

# Gold/Titania Core/Sheath Nanowires Prepared by Layer-by-Layer Assembly

Yu-Guo Guo,<sup>†</sup> Li-Jun Wan,\* and Chun-Li Bai\*

Center for Molecular Science, Institute of Chemistry, Chinese Academy of Sciences (CAS),  
Beijing 100080, China

Received: January 23, 2003; In Final Form: March 23, 2003

The strategy of layer-by-layer (LbL) self-assembly and calcining has been employed to prepare Au/TiO<sub>2</sub> core/sheath nanowires. Ordered arrays were achieved by using an LbL assembly of cationic polyelectrolytes and inorganic precursors on template-grown Au nanowires. The wires were investigated with SEM, TEM, and X-ray energy dispersion analysis. The prepared composite nanowires were found to possess anatase porous sheaths of TiO<sub>2</sub> with face-center-cubic polycrystallite Au cores. The assembly strategy will be useful in fabricating core/sheath nanowires. The first reported core/porous-sheath nanowire is expected to be an ideal nanostructure for chemical sensors and photocatalysis due to its composite and highly porous structure.

## Introduction

There is increasing interest in the fabrication of composite nanomaterials such as nanoparticles and nanowires consisting of organic or inorganic cores coated with sheaths of different chemical components.<sup>1–8</sup> Such nanomaterials have potential applications in capsule agents for drug delivery, catalysis, coatings, composite materials, and protection for sensitive agents such as enzymes and proteins. Self-assembly is a powerful technique in the preparation of these nanomaterials. One method to prepare core/sheath particles is to use a colloid-templating strategy that involves a layer-by-layer (LbL) assembly of polyelectrolytes and inorganic nanoparticles on submicrometer- and micrometer-sized polystyrene (PS) latex particles.<sup>9</sup> The basis of the LbL technique is an electrostatic attraction between the charged species deposited.<sup>10</sup> Preparing alternative core/sheath composite materials with desired morphology and improved order is an important issue for their use in nanotechnologies. Recently, a number of methods, including laser ablation, carbothermal reduction, and several solution-based methods have been developed to generate various one-dimensional nanostructures with coaxial structures.<sup>11–18</sup> Furthermore, it has been demonstrated that rod-shaped nanoparticles can be used as a substrate for LbL assembly of smooth, conformal films of insulating organic polyelectrolytes.<sup>19</sup>

Here, we report a novel nanowire-templating technique for the preparation of ordered Au/TiO<sub>2</sub> core/sheath nanowire arrays using a LbL self-assembly and calcining strategy. The template-grown Au nanowire array was used as a positive template. A cationic polyelectrolyte and an inorganic precursor were assembled on Au nanowires by the LbL technique. Then, calcining was applied for the conversion of the inorganic precursor to titania. An advantage of the LbL nanowire-templating approach over other methods is the nanoscale control that can be exerted over the sheath thickness by varying the number of deposition cycles.

Titania is one of the most investigated oxide materials owing to its technological importance. It has been widely used for photocatalysis and environmental cleanup applications,

due to its strong oxidizing power, chemical inertness, and non-toxicity.<sup>20,21</sup> Many methods including template synthesis<sup>22</sup> and sonochemical synthesis<sup>23</sup> have been developed to fabricate one-dimensional-structured titania. A series of semiconductor-metal composite nanoparticles have been shown to facilitate charge rectification in the semiconductor nanostructures.<sup>24</sup> The deposition of a noble metal on semiconductor nanoparticles is beneficial for maximizing the efficiency of photocatalytic reactions.<sup>25–27</sup> In this paper, the reported Au/TiO<sub>2</sub> core/sheath nanowires may also exhibit properties that are substantially different from those of either the TiO<sub>2</sub> sheath or the Au core separately, thus making them attractive from both a scientific and a technological viewpoint.

## Experimental Section

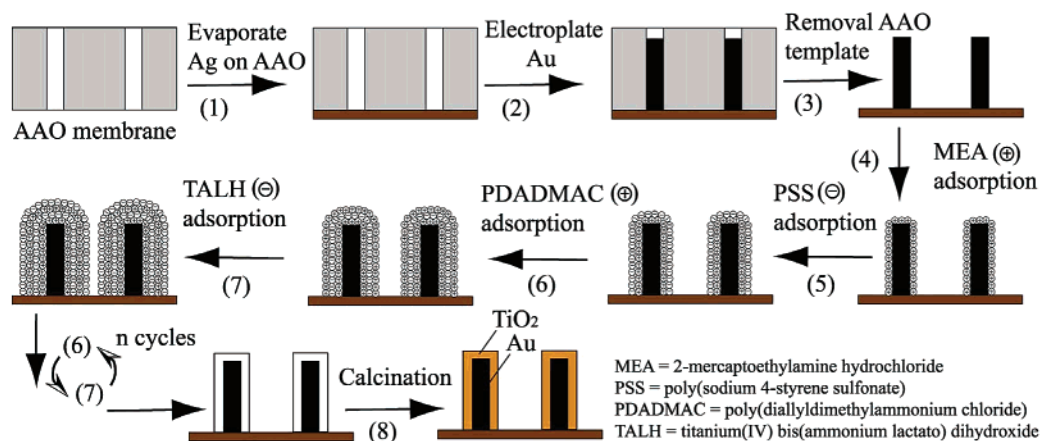
Fabrication of Au/TiO<sub>2</sub> core/sheath nanowires was carried out by the process shown schematically in Figure 1. Commercially available anodic aluminum oxide (AAO) membranes (200 nm pore size,  $8.9 \times 10^8$  pores cm<sup>-2</sup>, 60  $\mu$ m thickness) were used as negative templates for the fabrication of the Au nanowires by a slight modification of the method developed by Zhang et al.<sup>28</sup> Prior to electroplating Au, a layer of Ag (ca. 200 nm thick Ag) was deposited as an electrode onto one side of the AAO templates by using a vacuum evaporation apparatus. The AAO template with Ag substrate was used as the working electrode in a glass cell with a platinum counter electrode and a saturated calomel electrode (SCE) reference electrode. Au nanowires were electrodeposited by potentiostatic control at -0.9 V (vs SCE) from the following electrolytic bath: 20 g L<sup>-1</sup> HAuCl<sub>4</sub>·4H<sub>2</sub>O, 120 g L<sup>-1</sup> Na<sub>2</sub>SO<sub>3</sub>, 50 g L<sup>-1</sup> EDTA, and 80 g L<sup>-1</sup> (NH<sub>4</sub>)<sub>3</sub>C<sub>6</sub>H<sub>5</sub>O<sub>7</sub> (tri ammonium citrate). The pH of the electrolytic solution was controlled between 6.5 and 7.5. After deposition, the Au-filled membrane was then glued to a glass slide and the AAO template was dissolved with 2 M NaOH at 25 °C for 2 h.

To actualize LbL assembly of the polyelectrolyte, the surfaces of the Au nanowires must be charged. This was achieved by a 30 h adsorption of 2-mercaptoethylamine hydrochloride (MEA) (Alfa Aesar) onto the surfaces of the Au nanowires from a 2% ethanolic solution to render them positive.

The polyelectrolytes, poly(sodium 4-styrenesulfonate) (PSS) ( $M_w$  ca. 70 000) and poly(diallyldimethylammonium chloride)

\* To whom correspondence should be addressed. Tel. & Fax: +86-10-62558934. E-mail: wanlijun@iccas.ac.cn.

<sup>†</sup> Also in Graduate School of CAS, Beijing, China.



**Figure 1.** Schematic illustration of the procedure used to fabricate an Au/TiO<sub>2</sub> core/sheath nanowire array.

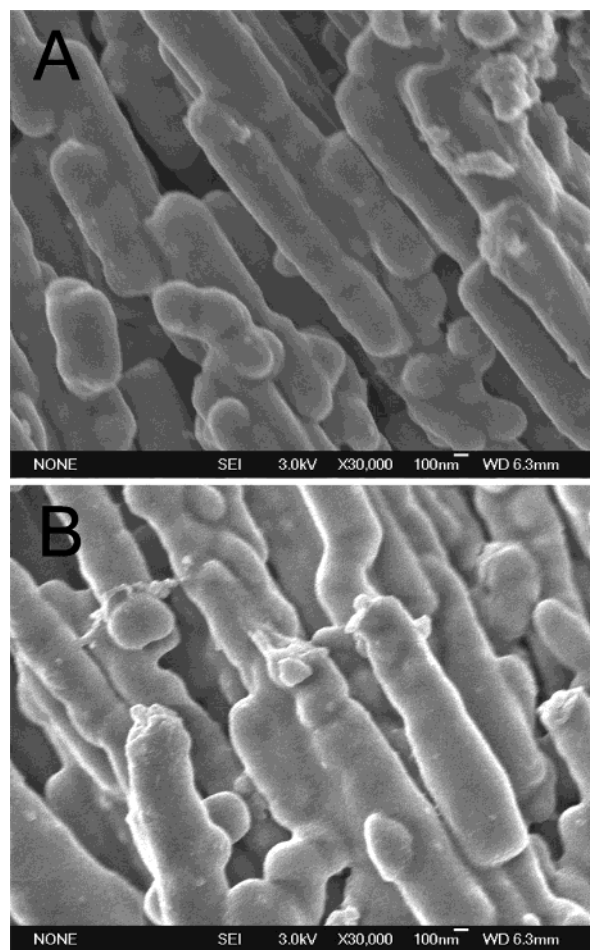
(PDADMAC) (20 wt % in water,  $M_w$  ca. 100 000–200 000) were purchased from Aldrich and used without further purification. The titanium precursor, titanium(IV) bis(ammonium lactate) dihydroxide (TALH) (chemical formula  $[\text{CH}_3\text{CH}(\text{O}-)\text{CO}_2\text{NH}_4]_2\text{Ti}(\text{OH})_2$ ), 50 wt % in aqueous solution, was purchased from Aldrich and diluted to 5 wt % with water before use. Ultrapure Millipore water (Millipore-Q) was used in all experiments.

Prior to deposition of TALH/PDADMAC multilayers, a precursor polyelectrolyte multilayer film (PSS/PDADMAC) was assembled onto the positively charged Au/MEA nanowires. The multilayers were achieved by successively immersing the nanowire array in the polymer and TALH solutions for 20 min. The solutions were as follows: PSS (1 mg mL<sup>-1</sup> containing 0.5 M NaCl), PDADMAC (1 mg mL<sup>-1</sup> containing 0.5 M NaCl), TALH (5 wt %). Each adsorption step was followed by removal of excess reagents by soaking the membrane in water for 10 min each of three times. After several cycles of the assemblies of TALH and PDADMAC, an Au/MEA/PSS/PDADMAC/(TALH/PDADMAC)<sub>*n*</sub> nanowire array was obtained. Au/TiO<sub>2</sub> core/sheath nanowire array was produced by drying the as-prepared TALH/PDADMAC-coated nanowire array at room temperature and then calcining (heating rate 10 K min<sup>-1</sup>) at 450 °C under N<sub>2</sub> for 4 h and then for a further 8 h under O<sub>2</sub>.

For SEM and TEM observations, the nanowire arrays were ultrasonically dispersed in ethanol and then dropped on mica and copper-grid surfaces, respectively. To increase conductance, the surface of mica was deposited on a layer of Au thin film prior to dropping. SEM measurements were performed on a JEOL JSM-6700F field emission scanning electron microscope. TEM and electron diffraction were carried out with a JEM-200CX microscope operated at 160 kV and equipped with energy-dispersive X-ray analyzer (EDAX 9100/6, Philips).

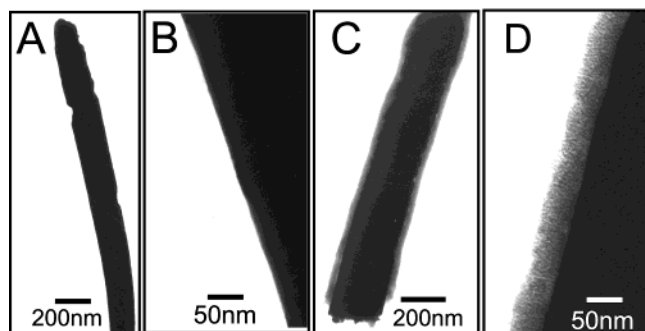
## Results and Discussion

Parts A and B of Figure 2 show the SEM images of Au and Au/MEA/PSS/PDADMAC/(TALH/PDADMAC)<sub>9</sub> nanowires, respectively. The varied length of the nanowires and the presence of other shaped nanoparticles were the results of ultrasonic dispersion treatment during the preparation of SEM samples. The nanowires in Figure 2A appear to have smooth and clear boundaries, whereas those in Figure 2B have slightly rough boundaries. It indicates that the polymer layers have successfully coated the Au nanowires. Further evidence can be found from their TEM images, as shown in Figure 3. Uncoated Au nanowires appear smooth both at low (Figure 3A) and high (Figure 3B) magnifications with average diameter 210 nm

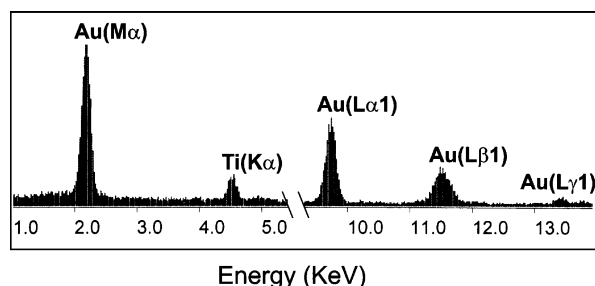


**Figure 2.** SEM images of Au nanowires (A) before and (B) after being coated with nine TALH/PDADMAC layer pairs. The coated were first primed with a precursor trilayer of MEA/PSS/PDADMAC.

corresponding to the pore diameter of AAO template used. A uniform polymer layer with a thickness of ca. 40 nm can be clearly seen in the TEM images of Au nanowires modified by nine alternate adsorptions of TALH and PDADMAC (Figure 3C,D). It should be noted that the channels of the AAO templates are not perfect cylinder-shaped pores. Consequently, the so-prepared Au nanowires had slightly varying diameters, which resulted in the varying diameters of the multilayer-coated Au nanowires, as seen in Figure 2B. However, the thicknesses



**Figure 3.** TEM images of Au nanowires before and after being coated with TALH and polyelectrolytes: (A) low-magnification and (B) high-magnification TEM images of an uncoated Au nanowire; (C) low-magnification and (D) high-magnification TEM images of an Au nanowire coated with nine TALH/PDADMAC layer pairs.



**Figure 4.** EDAX profile of an Au nanowire coated with nine TALH/PDADMAC layer pairs shown in Figure 3C.

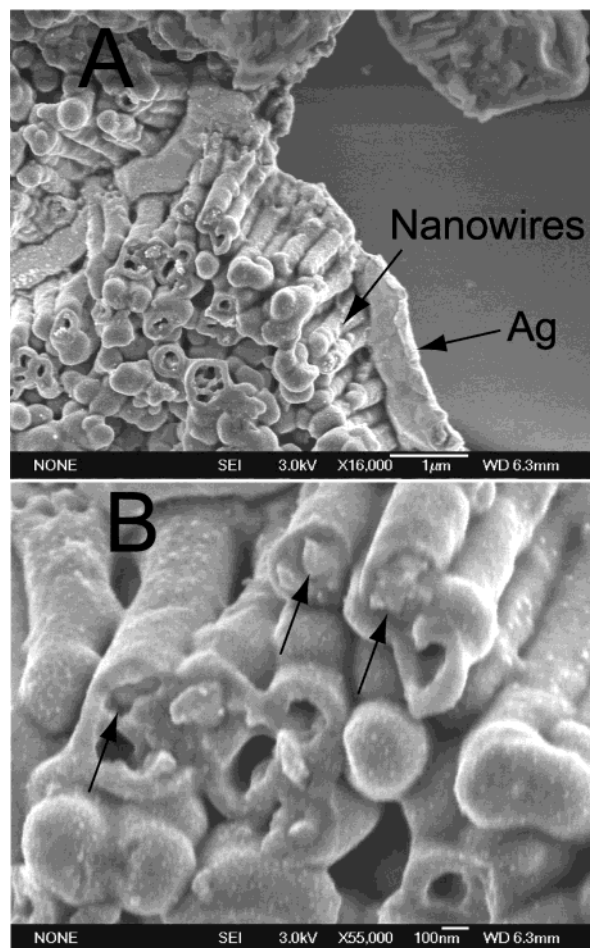
of the multilayers were uniform along the entire length of each nanowire confirmed by TEM observation in our experiment.

It was reported that MEA will bind to the surface of Au nanowires and form self-assembled monolayer with a thickness of ca. 0.5 nm.<sup>19</sup> From previous studies on the deposition of oppositely charged polyelectrolytes on colloid particles or planar substrates under similar conditions to those used in this study, the thickness of each PDADMAC layer and PSS was estimated to be approximately 2 and 1 nm, respectively.<sup>7,10,19</sup> Assuming such thicknesses for the polyelectrolyte layers, each deposition cycle of TALH causes a thickness increment of ca. 2 nm, implying that oligomers are deposited with each step. Therefore, the above data show that the thickness of the multilayer coatings can be tailored by the number of TALH/PDADMAC layers deposited. It should be noted that the precursor three-layer film of MEA/PSS/PDADMAC was an essential requirement to adsorb TALH onto the surface of Au nanowires. Attempts to deposit TALH directly onto uncoated Au nanowires were not successful. This is evident that the three-layer precursor film provides a uniformly charged and smooth polyelectrolyte surface that facilitates subsequent deposition of various species.<sup>7,9</sup>

As shown in Figure 4, energy-dispersive X-ray analysis (EDAX) of the coated Au nanowire shown in Figure 3C revealed the presence of Ti, also confirming the deposition of TALH.

The multilayer-coated nanowires were subsequently calcined to prepare Au/TiO<sub>2</sub> core/sheath nanowires. TALH is known to hydrolyze and condense at elevated temperatures to form nanoparticles.<sup>29</sup> Hence, the titanium precursor that was adsorbed within the multilayer film was expected to form a titania network comprising nanoparticles upon heating. The shape, structure, and wall thickness of the resulting composite nanowires were examined by SEM, TEM, and electron diffraction (ED).

Figure 5 shows SEM images of the Au/TiO<sub>2</sub> core/sheath

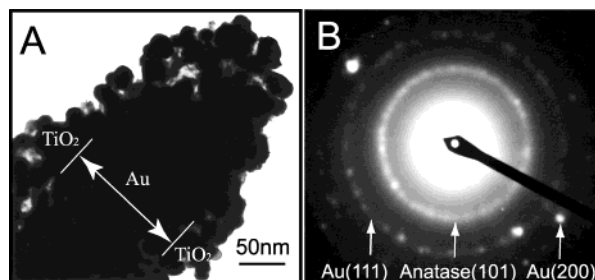


**Figure 5.** (A) Low-magnification and (B) high-magnification SEM images of an Au/TiO<sub>2</sub> core/sheath nanowire array prepared by calcination of composite nanowires consisting of an Au core coated with nine layer pairs of TALH and PDADMAC at 450 °C.

nanowires produced by heating Au nanowires coated with nine TALH/PDADMAC multilayers at 450 °C. An aligned nanowire array with a uniform length and diameter on an Ag film substrate can be clearly seen in Figure 5A. Although the nanowire surface becomes rougher after calcining, it appears to be completely covered by TiO<sub>2</sub> along the entire length of each nanowire, including its tip. This feature of the core/sheath structure can be found in the broken tips of nanowires in the high magnification SEM image (Figure 5B, indicated by arrows). Clearly, the nanowires become thicker than those of uncoated Au nanowires but slightly thinner than those of the corresponding Au/polymer nanowires. The former is because of the formation of the TiO<sub>2</sub> sheath and the latter is due to the shrinkage of polymer layer during heating, as observed in previous work using core-shell particles to produce hollow inorganic spheres.<sup>7,9</sup> The thickness of the sheath is about 36 nm. Given the thickness of 40 nm for the corresponding precursor polymer layer, the shrinkage rate was calculated to be 10%. As the SEM samples were prepared by dropping the suspension of Au/TiO<sub>2</sub> nanowire arrays dispersed in ethanol on mica surfaces and the SEM images were obtained from an oblique view, the real lengths of the nanowires were not easily measured from the images. However, the lengths of these core-sheath nanowires were mainly determined by the original gold nanowires and could be as long as 60 μm corresponding to the thickness of AAO template used.

TEM and ED were used to examine the structure of single composite nanowire. The TEM image in Figure 6A showed that





**Figure 6.** (A) TEM image of an Au/TiO<sub>2</sub> core/sheath nanowire prepared by calcination of composite nanowires consisting of an Au core coated with nine layer pairs of TALH and PDADMAC at 450 °C, and (B) corresponding ED pattern of the single nanowire.

the sheath of the composite nanowire was highly porous and composed of connected titania nanoparticles approximately 10–15 nm in diameter. The ED pattern of this core/sheath nanowire is shown in Figure 6B. The ED pattern confirms the anatase phase of the outer sheath of TiO<sub>2</sub> as well as the face-centered cubic (fcc) polycrystallites of the inner core of Au. This verifies the conversion of TALH to titania under the calcination conditions used.<sup>7</sup> EDAX of the composite nanowire also revealed the presence of Ti and Au. The first reported core/porous-sheath nanowire is expected to be an ideal nanostructure for chemical sensors and photocatalysis due to its composite and highly porous structure. Further investigation is in progress.

## Conclusions

To summarize, we have demonstrated a simple and effective stepwise route for preparing Au/TiO<sub>2</sub> core/sheath nanowires. With the LbL technique, the inorganic molecular precursor TALH has been sequentially adsorbed on the surfaces of the modified Au nanowires in alternation with PDADMAC at a density and distribution that is amenable to forming a TiO<sub>2</sub> sheath upon calcination. These core/sheath nanowires have well-defined diameters and lengths, largely determined by those of the AAO templates, and porous sheaths with thicknesses controlled by the number of layers deposited. This method opens a door to use a wide variety of nanowires available as the positive templates for the fabrication of core/sheath nanostructured materials for chemical sensors, photocatalysis, light energy conversion devices, and nanoscale electronic and optoelectronic devices. The properties of the novel core/porous-sheath structures of Au/TiO<sub>2</sub> and building advanced materials using these nanoscale blocks will be explored in future work.

**Acknowledgment.** Financial supports from National Natural Science Foundation of China (No. 20025308 and 20177025), National Key Project on Basic Research (Grant G2000077501), and the Chinese Academy of Sciences are gratefully acknowledged.

## References and Notes

- Giersig, M.; Ung, T.; Liz-Marzan, L. M.; Mulvaney, P. *Adv. Mater.* **1997**, *9*, 570.
- Walsh, D.; Mann, S. *Nature* **1995**, *377*, 320.
- Kawahashi, N.; Matijevic, E. *J. Colloid Interface Sci.* **1991**, *143*, 103.
- Antipov, A. A.; Sukhorukov, G. B.; Donath, E.; Möhwald, H. *J. Phys. Chem. B* **2001**, *105*, 2281.
- Gittins, D. I.; Caruso, F. *J. Phys. Chem. B* **2001**, *105*, 6846.
- Liz-marzan, L. M.; Giersig, M.; Mulvaney P. *J. Chem. Soc., Chem. Commun.* **1996**, 731.
- Caruso, F.; Shi, X. Y.; Caruso, R. A.; Susha, A. *Adv. Mater.* **2001**, *13*, 740.
- Philipse, A. P.; Bruggen, M. P. B.; Pathmanathan, C. *Langmuir* **1994**, *10*, 92.
- Caruso, F.; Caruso, R. A.; Möhwald, H. *Science* **1998**, *282*, 1111.
- Decher, G. *Science* **1997**, *277*, 1232.
- Morales, A. M.; Lieber, C. M. *Science* **1998**, *279*, 208.
- Shi, W. S.; Peng, H. Y.; Xu, L.; Wang, N.; Tang, Y. H. H.; Lee, S. T. *Adv. Mater.* **2000**, *12*, 1927.
- Yin, Y. D.; Lu, Y.; Sun, Y. G.; Xia, Y. N. *Nano Lett.* **2002**, *2*, 427.
- Wen, X. G.; Yang, S. H. *Nano Lett.* **2002**, *2*, 451.
- Zhang, L. D.; Meng, G. W.; Phillipp, F. *Mater. Sci. Eng.* **2000**, *A286*, 34.
- Jang, J.; Lim, B.; Lee, J.; Hycon, T. *Chem. Commun.* **2001**, 83.
- Xie, Y.; Qiao, Z.; Chen, M.; Liu, X.; Qian, Y. *Adv. Mater.* **1999**, *11*, 1512.
- Obare, S. O.; Jana, N. R.; Murphy, C. J. *Nano Lett.* **2001**, *1*, 601.
- Yu, J. S.; Kim, J. Y.; Lee, S.; Mbindyo, J. K. N.; Martin, B. R.; Mallouk, T. E. *Chem. Commun.* **2000**, 2445.
- Andersson, M.; Österlund, L.; Ljungström, S.; Palmqvist A. *J. Phys. Chem. B* **2002**, *106*, 10674.
- Imai, H.; Matsuda, M.; Shimizu, K.; Hirashima, H.; Negishi, N. *J. Mater. Chem.* **2000**, *10*, 2005.
- Jung, J. H.; Kobayashi, H.; Bommel, K. J. C.; Shinkai, S.; Shimizu, T. *Chem. Mater.* **2002**, *14*, 1445.
- Zhu, Y. C.; Li, H. L.; Koltypin, Y.; Hachon, Y. R.; Gedanken, A. *Chem. Commun.* **2001**, 2616.
- Subramanian, V.; Wolf, E.; Kamat, P. V. *J. Phys. Chem. B* **2001**, *105*, 11439.
- Tada, H.; Suzuki, F.; Ito, S.; Akita, T.; Tanaka, K.; Kawahara, T.; Kobayashi, H. *J. Phys. Chem. B* **2002**, *106*, 8714.
- Dawson, A.; Kamat, P. V. *J. Phys. Chem. B* **2001**, *105*, 960.
- Zwijnenburg, A.; Goossens, A.; Sloof, W. G.; Crajé, M. W. J.; Kraan, A. M.; Jongh, L. J.; Makkee, M.; Moulijn, J. A. *J. Phys. Chem. B* **2002**, *106*, 9853.
- Zhang, X. Y.; Zhang, L. D.; Lei, Y.; Zhao, L. X.; Mao, Y. Q. *J. Mater. Chem.* **2001**, *11*, 1732.
- Möckel, H.; Giersig, M.; Willig, F. *J. Mater. Chem.* **1999**, *9*, 3051.