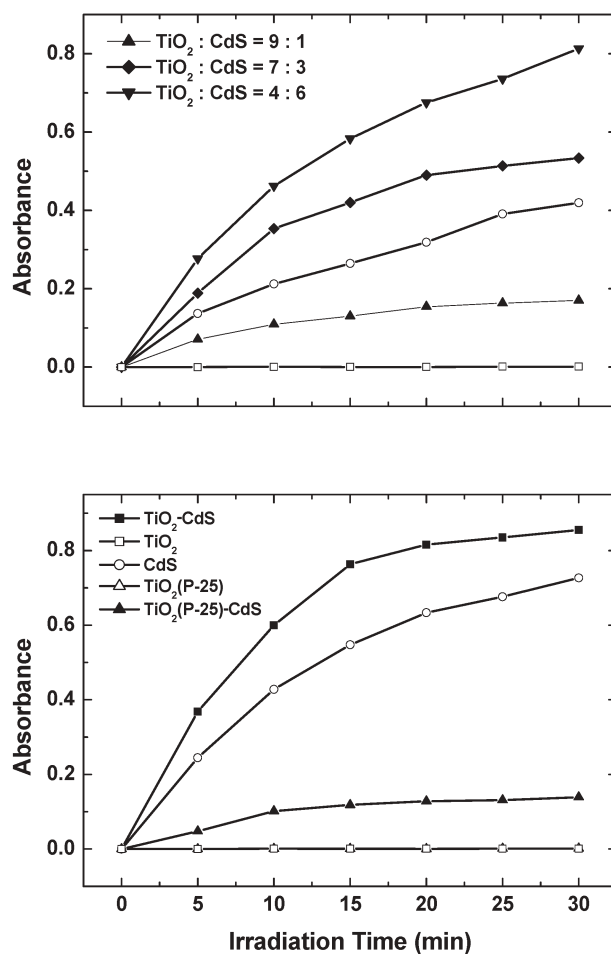Photocatalytic activities of TiO$_2$–CdS composites as well as CdS NPs and TiO$_2$ nanotubes were examined by measuring the reduction rate of methyl viologen (MV) dichloride included in the samples. For various photoredox systems, MV^{2+} is widely used as an electron acceptor, which can be readily reduced to MV$^+$ by chemical and photochemical methods.[8] In our experiments 2 mg of the sample was dispersed in 10 mL of deionized water containing 1 mM of MV^{2+}, which was then irradiated using a 450 W Xe-arc lamp (Oriel Corporation) with a 420 nm cut-off and water filters to eliminate undesirable UV and IR radiation, respectively. The nominal concentration ratio of TiO$_2$: CdS was altered between 1 : 9 and 9 : 1 to find the optimal composition showing the highest catalytic activity. For comparison, catalytic activities of TiO$_2$ nanotubes and CdS NPs were also investigated. Upon reduction the sample containing MV^{2+} immediately turns light blue in color, producing a distinctive absorption peak at 602 nm in the UV-visible spectra due to the reduction of MV^{2+}. Fig. 4(a) shows the intensity changes of the peak at 602 nm for TiO$_2$–CdS composites as a function of irradiation time. The reduction rate of MV^{2+} under visible light increases in the order TiO$_2$ < TiO$_2$–CdS (9 : 1) < CdS < TiO$_2$–CdS (7 : 3) < TiO$_2$–CdS (4 : 6), indicating that absorption of visible light by the TiO$_2$–CdS composite yields an efficient transfer of the excited electrons from CdS NPs to the conduction band of TiO$_2$ nanotubes through DMSA without back-electron transfer. As can be seen in the top panel of Fig. 4, the TiO$_2$–CdS composite having a 4 : 6 ratio exhibits the highest activity, which was used for the subsequent experiments.

In order to estimate the catalytic property of the TiO$_2$–CdS composite based on the titania nanotubes, we have investigated a composite of TiO$_2$(P25)–CdS where CdS NPs were similarly

Fig. 3 UV-visible diffuse reflectance spectra of TiO$_2$ nanotubes, CdS NPs, CdSe NPs, TiO$_2$ nanotubes–CdS NPs, and TiO$_2$ nanotubes–CdSe NPs.

Fig. 4 Changes of absorption peak at 602 nm in the UV-visible spectra for various composites of TiO$_2$ nanotubes–CdS NPs as a function of irradiation time (top). The bottom shows similar experimental data for a composite of TiO$_2$(P25)–CdS NPs as well as TiO$_2$(P25) and CdS NPs.

anchored on TiO_2 NPs (Degussa P25) frequently used as a reference material. As given in the bottom panel of Fig. 4, our TiO_2–CdS composite clearly shows better catalytic activity than the TiO_2(P25)–CdS composite. It has been known that the anatase phase of TiO_2 shows a higher photocatalytic activity than the rutile one largely because the anatase phase has a lower dielectric constant.[9] Accordingly, the most likely cause of the higher activity in the nanotube composite is that it consists exclusively of the anatase phase. On the other hand, the TiO_2(P25) particles show a mixture of anatase and rutile forms. Another plausible cause is that the titania tubes have more room to anchor sensitizing CdS NPs due to the larger internal and external spaces than the particulate sample. In fact, BET measurements reveal that the surface area of the nanotubes ($62 \ m^2 \ g^{-1}$) is larger than that of Degussa P25 ($50 \ m^2 \ g^{-1}$).

In summary, we have successfully fabricated a new CdS–TiO_2 composite in which CdS NPs are evenly dispersed and coordinated to the titania surface *via* bifunctional linker molecules. The photocatalytic studies suggest that the TiO_2–CdS composite based on the titania nanotubes has a significantly enhanced effect on the efficiency of photoreduction of MV ions under visible irradiation. Our preliminary studies also show that the nanotube-based composite has an enhanced efficiency of the water splitting reaction under visible light, which is about 3 times higher than the TiO_2(P25)–CdS composite. Hence, this nanotube-based composite might provide a new model for efficient light absorption and charge separation structures that can induce useful photochemical reactions.

Notes and references

1 (*a*) T. Asahi, A. Furube and H. Masuhara, *Chem. Phys. Lett.*, 1997, **275**, 234; (*b*) X. Du, Y. Wang, Y. Mu, L. Gui, P. Wang and Y. Tang, *Chem. Mater.*, 2002, **14**, 3953.
2 B. Tan and Y. Wu, *J. Phys. Chem. B*, 2006, **110**, 15932.
3 (*a*) M. Mrowetz, W. Balcerski, A. J. Colussi and M. R. Hoffmann, *J. Phys. Chem. B*, 2004, **108**, 17269; (*b*) J. C. Yu, J. Yu, W. Ho, Z. Jiang and L. Zhang, *Chem. Mater.*, 2002, **14**, 3808; (*c*) E. Bae and W. Choi, *Environ. Sci. Technol.*, 2003, **37**, 147; (*d*) J. C. Yu, L. Wu, J. Lin, P. Li and Q. Li, *Chem. Commun.*, 2003, 1552; (*e*) H. G. Kim, D. W. Hwang and J. S. Lee, *J. Am. Chem. Soc.*, 2004, **126**, 8912; (*f*) S. U. M. Khan, M. Al-Shahry and W. B. Ingler, Jr., *Science*, 2002, **297**, 2243.
4 (*a*) G. K. Mor, K. Shankar, M. Paulose, O. K. Varghese and C. A. Grimes, *Nano Lett.*, 2005, **5**, 191; (*b*) L. Qian, Z.-S. Jin, S.-Y. Yang, Z.-L. Du and X.-R. Xu, *Chem. Mater.*, 2005, **17**, 5334.
5 (*a*) N. Serpone, P. Maruthamuthu, P. Pichat, E. Pelizzetti and H. Hidaka, *J. Photochem. Photobiol., A*, 1995, **85**, 247; (*b*) D. Lawless, S. Kapoor and D. Meisel, *J. Phys. Chem.*, 1995, **95**, 10329.
6 (*a*) W. William Yu, Lianhua Qu, Wenzhuo Guo and Xiaogang Peng, *Chem. Mater.*, 2003, **15**, 2854; (*b*) C. B. Murray, D. J. Norris and M. G. Bawendi, *J. Am. Chem. Soc.*, 1993, **115**, 8706.
7 (*a*) H. Weib, A. Fernandez and H. Kisch, *Angew. Chem., Int. Ed.*, 2001, **40**, 3825; (*b*) Y. Bessekhouad, D. Robert and J. V. Weber, *J. Photochem. Photobiol., A*, 2004, **163**, 569.
8 (*a*) D. Duonghong, J. Ramsden and M. Gratzel, *J. Am. Chem. Soc.*, 1982, **104**, 2977; (*b*) K. T. Ranjit and L. Kevan, *J. Phys. Chem. B*, 2002, **106**, 1104.
9 J. Y. Kim, D.-W. Kim, H. S. Jung and K. S. Hong, *Jpn. J. Appl. Phys.*, 2005, **44**, 6148.