A general protocol to coat titania shell on carbon-based composite cores using carbon as coupling agent

Rongbo Zheng [a,b], Xianwei Meng [a], Fangqiong Tang [a,*]

[a] Laboratory of Controllable Preparation and Application of Nanomaterials, Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing 100190, PR China
[b] Graduate School of Chinese Academy of Sciences, Beijing 100039, PR China

ABSTRACT

We present herein a general protocol to coat titania shell on carbon-based composite cores via the hydrolysis of titanium tetrabutoxide in a mixed solvent with the catalysis of ammonia. As coupling agent, their carbonaceous component can adsorb counter-charged NH_4^+, and then the negatively charged $\equiv TiO^-$ species are adsorbed via electrostatic interaction to form TiO_2 shell. Various carbon-based cores with different functional components, such as Ag/C core/shell spheres, Ag/C nanocables, as well as magnetic ($C-Fe_3O_4$) hollow spheres can be coated with titania shell to form corresponding core/shell composites. Their optical or magnetic property is also investigated. Finally, anatase-phase titania shell with rough surface can be generated via hydrothermal treatment of aforementioned titania coated composites, which can further introduce the properties of anatase-phase titania to the composites.

© 2009 Elsevier Inc. All rights reserved.

1. Introduction

Recently, the design of core/shell structured composites has been received much attention, not only as a means to improve the stability and surface chemistry of the core materials but also as a way to obtain unique structures, properties, and applications via combination of different characteristics of the components, which are not available with their single-component counterparts [1–7]. As an important metal oxide, titania is of interest for coating applications because it has been widely used in pigments, cosmetics, catalyst supports, dielectric materials, and photocatalysts [8–10]. That is, a titania shell can increase stability, alter the optical properties, as well as introduce new properties to the core/shell composites [11,12]. For instance, Wu et al. [11] had demonstrated that titania coating could obviously enhance the UV shielding property and even thermal stability of the organic pigment (e.g. yellow 109). Gao's group found that TiO_2/SiO_2-coated magnetic spheres show good photocatalytic activities in the degradation of methylene blue [12].

Up to date, various methods have been developed to prepare titania coated core-shell composites [7,13–21]. For instance, as a general methodology, layer-by-layer (LBL) self-assembly technique, pioneered by Caruso et al., has been demonstrated to be a successful route to form core/shell structures including Au/TiO_2 [22], PS/TiO_2 core/shell nanospheres [23], as well as Ni/TiO_2 core/shell nanorods [24]. The shell thickness can be controlled either through the concentration of the coating materials or through the LBL cycling time. However, LBL process is time consuming in order to obtain the desired thickness of shell and a lot of redundant polymer is also incorporated into the shell. A second approach is to deposit TiO_2 by controlled precipitation of titania precursors onto the core particles, in some cases assisted by a coupling agent [3,18]. Typically, titania precursors are hydrolyzed in the presence of various particles to effect coating. For example, Kotov et al. [7] have demonstrated that a thin shell of TiO_2 can be coated on silver nanospheres by a one-pot route, which combines two processes that occur sequentially—the formation of the silver core and the coating. Gu's group have reported that Mn–Zn ferrite nanoparticles also can be coated with titania shell by hydrolysis of $TiCl_4$ in the presence of stearic acid-stabilized pre-prepared Mn–Zn ferrite nanoparticles [21]. More recently, our group has developed a mixed solvent method to coat anionic polystyrene (PS) spheres with titania, in which mixed solvent not only lower the hydrolysis rate but also lower the diffusion rate of titania precursors to form dense, smooth titania coating [18]. However, PS spheres were exploited simply as core to obtain hollow titania spheres via further remove PS spheres. Titania coating are generally exceptionally difficult to synthesize on different kind and morphology cores by a general method. Because the titania precursors are highly reactive, a tiny variation in core surface easily causes titania to form secondary particles or results cores to aggregate [3,18]. Hence, general and efficient strategies enabling the fabrication of titania coatings on different cores remain highly challenging.

Herein, we develop a mixed solvent method to coat titania shell on various carbon-based functional cores, in which carbon is used as a coupling agent, the cores are retained as functional

* Corresponding author. No. 2 Beiyitiao Zhongguancun Beijing 100190, PR China.
Fax: +86 10 62554670.
E-mail addresses: tangfq@mail.ipc.ac.cn, tangnano@sohu.com (F. Tang).

components to the composites instead of simply as template [18]. Taking noble metal (Ag/C nanospheres and Ag/C nanocables), metal oxide (magnetite, i.e. C–Fe$_3$O$_4$) hollow microspheres, and pure carbon spheres as examples, titania can be coated on aforementioned cores. The key is to use their carbon component (possess affluent functional groups such as OH, and COO$^-$) as coupling agent that can adsorb counter-charged NH$_4^+$, and then the negatively charged ≡TiO$^-$ species are deposited to form titania shell. Due to a high refractive index of the TiO$_2$ shell, the UV–vis absorption spectra of Ag/C/TiO$_2$ nanoparticles are first time to be reported that can be red-shift from 437 and 571 nm (the absorption spectra of Ag/TiO$_2$ nanoparticles) to about 500 and 720 nm, respectively. In addition, anatase-phase titania (A–TiO$_2$) shell with rough surface can be generated via hydrothermal treating at 180 °C for 12 h.

2. Experimental

2.1. Materials

Titanium tetrabutoxide (TBOT), acetonitrile, and ammonia were purchased and used without further purification. Carbon submicrospheres, Ag/C nanospheres, Ag/C nanocables, and C–Fe$_3$O$_4$ hollow microspheres were obtained according to the previous literatures [25–27]. Ag/C nanospheres were prepared via according to the previous literature [26]. That is, a 0.5 mL portion of AgNO$_3$ aqueous solution (0.1 M) was added drop by drop into 35 mL glucose aqueous solution (0.63 M) under vigorous stirring. After being stirred for more than 10 min, the solution was transferred and sealed in a 40 mL Teflon-sealed autoclave. Ag/C nanospheres with size of 170 and 380 nm could be synthesized when the autoclave was kept at 170 °C for 4 and 6 h, respectively. Ag/C nanocables were prepared via the following synthesis. Ag$_2$CO$_3$ were prepared via adding AgNO$_3$ (0.15 g) and Na$_2$CO$_3$ (0.05 g) into deionized water (35 mL) in sequence. Subsequently, NH$_2$SO$_3$H (0.17 g) was added into the above solution with stirring. Finally, salicylic acid (0.24 g) was put into it. After agitation for several minutes, the solution was transferred and sealed in a 40 mL Teflon-sealed autoclave and heated at 170 °C for 60 h. As for carbon submicrospheres, they were produced via hydrothermal treatment (160 °C for 4 h) of glucose aqueous solution (0.5 M). C–Fe$_3$O$_4$ hollow microspheres were obtained via ultrasonic spray pyrolysis. The experimental setup is similar to that of Suslick's group [28,29]. For nebulization, a Yuyue household ultrasonic humidifier was used to nebulize FeCl$_2$ saturated aqueous solution into a fine mist. The furnace temperature was set as 700 °C with a nitrogen flow rate of 2 SLPM (standard liters per minute).

2.2. Titania coated core/shell nanostructures

Titania shell can be coated on pure carbon spheres or carbon-based composites encapsulating various functional materials such as Ag and Fe$_3$O$_4$ via present method (Table 1). In a typical experiment, the requisite carbon-based composites were dispersed in 40 mL of ethanol/acetonitrile (3:1 v/v) so as to form a solution of concentration 0.003–0.03 M and then mixed with 0.3 mL of ammonia under ambient conditions. Finally, a solution of 0.6 mL TBOT in 10 mL of ethanol/acetonitrile (3:1 v/v) was added to the above suspension under stirring. After reacting for 2 h, the composite particles were cleaned by three cycles of centrifugation and ultrasonic dispersion in ethanol. The thickness of titania shell could be tuned via either changing the concentration of carbon-based composites or the size of carbon-based composites.

Table 1
Synthesis conditions of the samples.

Sample	Carbonaceous cores and amount			
	Ag/C spheres/g	Ag/C cables/g	C–Fe$_3$O$_4$ hollow spheres/g	C spheres/g
AS 1	0.02 (170 nm)			
AS 2	0.04 (170 nm)			
AS 3	0.02 (380 nm)			
AC 1		0.02		
AC 2		0.03		
FS			0.01	
CS				0.03

2.3. Formation of anatase-phase titania shell with rough surface

C/TiO$_2$ core/shell spheres of 0.1 g were re-dispersed in 16 mL deioned water to form suspension, which were put into Teflon-lined stainless steel autoclave with a volume of 20 mL. The autoclave was maintained at 180 °C for 12 h. After the autoclave was cooled naturally to room temperature, the resulting precipitate was separated centrifugally and washed with distilled water and then absolute ethanol three more times.

2.4. Characterization

The obtained products were characterized by XRD (Rigaku Dmax2000 with Cu Kα radiation), SEM and EDS (XL30ESEM FEG), TEM (JEOL 2010), UV–vis–near-infrared (Cary 500 Scan UV–vis–NIR spectrophotometer), ξ-potential (Malvern Zetasizer 3000 H), and the vibrating-sample magnetometer (VSM LDJ-9600).

3. Results and discussion

3.1. Carbon-based composite cores

Recently, carbon spheres have been prepared via the dehydration of polysaccharides aqueous solution via either hydrothermal route [25] or ultrasonic spray pyrolysis [28,29]. On the other hand, various functional components such as noble metal [26], oxides [30–35], have been encapsulated in the carbonaceous structures to form core-shell structures via different route. According to the results of IR, Raman, and EDS studies of previous literatures [25,26], their surface was hydrophilic, being functionalized with OH, and COO$^-$ groups. The ξ-potential of as-prepared carbon spheres, Ag/C core/shell nanospheres, Ag/C nanocables, and C–Fe$_3$O$_4$ was −40.8, −36.7, −33.2, and −11.6 mV, respectively.

3.2. Formation mechanism of carbon-based core/TiO$_2$ shell

Due to the presence of carbon component, aforementioned carbon-based composites possess negative-charge surface (revealed by the negative value of ξ-potential), which can adsorb counter-charged NH$_4^+$, and then the negatively charged ≡TiO$^-$ species to form titania shell [18]. As shown in Scheme 1, the present coating process include the following steps: (1) The NH$_4^+$ species can be held by the negatively charged surface of carbon-based cores terminating in the functional groups such as COO$^-$ and OH$^-$ via the electrostatic interaction; (2) With the accumulation of NH$_4^+$ species on the surface of carbon-based core, the negatively charged titania precursor (≡TiO$^-$) are adsorbed by the NH$_4^+$ species onto the surface of carbon-based core. (3) The condensation process by the catalysis of NH$_4^+$ species will occur easily on the surface of carbon-based core to form the core-shell

nanostructures with titania coating. Taking C, Ag/C, and C–Fe$_3$O$_4$ as examples, we can demonstrate that aforementioned route is a general protocol to form titania shell on carbon-based cores with various functional components.

3.3. TiO$_2$ coated Ag/C core/shell nanocomposites

According to above coating mechanism, Ag/C core/shell nanospheres were selected as cores to be coated with titania shell. The morphologies of the Ag/C and Ag/C/TiO$_2$ core-shell composites are investigated by SEM and images are shown in Fig. 1. From Fig. 1 we can see that the obtained products feature the core/shell structures due to the contrast difference between the core and the shell of the nanospheres. The TEM images further demonstrated that the Ag/C nanospheres were coated with TiO$_2$ shell (inset of Fig. 1B). Though there are some larger nanospheres encapsulating more than one Ag nanoparticles in one shell, most nanospheres encapsulate one Ag nanoparticles in a single shell. Before coated with TiO$_2$, the size of Ag core is in the range of 100–140 nm, while the carbon shell is about 25 nm. That is the mean size of Ag/C nanospheres is about 170 nm. After coated with
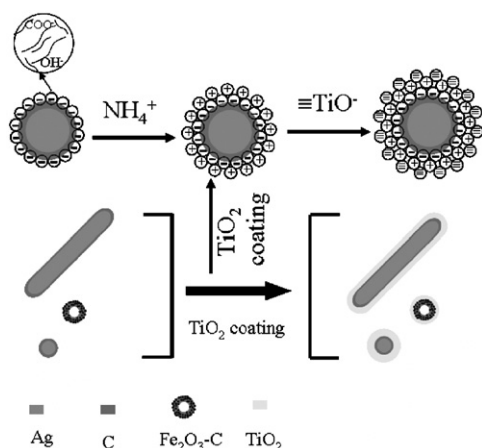
TiO$_2$, the size increases to about 350 nm, which means the thickness of titania shell is about 90 nm.

Similarly, Ag/C/TiO$_2$ nanocables can be generated when Ag/C nanocables are used as target core. As shown in Fig. 1C and D, the diameters of nanocables increase from 170 nm (the size of Ag/C nanocables) to 410 nm after coated with TiO$_2$ shell. Magnification image (the inset of Fig. 1D) further demonstrates that obtained products feature the cable-like structures due to the contrast difference between the bright Ag core and the dark TiO$_2$ sheath.

The thickness of TiO$_2$ shell can be adjusted via either changing the amount or the size of Ag/C nanoparticles. As shown in Fig. 2A, the thickness of TiO$_2$ shell decreases to about 40 nm when the amount of Ag/C nanoparticles increases to about 0.04 g (sample AS 2). The thickness of TiO$_2$ shell increases to about 140 nm when the size of Ag/C nanoparticles is about 360 nm (sample AS 3). It should be noted that some TiO$_2$ nanospheres with size of about 260 nm coexist with the Ag/C/TiO$_2$ nanospheres. That is, the thickness of TiO$_2$ shell should be less than 90 nm; otherwise some TiO$_2$ solid nanospheres would be formed as a result of unsuppressed homogeneous nucleation. Similarly, the thickness of TiO$_2$ sheath can be reduced to about 90 nm (Fig. 2D) when the amount of Ag/C nanocables is 0.03 g (sample AC 2).

Fig. 3 shows the UV–vis absorption spectra of Ag/C nanoparticles (curve a) and Ag/C/TiO$_2$ nanoparticles (curve b) suspensions. Typically, there are three peaks at 363, 437, and 571 nm, respectively. The former two peaks can be attributed to typical extinction spectra of Ag/C nanoparticles, similar to the result of Li [26]. As for the peak at 571 nm, it may result from the co-contribution of the in-plane dipole resonance of Ag nanoplates [34] and the coating of C shell. It is interesting that the peaks at 437 and 571 nm further red-shift to about 500 and 720 nm, respectively, which is caused by a high refractive index of the TiO$_2$ shell. That is, the absorption peak can be red-shift about 150 nm when the thickness of TiO$_2$ coating is 90 nm. To the best of our knowledge, this is the first time to report that absorption spectra of Ag nanoparticles can be red-shifted to 720 nm via the coating with high refractive index shell.

3.4. TiO$_2$ coated C–Fe$_3$O$_4$ hollow microspheres composites

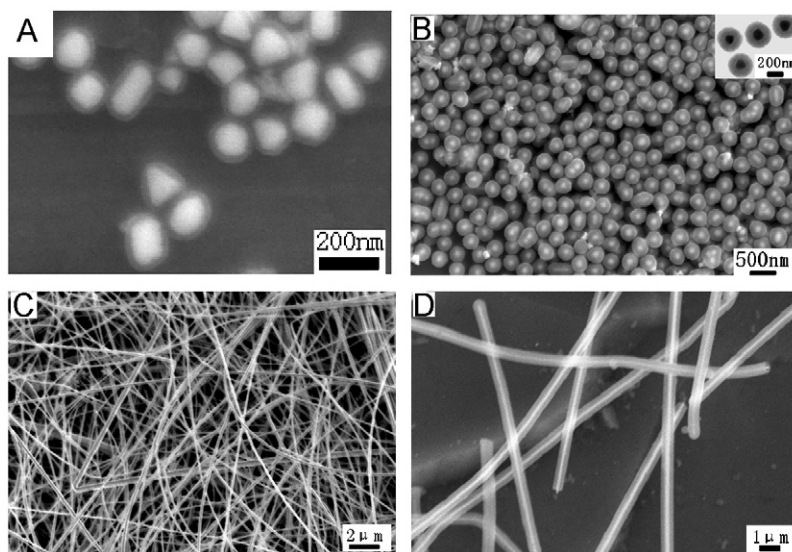Besides noble metal such as Ag encapsulated in carbon shell, carbon-metal oxide composites such as carbon-magnetite

Scheme 1. Illustration of the formation mechanism of the titania coated core/shell composites.

Fig. 1. SEM and TEM images of (A) Ag/C nanoparticles; (B) Ag/C/TiO$_2$ core/shell spheres (AS 1); (C) Ag/C nanocables; (D) Ag/C/TiO$_2$ nanocables (AC 1). The inset of B and D is the magnification images of Ag/C/TiO$_2$ spheres and nanocables, respectively.
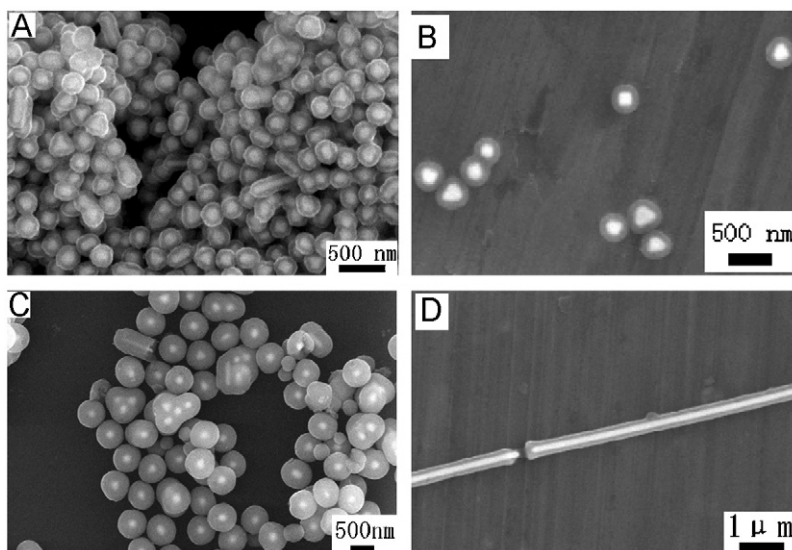
Fig. 2. SEM images of (A) Ag/C/TiO$_2$ core/shell spheres (AS 2); (B) Ag/C nanospheres with size of about 360 nm; (C) Ag/C/TiO$_2$ core/shell spheres (AS 3); (D) Ag/C/TiO$_2$ nanocables (AC 2).
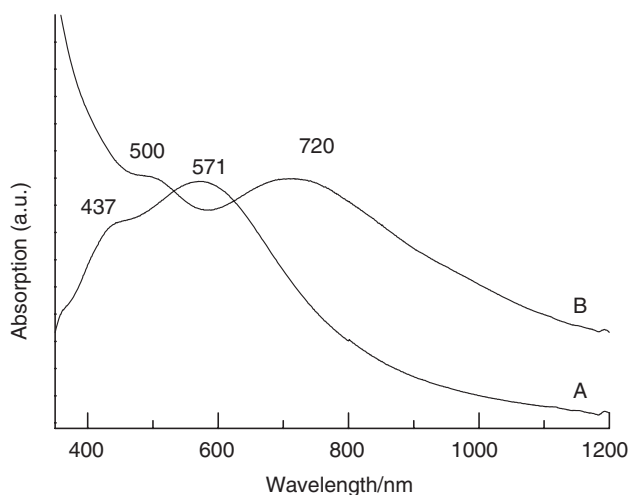

Fig. 3. UV–vis absorption of (A) Ag/C nanospheres; and (B) Ag/C/TiO$_2$ nanospheres (AS 1).

(C–Fe$_3$O$_4$) composites also can be used as target core to be coated with titania shell. Fig. 4A and B show the morphologies of aforementioned C–Fe$_3$O$_4$ hollow spheres and TiO$_2$ coated C–Fe$_3$O$_4$ hollow composites, respectively. Due to the polydispersity in size of C–Fe$_3$O$_4$ hollow spheres, it is hard to judge whether TiO$_2$ is coated on the surface of C–Fe$_3$O$_4$ hollow spheres via the variation of their size. The TEM images (the inset of Fig. 4B) indicates that the thickness of TiO$_2$ coating is about 20 nm. The result of EDS further demonstrates that TiO$_2$ is successfully coated on the surface of C–Fe$_3$O$_4$ hollow composites, as shown in Fig. 4. The molar ratio of Ti to Fe is about 1:5. The magnetic properties of the TiO$_2$ coated C–Fe$_3$O$_4$ hollow composites are investigated using vibrating sample magnetometer. From Fig. 4d, we can see that aforementioned hollow composites exhibit ferrimagnetism with saturation magnetization M_s = 31.1 emu/g, remnant magnetization M_r = 1.8 emu/g, and coercive field H_c = 37.0 Oe. Our magnetic TiO$_2$ hollow microspheres should widen their applications in catalyst, drug delivery, as well as environmental remedy via the combination of magnetic property and catalytic properties.

3.5. Carbon spheres coated with anatase-phase titania (A–TiO$_2$) shell of rough surface

In order to demonstrate the key role of carbonaceous component plays in the present route, the following controlled experiments were conducted. If poly(vinyl pyrrolidone) stabilized Ag nanowires were used as cores, no titania shell could be coated on the surface of Ag nanowires. Contrarily, titania nanoparticles were generated via the homogeneous nucleation of titania (data not show). On the other hand, if pure carbonaceous spheres were used as core, C/TiO$_2$ core/shell spheres would be formed via the same procedure. As shown in Fig. 5, the size of C/TiO$_2$ spheres increases from about 400 nm (the size of carbonaceous spheres) to about 480 nm, which means that TiO$_2$ shell with thickness of about 40 nm was successfully coated on the surface of pure carbonaceous spheres. Therefore, we can conclude that carbon surface plays an important role in the coating of titania shell on carbon-based composites, and present route is a general protocol for obtaining TiO$_2$ coated carbon-based core-shell composites.

A–TiO$_2$ shell with rough surface is prepared via hydrothermal treatment of aforementioned C/TiO$_2$ core/shell spheres. It is known that TiO$_2$ coating obtained from sol–gel processing of TBOT were amorphous in nature [11–18]. Herein, A–TiO$_2$ coating is generated via hydrothermal treatment of amorphous TiO$_2$ shell. Fig. 5C reveals the SEM image of powder obtained via hydrothermal treatment at 180 °C for 12 h. From Fig. 5C, we can see that the surface of C/A–TiO$_2$ spheres becomes rough, which is composed of anatase nanocrystals (<10 nm). At the same time, the size increases from 480 to 500 nm, which may result from the larger space between the anatase nanocrystals. Fig. 5D shows XRD pattern of the samples before and after hydrothermal treatment. TiO$_2$ shell can be transformed from amorphous (line 1 of Fig. 5D) to anatase-phase titania (JCPDS file No. 21-1272) via hydrothermal treatment.

4. Conclusion

In summary, we develop a general protocol for generating titania coated core/shell composites utilizing their negatively charged carbonaceous surface as coupling agent that can adsorb counter-charged NH$_4^+$, and then the negatively charged ≡TiO$^-$
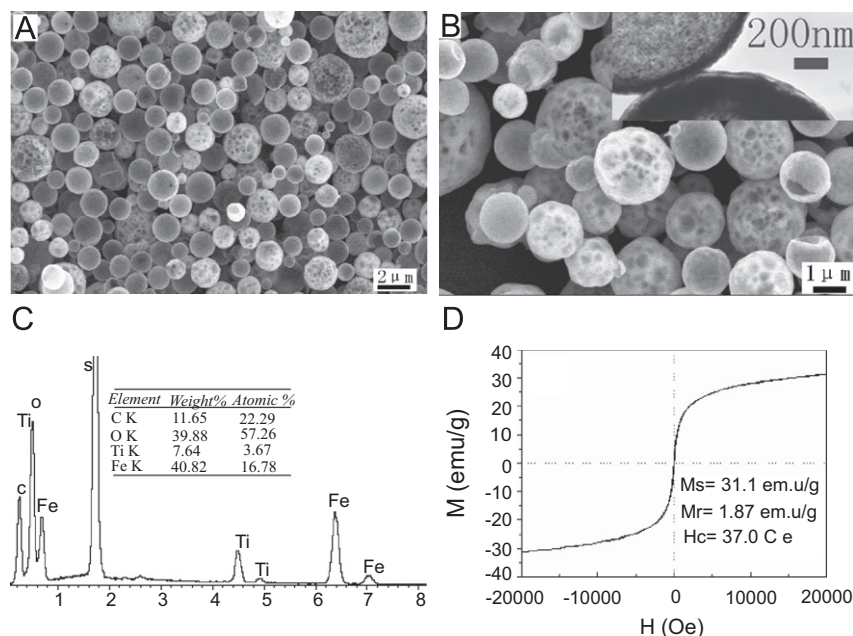
Fig. 4. SEM images of (A) C–Fe$_3$O$_4$ hollow spheres and (B) Titania coated C–Fe$_3$O$_4$ hollow spheres (FS). The inset of Fig. 4B is its TEM image. (C) EDS of Titania coated C–Fe$_3$O$_4$ hollow spheres. (D) The M–H hysteresis loop for titania coated C–Fe$_3$O$_4$ hollow spheres measured at room temperature.
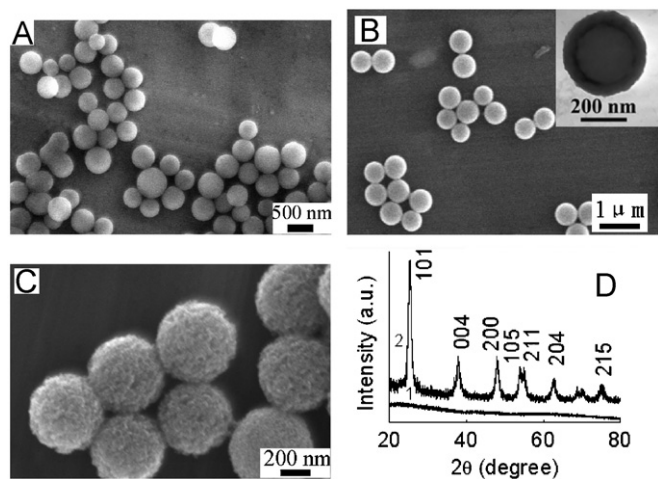

Fig. 5. SEM images of (A) carbonaceous spheres; C/TiO$_2$ core/shell spheres before; (B) and after; (C) hydrothermal treatment; and (D) XRD pattern of C/TiO$_2$ core/shell spheres before (1) and after (2) hydrothermal treatment.

species are deposited to form titania shell. Herein, C spheres, Ag/C core/shell spheres and C–Fe$_3$O$_4$ hollow spheres, as well as Ag/C nanocables are used as target cores to coat TiO$_2$ shell. Furthermore, the amorphous TiO$_2$ coating can be converted to A–TiO$_2$ coating with rough surface (composed of anatase nanoparticles with the size of less than 10 nm) via hydrothermal treatment. Due to a high refractive index of the TiO$_2$ shell, the UV–vis absorption spectra of Ag/C/TiO$_2$ nanoparticles are the first time to be reported that can be red-shift from 437 and 571 nm to about 500 and 720 nm, respectively. The M_s of titania coated C–Fe$_3$O$_4$ hollow microspheres is as high as 31.1 emu/g. Titania coating functional composites (such as metal, matnetic properties) may have potential applications in photocatalysts, environmental remediation, magnetic separation of biomolecules, photochromic materials, etc.

References

[1] F. Caruso, Adv. Mater. 13 (2001) 11.
[2] A.H. Lu, E.L. Salabas, F. Schüth, Angew. Chem. Int. Ed. 46 (2007) 1222.
[3] L.M. Liz-Marzán, P. Mulvaney, J. Phys. Chem. B 107 (2003) 7312.
[4] Y.D. Yin, Y. Lu, Y.G. Sun, Y.N. Xia, Nano Lett. 2 (2002) 427.
[5] X. Wang, Q. Peng, Y.D. Li, Acc. Chem. Res. 40 (2007) 635.
[6] G. Oldfield, T. Ung, P. Mulvaney, Adv. Mater. 12 (2000) 1519.
[7] I. Pastoriza-Santos, D.S. Koktysh, A.A. Mamedov, M. Giersig, N.A. Kotov, L.M. Liz-Marzán, Langmuir 16 (2000) 2731.
[8] A. Fujishima, K. Honda, Nature 238 (1972) 37.
[9] B. O'Regan, M. Graetzel, Nature 353 (1991) 737.
[10] S.U.M. Khan, M. Al-Shahry, W.B. Ingler, Science 297 (2002) 2243.
[11] J.J. Yuan, S.X. Zhou, L.M. Wu, B. You, J. Phys. Chem. B 110 (2006) 388.
[12] X.F. Song, L. Gao, J. Am. Ceram. Soc. 12 (2007) 4015.
[13] J.M. Du, J.L. Zhang, Z.M. Liu, B.X. Han, T. Jiang, Y. Huang, Langmuir 22 (2006) 1307.
[14] X.M. Sun, J.F. Liu, Y.D. Li, Chem. Eur. J. 12 (2006) 2039.
[15] K. Kamata, Y. Lu, Y.N. Xia, J. Am. Chem. Soc. 125 (2003) 2384.
[16] Z.Z. Yang, Z.W. Niu, Y.F. Lu, Z.B. Hu, C.C. Han, Angew. Chem. Int. Ed. 42 (2003) 1943.
[17] H. Sakai, T. Kanda, H. Shibata, T. Ohkubo, M. Abe, J. Am. Chem. Soc. 128 (2006) 4944.
[18] P. Wang, D. Chen, F.Q. Tang, Langmuir 22 (2006) 4832.
[19] A. Imhof, Langmuir 17 (2001) 3579.
[20] Z.Y. Zhong, Y.D. Yin, B. Gates, Y.N. Xia, Adv. Mater. 12 (2000) 206.
[21] M. Ma, Y. Zhang, X.B. Li, D.G. Fu, H.Q. Zhang, N. Gu, Colloids Surfaces A 224 (2003) 207.
[22] K.S. Mayya, D.I. Gittins, F. Caruso, Chem. Mater. 13 (2001) 3833.
[23] F. Caruso, X.Y. Shi, R.A. Caruso, A. Susha, Adv. Mater. 13 (2001) 740.
[24] K.S. Mayya, D.I. Gittins, A.M. Dibaj, F. Caruso, Nano Lett. 1 (2001) 727.
[25] X.M. Sun, Y.D. Li, Angew. Chem. Int. Ed. 43 (2004) 597.
[26] X.M. Sun, Y.D. Li, Langmuir 21 (2005) 6019.
[27] D.K. Ma, M. Zhang, G.C. Xi, J.H. Zhang, Y.T. Qian, Inorg. Chem. 45 (2006) 4845.
[28] S.E. Skrabalak, K.S. Suslick, J. Am. Chem. Soc. 128 (2006) 12642.
[29] S.E. Skrabalak, K.S. Suslick, J. Phys. Chem. C 111 (2007) 17807.

[30] L.Q. Xu, W.Q. Zhang, Y.W. Ding, Y.Y. Peng, S.Y. Zhang, W.C. Yu, Y.T. Qian, J. Phys. Chem. B 108 (2004) 10859.

[31] A.B. Fuertes, M. Serilla, T. Valdes-Solis, P. Tartaj, Chem. Mater. 19 (2007) 5418.

[32] A.H. Han, T.W. Kim, D.H. Park, S.J. Hwang, J.H. Choy, J. Phys. Chem. B 111 (2007) 11347.

[33] R. Demir-Cakan, Y.S. Hu, M. Antonietti, J. Maier, M.M. Titirici, Chem. Mater. 20 (2008) 1227.

[34] I. Wahio, Y.J. Xiong, Y.D. Yin, Y.N. Xia, Adv. Mater. 18 (2006) 1749.

[35] Y. Ohko, T. Tatsuma, T. Fujii, K. Naoi, C. Niwa, Y. Kubota, A. Fujishima, Nature Mater. 2 (2003) 29.