JOURNAL OF MATERIALS SCIENCE **38** (2003) 4911–4916

Preparation of PS/TiO_2 core-shell microspheres and TiO_2 hollow shells

JILIANG YIN, HONGJIN CHEN, ZHONGKAI LI, XUEFENG QIAN*, JIE YIN
Research Institute of Polymer Materials, School of Chemistry & Chemical Technology,
State Key Laboratory of Composite Materials, Shanghai Jiao Tong University,
Shanghai 200240, People's Republic of China
E-mail: xfqian@mail.sjtu.edu.cn

MEIWU SHI, GUOTAI ZHOU
The Quartermaster Research Institute of CPLA, Beijing, People's Republic of China

PS/TiO_2 core-shell microspheres were prepared by a hydro-thermal method at 105°C. Different-sized PS/TiO_2 core-shell microspheres were obtained with various PS cores, which were prepared by emulsion polymerization and seeds polymerization. Furthermore, intact hollow TiO_2 shells with different shell thickness were obtained by calcining PS/TiO_2 core-shell microspheres at 600°C. Light scattering of core-shell microspheres and hollow shells was tested. © *2003 Kluwer Academic Publishers*

1. Introduction

Core-shell microspheres and hollow shells have extensive applications in the fields of biology, electronics, magnetics, optics, medical analysis, chemistry, coating, and so on [1–8]. A variety of techniques have been employed to deposit coatings from solutions onto suspended core particles, which involve sol-gel process, chemical precipitation, microemulsion, and sonochemical process. Inorganic (SiO_2 beads, glass bubble) and organic (polystyrene (PS), poly(methylmethacylate) (PMMA) and copolymer beads) materials can be used as cores [7–11]. Because polymer cores can be removed from core-shell microspheres easily and polymer microspheres can be prepared easily, they were usually adopted to produce core-shell and hollow microspheres.

Several-sized core-shell microspheres and hollow TiO_2 shells with different shell thickness were prepared in this study. Submicron-sized monodispersed PS microspheres were coated with uniform layers of amorphous TiO_2 by hydrolysis of tetrabutyl titanate in an ethanol solution containing PS microspheres. The coating layers of different thickness were obtained by adjusting the concentrations of tetrabutyl titanate and PS. And then the core-shell microspheres were calcined into hollow shells.

2. Experiment

2.1. Materials

Styrene (AR, Shanghai Lingfeng Chemical Reagent Co. Ltd.) was purified by reduced pressure distillation. Lauryl sodium sulfate (AR, Shanghai Lingfeng Chemical Reagent Co., Ltd.) and potassium persulphate (AR, Shanghai Qianjin reagent factory) were recrystallized twice in water. Tetrabutyl titanate (CP, Shanghai Reagent Company), poly(vinylpyrrolidone) (PVP, weight-average molecular weight 30,000, Shanghai Reagent Company), ethanol (AR, Shanghai Zhengxing Chemical Reagent Company) were used without further purification.

2.2. Preparation of microspheres

2.2.1. PS microspheres

Emulsion polymerization method was used to prepare sub-micron PS spheres. The reaction condition is listed in Table I. In a 500 ml round flask, styrene, lauryl sodium sulfate and distilled water were added in sequence. Then the solution was purged with nitrogen in order to eliminate the inhibition effect of oxygen before the polymerization was initiated. Then the solution was heated to 80°C, and the initiator potassium persulphate was added. The polymerization was continued for 6 h, and the conversions exceeded 99%. Then ethanol and sodium chloride aqueous solution were used as de-emulsifier. By filtration, the microspheres were collected and dried in vacuum oven.

In order to obtain larger monodispersed PS microspheres, seeded polymerization was employed. In a 250 ml round flask, the as-prepared PS microspheres were dispersed into distilled water, and lauryl sodium sulfate, styrene, were added. The following treatment is similar to emulsion polymerization process.

2.2.2. Core-shell microspheres

The coating procedure consisted of controlled hydrolysis of ethanol solution of tetrabutyl titanate in the presence of PS microspheres and hydro-thermal treatment.

---

*Author to whom all correspondence should be addressed.

0022–2461

TABLE I Experimental condition in the preparation of PS microspheres at 80°C

Sample	A	B	C	D
Seeds size (nm)	–	–	265	540
Seeds amount (g)	–	–	2.0	2.0
Styrene (g)	9.06	9.06	14.0	14.0
Potassium persulfate (g)	0.1	0.1	0.16	0.16
Sodium dodecyl sulfate (g)	0.08	0.03	0.048	0.048
Water (g)	56	56	94	94
Sphere size (nm)	130	265	540	950

The PS microspheres were dispersed in PVP ethanol solution by ultrasonic treatment. And tetrabutyl titanate was added into ethanol with the help of ultrasonic agitation. Then distilled water was added for further hydrolysis of tetrabutyl titanate with vibration. After being treated in a 50 ml Teflon autoclave at 105°C for 1.5 h, the system was centrifuged at 4000 rpm for 20 min. The microspheres were washed several times with ethanol and Milli-Q water. Purified core-shell microspheres were dried in a vacuum oven at room temperature.

2.2.3. Hollow shells

Hollow TiO_2 shells were obtained by calcining the PS/TiO_2 microspheres at 600°C under static air for 3 h.

2.3. Characterization

The size of the PS/TiO_2 core-shell microspheres and TiO_2 hollow shells was determined by a Hitachi H-8100 transmission electron microscope (accelerating voltage = 200 kV). The shell thickness was estimated from TEM micrographs. Light scattering of the microspheres and shells was analyzed with a Cary 500 UV/vis/NIR spectrometer. The powder X-ray diffraction (XRD) patterns of core-shell microspheres and hollow shells were examined on a Shimadu XD-3A X-ray diffractometer at a scanning rate of 4°/min in 2θ ranging from 20° to 100° with Cu K_α radiation ($\lambda = 0.15418$ nm). The thermogravimetric analysis (TGA) was operated on a Perkin-Elmer TGA 7 analyzer at a heating rate of 20°C/min under the a nitrogen stream.

TABLE II Properties of core-shell microspheres obtained in 50×10^{-6} m^3 ethanol containing 1.5×10^{-6} m^3 water by aging at 105°C for 1.5 h

Sample	PS (nm)	PS (g)	PVP (g)	Tetrabutyl titanate (g)	Shell (nm)	Ratio of inner/ outer diameter
1	130	0.075	0.06	0.3	19	130/168
2	265	0.075	0.06	0.3	42.5	265/350
3	540	0.075	0.06	0.3	55	540/650
4	540	0.075	0.06	0.2	36	540/612
5	540	0.1	0.08	0.3	41.5	540/623
6	950	0.075	0.06	0.3	125	950/1200
7	950	0.075	0.06	0.2	87.5	950/1125
8	950	0.1	0.08	0.3	105	950/1160

3. Results and discussion

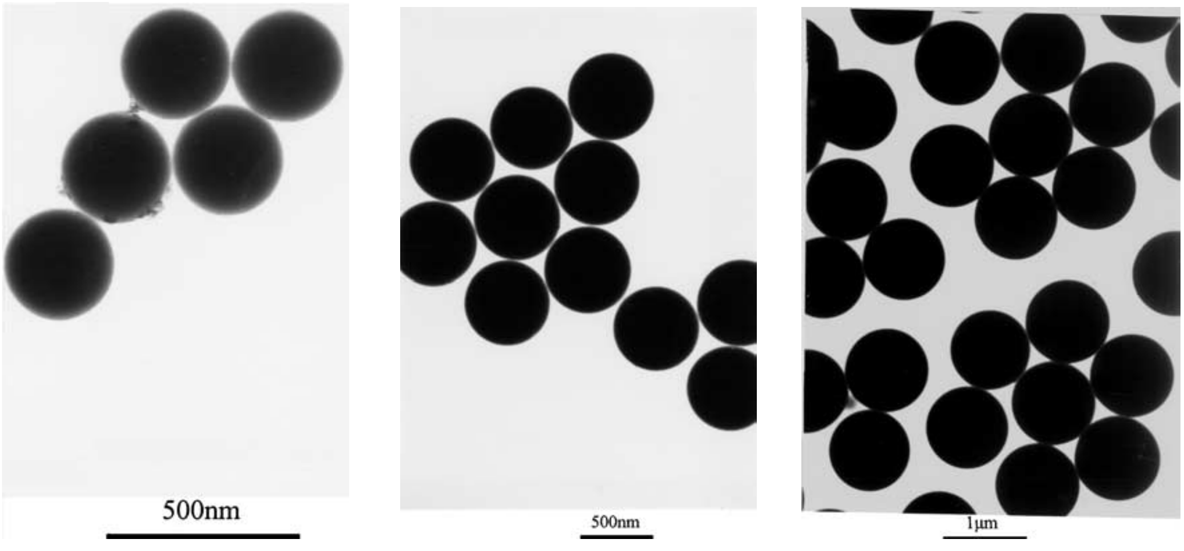
3.1. Preparation of PS microspheres

The typical TEM photographs of the as-prepared PS microspheres are shown in Fig. 1, from which we can see microspheres prepared from emulsion polymerization and seeded polymerization are monodispersed. The size of the PS microspheres is estimated from TEM photos and listed in Table I (A and B).

PS microspheres of desired size can be obtained from seeded polymerization. The amount of monomer was decided by the amount of seeds and the desired microspheres size. The mass of styrene changes according to:

$$m_1 = m_0 \times \left[\left(\frac{R_1}{R_0}\right)^3 - 1\right]$$

where R_0 and R_1 are the radii of seeds and PS microspheres, respectively; m_0 and m_1 are the masses of seeds and styrene monomer, respectively.



(a) (b) (c)

Figure 1 TEM photographs of PS microspheres: (a) 265 nm PS microspheres obtained by emulsion polymerization (Table I), (b) 540 nm PS microspheres, and (c) 950 nm PS microspheres obtained by seeds polymerization (Table I).

The results reveal that the sizes of PS microspheres obtained from seeded polymerization were in good agreement with the target values (Table IC and D).

3.2. Preparation of core-shell microspheres

PS microspheres of different sizes were used as core to prepare various core-shell microspheres, and the preparation conditions and results were listed in Table II. Without protective agent, the finished core-shell microspheres were slightly aggregated, although PS microspheres were well dispersed in ethanol. So PVP was used to prevent microspheres aggregation.

Fig. 2 shows typical TEM images of the as-prepared core-shell microspheres, which shows that the coating on 130 nm (Fig. 2a) and 265 nm (Fig. 2b) PS core was smooth and there were few secondary TiO_2 particles. However it was found that more free TiO_2 particles formed when 540 nm (Fig. 2c) and 950 nm (Fig. 2d) PS microspheres were used as cores with the same

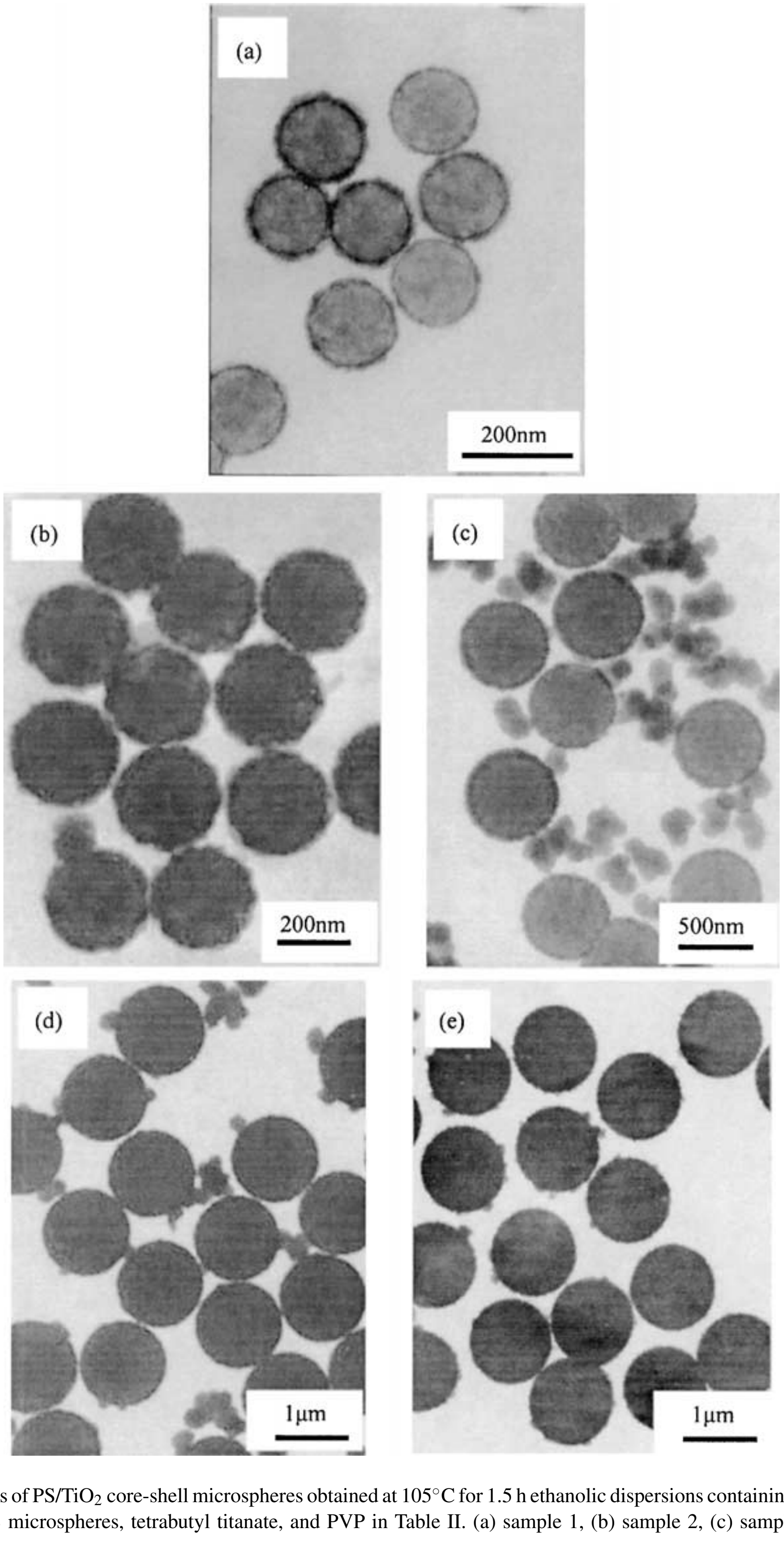


Figure 2 TEM photographs of PS/TiO_2 core-shell microspheres obtained at 105°C for 1.5 h ethanolic dispersions containing 1.5 g H_2O in the presence of different amounts of PS microspheres, tetrabutyl titanate, and PVP in Table II. (a) sample 1, (b) sample 2, (c) sample 3, (d) sample 6, and (e) sample 8.

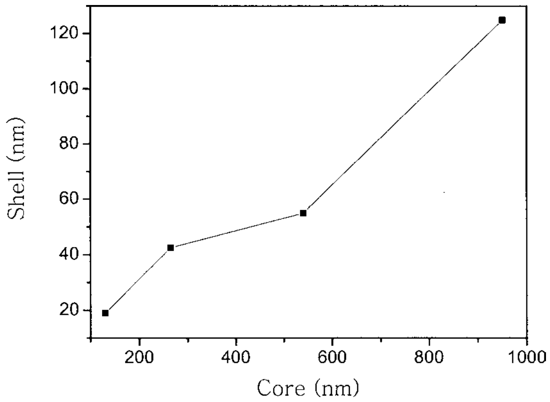


Figure 3 Relationship between TiO_2 shell thickness and PS core diameter at a constant concentration of tetrabutyl titanate and weight fraction of PS.

concentration of tetrabutyl titanate and weight fraction of PS cores. This is because the specific surface of bigger PS microspheres was smaller. Thus the larger PS microspheres with the same weight fraction have smaller surface area to adsorb the TiO_2 particles. The hydrolysis is very fast. To ensure the formation of a smooth coating and to prevent the formation of secondary TiO_2 particles, the hydrolyzed TiO_2 species must be captured rapidly by the PS microspheres [12]. TiO_2 coating on 540 and 950 nm PS cores became smooth by increasing the weight fraction of PS core (Fig. 2e).

From Table II, it is found that the thickness of the TiO_2 shell increases with the increase of seed diameter at the decided tetrabutyl titanate concentration (sample 1, 2, 4, 7 in Table II). Further analysis shows that the

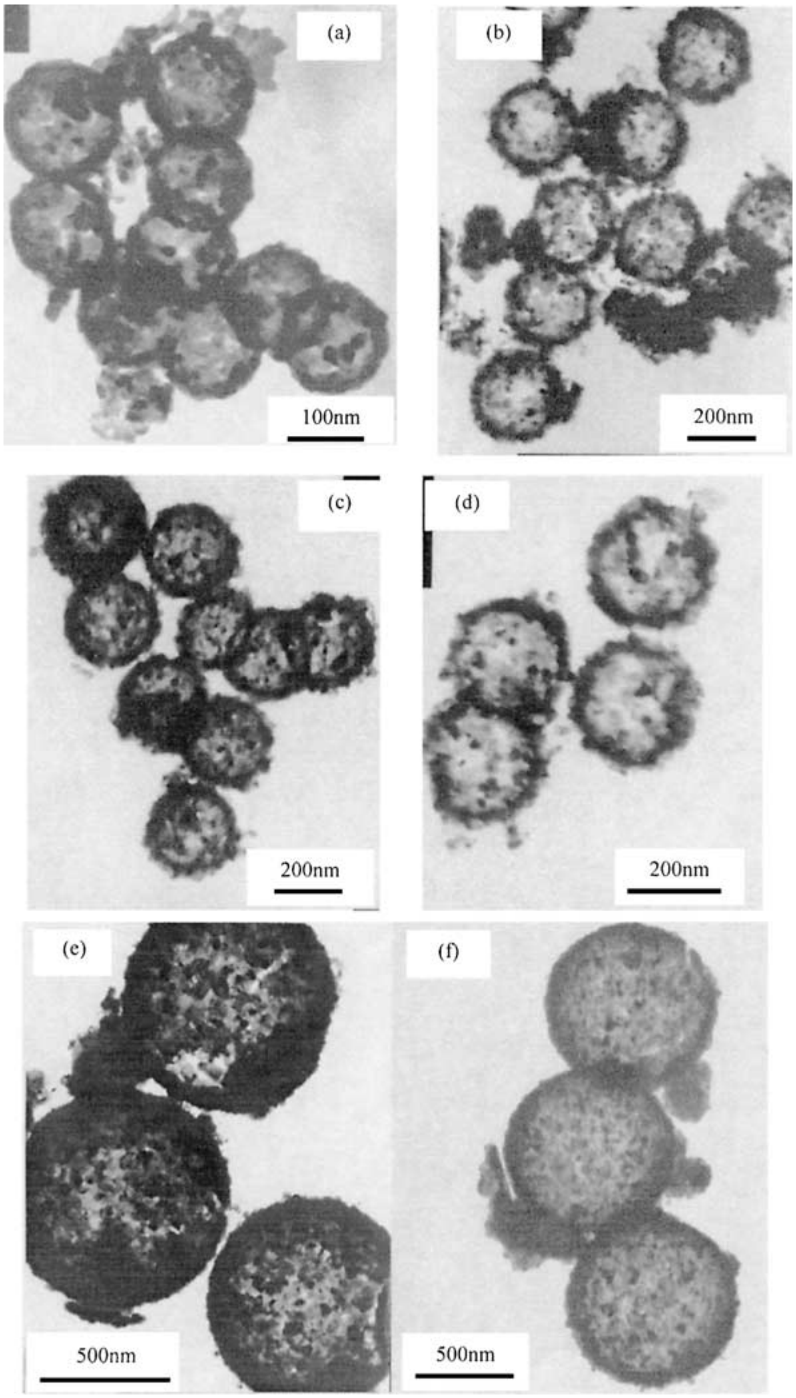


Figure 4 TEM photographs of TiO_2 hollow shells obtained by calcining the PS/TiO_2 core-shell microspheres, (a) sample 1, (b)–(d) sample 2, (e)–(f) sample 6.

thickness of the TiO_2 coating layer is dependent on the diameter of the PS core at a given concentration of tetrabutyl titanate and mass of PS core. The relationship between the TiO_2 shell thickness and PS core diameter can be derived as following:

$$\frac{4}{3}\pi[(R+d)^3 - R^3]\rho_2 n = m_2, \quad \text{and} \quad n = \frac{m_3}{\frac{4}{3}\pi R^3 \rho_3}$$

$$\frac{(R+d)^3 - R^3}{R^3} = \frac{m_2\rho_3}{m_3\rho_2}, \quad \text{so}$$

$$d = \left(\sqrt[3]{\frac{m_2\rho_3}{m_3\rho_2} + 1} - 1\right)R$$

where n is the number of PS microspheres; R is radius of PS core; d is thickness of TiO_2 coating, and m_2, ρ_2 m_3, ρ_3 are the mass and density of TiO_2 nanoparticles cluster and PS, respectively.

At a given concentration of PS core and tetrabutyl titanate, theoretical calculation indicates that the thickness of the TiO_2 shell is linearly related to the diameter of the PS core microspheres. The relationship between the TiO_2 shell thickness and PS core diameter obtained by the experiment at a constant concentration of tetrabutyl titanate and weight fraction of PS is shown in Fig. 3.

The relationship between the TiO_2 coating thickness and the PS core diameter is shown in Fig. 4; it was almost linear, which was in good agreement with the theoretical prediction.

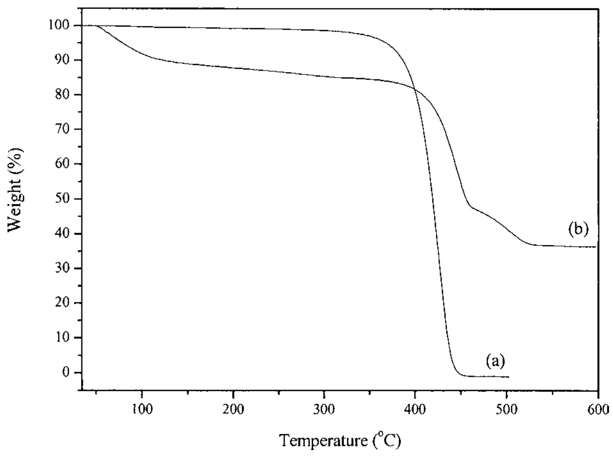


Figure 5 Thermogravimetric trace of (a) PS microspheres and (b) TiO_2/PS core-shell of sample 1.

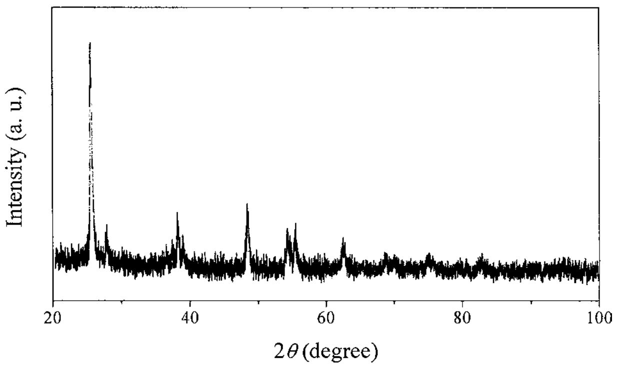
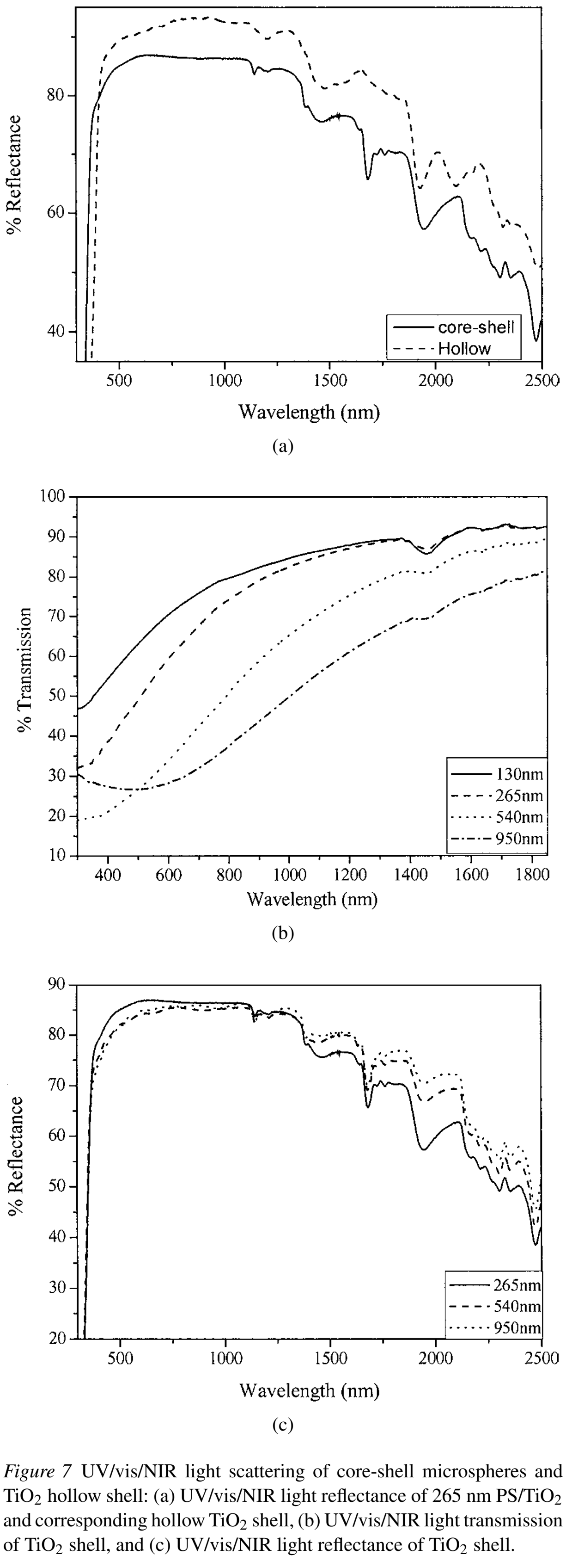


Figure 6 X-ray diffraction patterns of TiO_2 shell obtained by calcining core-shell microspheres (sample 2) at 600°C.

3.3. TiO_2 hollow shells

Fig. 4 shows typical TEM images of TiO_2 hollow shells of sample 1, sample 2 and sample 6 in Table II, from which we can see that most hollow shells were kept



(a)

(b)

(c)

Figure 7 UV/vis/NIR light scattering of core-shell microspheres and TiO_2 hollow shell: (a) UV/vis/NIR light reflectance of 265 nm PS/TiO_2 and corresponding hollow TiO_2 shell, (b) UV/vis/NIR light transmission of TiO_2 shell, and (c) UV/vis/NIR light reflectance of TiO_2 shell.

intact and the diameter of the hollow shells was about 155 nm, 285 nm and 850 nm respectively. Compared with the size of core-shell microspheres in Table II the hollow shells are slightly shrunk after calcination. This is due to the disappearance of the PS core and the crystal growth of the TiO_2 nanoparticles. Some TiO_2 particles were found in Fig. 4a, b, e and f. The TiO_2 particles in Fig. 4a and b are attributed to the secondary particles formed in the autoclave and hollow spheres broken during the calcination. The hollow spheres broken during the calcination at 600°C were few, estimated from the TEM photographs. The TiO_2 particles in Fig. 4a and b are attributed to the secondary particles formed in the autoclave, and no hollow spheres were broken during the calcination at 600°C.

In order to observe the weight loss of PS/TiO_2 core-shell microspheres at the calcination, thermogravimetric analysis (TGA) was adopted. Fig. 5a shows the PS weight loss was centred at 350–460°C, which is associated with the decomposition of PS. The first weight loss stage of Fig. 5b (sample 1) was associated with the release of water between 50 and 200°C, and the second weight loss stage, at 350–460°C, was associated with the decomposition of PS. The thermogravimetric curve also shows the transformation of amorphous TiO_2 into anatase at 460–520°C, which was confirmed by XRD. The weight loss of core-shell microspheres was about 60% during the calcination.

3.4. X-ray powder diffraction pattern

The X-ray powder diffraction pattern showed PS/TiO_2 core-shell microspheres were amorphous. After being calcined at 600°C, they were turned into anatase (Fig. 6).

3.5. Light scattering

The light scattering of PS/TiO_2 core-shell microspheres and TiO_2 shells (Fig. 7a) shows that the anatase TiO_2 shells have higher reflectance than the corresponding core-shell microspheres. Fig. 7b is the transmission spectrum taken in ethanol suspension. A shift in reflectance peak was observed to longer wavelengths with the increase of shell diameter. Fig. 7c is the reflective spectra of hollow TiO_2 shells with different diameters, which indicates that the reflectance of hollow shells was independent of the shell size (Fig. 7c).

4. Conclusions

Amorphous TiO_2 was coated of PS microspheres, which were prepared through emulsion polymerization and seeded polymerization, without further surface modification. The treatment was carried out in an autoclave at 105°C. Different-sized PS/TiO_2 core-shell microspheres were obtained by using various-sized PS cores. Anatase TiO_2 hollow shells were obtained by calcining the PS/TiO_2 microspheres to eliminate PS cores. These hollow microspheres had a higher reflectance than the PS/TiO_2 microspheres.

References

1. M. C. NEVES and T. TRINDADE, *Mater. Res. Bulletin* **36** (2001) 1099.
2. X. A. FU and S. QUTUBUDDIN, *Coll. Surf. A: Physicochem. Eng. Asp.* **179** (2001) 65.
3. M. L. BREEN, A. D. DINSMORE, R. H. PINK, S. B. QADRI and B. R. RATNA, *Langmuir* **3** (2001) 903.
4. P. H. WANG and C. Y. PAN, *Coll. Polym. Sci.* **278**(3) (2000) 245.
5. *Idem.*, *ibid.* **278**(6) (2000) 581.
6. *Idem.*, *ibid.* **280**(2) (2002) 152.
7. H. SHIHO and N. KAWAHASHI, *ibid.* **278**(3) (2000) 270.
8. MICHAEL S. WONG and JENNIFER N. CHA, *Nano Lett.* **2** (2002) 583.
9. MÁRCIA C. NEVES, TITO TRINDADE, ANA M. B. TIMMONS and JÚLIO D. PEDROSA DE JESUS, *Mater. Res. Bull.* **36** (2001) 1099.
10. P. SOMASUNDARAN, TSUNG-YUAN CHEN and D. SARKAR, *Mater. Res. Innovat.* **2** (1999) 325.
11. N. ARUL DHAS, A. ZABAN and A. GEDANKEN, *Chem. Mater.* **11** (1999) 806.
12. A. IMHOF, *Langmuir* **17** (2001) 3579.

Received 4 December 2002
and accepted 14 August 2003