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Hydrothermal Synthesis of TiO_2 Hollow Nanospheres *via* Self-Assembly Process

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One-step self-assembly process was proposed to synthesize anatase TiO_2 hollow nanospheres from octadecyltrimethoxysilane and tetrabutyl titanate at 120 ºC. The as-prepared product was characterized by X-ray diffraction, field-emission scanning electron microscopy and transmission electron microscopy, respectively. The morphology and size of the as-prepared sample can be adjusted by varying the temperature and the amount of octadecyltrimethoxysilane. Octadecyltrimethoxysilane plays a key role in the formation of hollow nanospheres of anatase TiO_2. In particular, the as-synthesized TiO_2 hollow nanospheres will be of great importance due to their potential applications in photocatalysis, drug delivery, separations and cell targeting, *etc*.

Key Words: Crystal growth, Hollow nanospheres, TiO_2, Hydrothermal synthesis.

INTRODUCTION

Metal oxides hollow structures have received great attention because of their wide applications in many fields such as photocatalysis[1,2] gas-sensing material[3,4], electrode material[5,6], drug delivery[7], chemical/biological separation[8]. Over the past decades, much effort has been devoted to synthesize the hollow structures, which have been used as microreactor[9] and high selectivity of catalyst[10]. Huang and his coworkers[11] have proposed a method to fabricate hollow bipyramid β-MnO_2 by simply varying hydrothermal reaction temperature without any template or surfactant, which has excellent electrochemical performance for lithium storage. Wang *et al.*[12] had synthesized Fe_2O_3 using F127 as template and a mixture of propanol and ethylene glycol as solvent. The sample which had highly sensitive gas sensors and high capacity was used as anode materials in lithium ion batteries. In particular, titania is known as the most important and popular photocatalyst which has received much attention due to its promising applications in photocatalysis[13-15], solar cells[16-17] and lithium ion batteries[18,19] *etc*. Over the past decades, many efforts have been paid to develop different techniques to fabricate the hollow nanospheres and nanotubes of titania such as sol-gel method[20], solvothermal method[21], hydrothermal method[22], chemical vapour deposition[23], physical vapour deposition[24], *etc*.

In contrast to other preparation methods, solution approaches are usually carried out in an easy and mild way. Herein, a facile solution approach has been proposed to synthesize TiO_2 hollow nanospheres using octadecyltrimethoxysilane (C18TMS) as structure-directing agent and tetrabutyl titanate as titanium source. Octadecyltrimethoxysilane molecules are quickly degraded to the siloxane polymer, which has hydrophobic chain (Si-R) and hydrophilic end (Si-OH) resulting in the formation of sphere-like microemulsion[25]. The nucleation and the nucleus growth of TiO_2 would be carried out on the surface of the formed microemulsion to form hollow TiO_2 nanospheres *via* self-assembly process (Fig. 1). The suitable amount of octadecyltrimethoxysilane and temperature played key roles in producing hollow TiO_2 nanospheres.

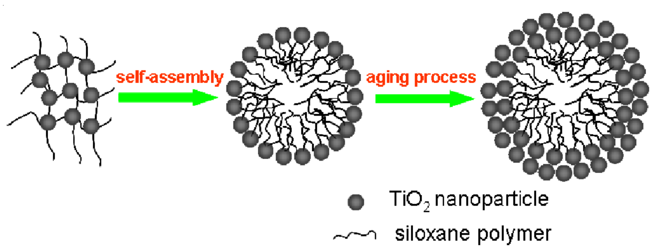

Fig. 1. Schematic illustration of the formation of the TiO_2 hollow microspheres

EXPERIMENTAL

All chemicals are analytical grade and were used without further purification.

Octadecyltrimethoxysilane was received from Sigma Ltd. and all chemicals are of analytical grade and used as received. In a typical synthesis, 100 mL tetrabutyl titanate and 40 mL octadecyltrimethoxysilane were dissolved in 21 mL of absolute ethanol, respectively, with vigorous magnetic stirring, then 1 mL 1 M HCl was added to the previous solution to form an aqueous solution which was then transferred to a Teflon-lined stainless steel autoclave (30 mL in total volume), sealed and maintained at 120 ºC for 12 h. The autoclave was allowed to cool to room temperature naturally. Finally, the product was collected by centrifugation, washed with absolute ethanol three times and then dried at 60 ºC for 4 h.

The phase of the as-prepared product was characterized by X-ray diffraction analyses, which was carried out on a Philips X'Pert PRO SUPER X-ray diffractometer equipped with graphite monochromatized CuK_{α} radiation and the operation voltage and current were maintained at 40 kV and 40 mA, respectively. The morphology and size of the samples were investigated by field-emission scanning electron microscopy (FESEM, JEOL-6700F) and transmission electron microscopy (TEM, JEOL 3010).

Photocatalytic activity testing on the degradation of rhodamine-B was carried out in a 100 mL beaker containing 50 mL rhodamine-B with a concentration of 3 mg L^{-1} and 40 mg of the as-prepared TiO_2 composite microspheres were irradiated by UV light of a 10 W Hg lamp. The concentration of rhodamine-B was measured by a UV-visible spectrophotometer (2401 PC model; Shimadzu, Kyoto, Japan) in the wavelength range of 200-800 nm at 15 min intervals during the degradation process of rhodamine-B.

RESULTS AND DISCUSSION

The morphology of the as-prepared sample was investigated by FESEM and TEM, which are shown in Fig. 2. A general overview SEM image (Fig. 2a) shows that the as-prepared sample synthesized by tetrabutyl titanate and octadecyltrimethoxysilane at 120 ºC was composed of nanospheres with 700 nm in diameter. Fig. 2b shows that the as-prepared sample was hollow nanospheres and the hollow architectures with a shell width of 30 nm and the shell consisted of well closed small nanoparticles, which have been confirmed by TEM (Fig. 2c and 2d). Fig. 2e shows that the high resolution TEM images taken from the rectangle section shown in Fig. 2d and the lattice spacing is 0.35 nm, which is corresponded to the (101) lattice planes of anatase phase TiO_2. The above analyses indicated that the TiO_2 composite hollow microspheres were crystalline.

The phase of the as-prepared product was characterized by X-ray diffraction analyses. Fig. 3 shows the XRD patterns of the as-prepared sample obtained from tetrabutyl titanate and octadecyltrimethoxysilane at 120 ºC, in which all the peaks can be readily indexed to the anatase phase TiO_2 (JCPDS no. 21-1272) with a cell constant (a = 3.785 Å, c = 9.513 Å) and without impurity peaks detected[26]. The size of the formed anatase TiO_2 nanoparticles is with an average diameter of 700 nm, which is calculated according to the Scherer equation ($R_m = k\lambda/\beta_{1/2} \cos\theta$). Fig. 4 shows the energy-dispersive X-ray analysis (EDX) of the as-prepared hollow TiO_2 nanospheres, in which the elements O, Si, Ti and Cu were observed and the element Cu came from Cu grid which was used as the samples' substrate for TEM observation. The elemental compositions of the as-prepared anatase hollow nanospheres have been given in Table-1.

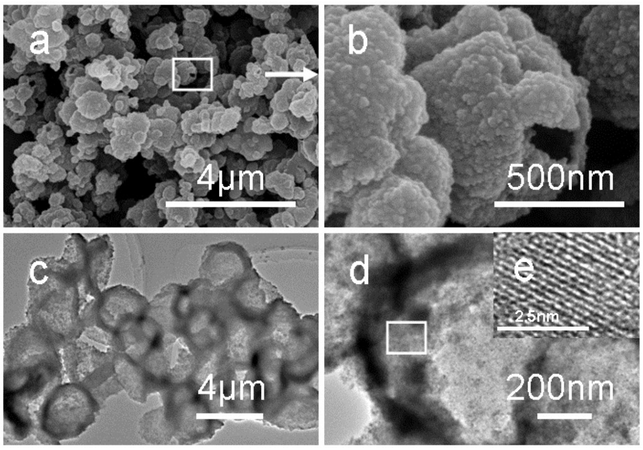

Fig. 2. FESEM and TEM images of the as-prepared product obtained from 100 mL tetrabutyl titanate in presence of 40mL octadecyltrimethoxysilane and 1 mL 1 M HCl at 120 ºC; (a) a general view of the as-prepared TiO_2 composite hollow microspheres; (b) a magnified SEM image of the hollow microspheres; (c)-(e) TEM and HRTEM images of the hollow microspheres

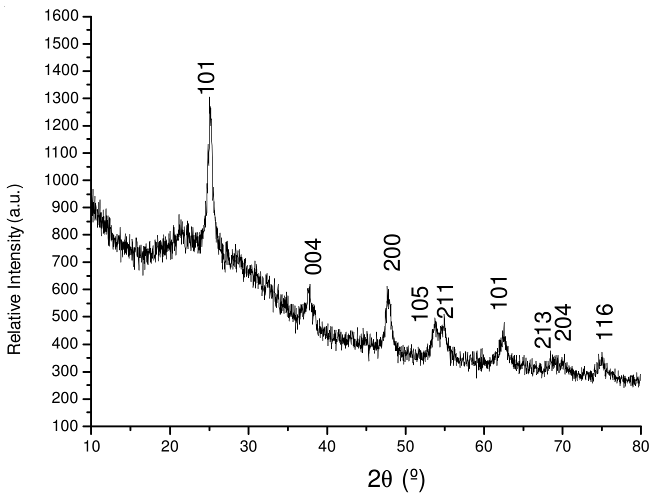

Fig. 3. XRD pattern of the as-prepared product obtained from 100 μL tetrabutyl titanate, 40 μL octadecyltrimethoxysilane and 1 mL 1 M HCl at 120 ºC for 12 h

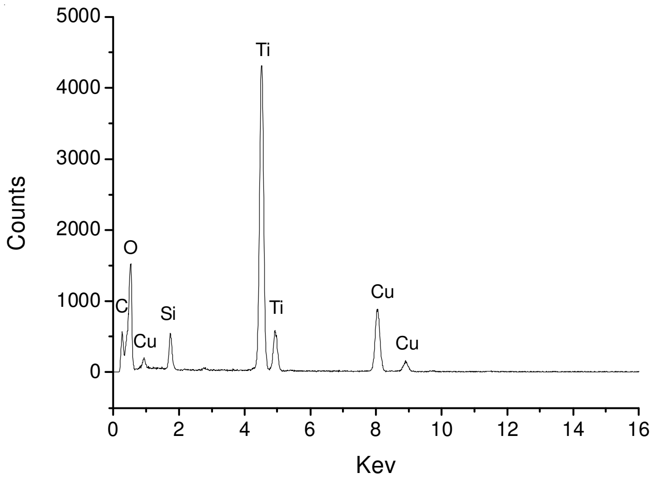

Fig. 4. EDX analyses of elemental composition of the as-prepared TiO_2 hollow nanospheres

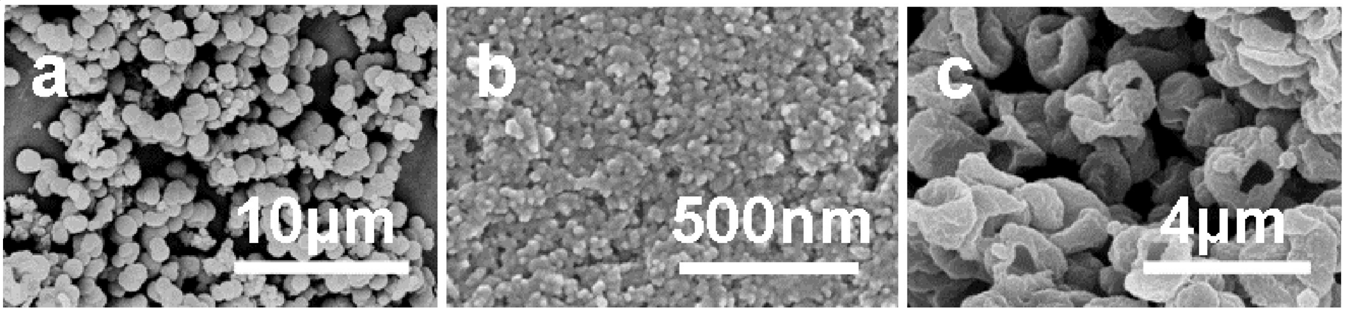

Fig. 5. FESEM images of the as-prepared products obtained from 100 μL tetrabutyl titanate, 1 mL 1 M HCl and different amount of octadecyltrimethoxysilane at different temperature, while other experimental conditions were kept the same. (a) 40 μL, 60 ºC; (b) 0 μL, 120 ºC; (c) 20 μL, 120 ºC

TABLE-1
ELEMENT COMPOSITIONS OF THE AS-PREPARED TiO_2 HOLLOW MICROSPHERES FROM EDX

Element	Weight (%)	Atomic (%)
C	09.70	22.50
O	08.70	35.20
Si	04.50	03.50
Ti	58.60	30.70
Cu	18.50	08.00
	Totals 100	

Octadecyltrimethoxysilane is an organosilicon compound, which is used for preparing hydrophobic coatings and self-assembled monolayers[27]. The self-assembly process for the synthesis of TiO_2 hollow nanospheres are strongly dependent on the reaction kinetics and the amount of the octadecyltrimethoxysilane. To gain a better understanding on the growth mechanism of these hollow nanospheres, the products formed at early stage were collected for TEM analysis. The product in white obtained at 120 ºC for 1 h is composed of TiO_2 nanoparticles with *ca*. 5-6 nm in diameter (data not shown). In addition, for comparison, the experiments were carried out under different temperature and in presence of different amount of octadecyltrimethoxysilane, while other experimental conditions were kept the same. Fig. 5b showed that the only TiO_2 nanoparticles were obtained in absence of octadecyltrimethoxysilane and hollow semi-spherical could be obtained when the amount of octadecyltrimethoxysilane was increased to 20 μL (Fig. 5c). Fig. 5a shows that hard nanospheres could be obtained when the experiment was carried out at 60 ºC[26]. The proposed growth mechanism for the anatase TiO_2 hollow nanospheres was illustrated in Fig. 1. In a word, the suitable amount of octadecyltrimethoxysilane and temperature played key roles in producing hollow TiO_2 nanospheres.

In order to evaluate the photocatalytic property of the as-prepared sample, 40 mg the as-prepared sample was used to degradation rhodamine-B with a concentration of 3 mg/L. Before photodegradation under UV irradiation, the catalysts and rhodamine-B mixed solution were kept in the dark for 0.5 h to ensure that rhodamine-B was adsorbed to reach saturation on the surface of catalysts. The concentration of rhodamine-B is determined by UV-visible spectrophotometer according to the absorption of at 553 nm. Fig. 6 shows the adsorption curve of rhodamine-B aqueous solution after UV irradiation with different time by using the as-prepared sample as catalysts. With the extension of irradiation, the concentration of rhodamine-B was decreased gradually. When the irradiation time increased to 75 min, the degradation of rhodamine-B is completely finished.

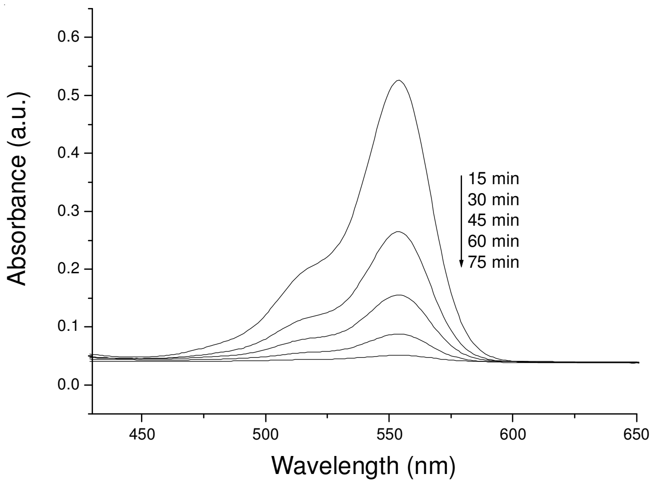

Fig. 6. UV-visible adsorption spectra showing UV-degradation of rhodamine-B using the as-prepared TiO_2 hollow microspheres

Conclusion

In summary, anatase TiO_2 hollow nanospheres were successfully synthesized from tetrabutyl titanate using octadecyltrimethoxysilane as structure-directing agent at 120 ºC. Octadecyltrimethoxy-silane and temperature played key roles in producing hollow TiO_2 nanospheres. The anatase TiO_2 hollow nanospheres are with 700 nm in diameter and 30 nm in shell width. The morphology and size of the as-prepared sample can be adjusted by varying the temperature and the amount of octadecyltrimethoxysilane. On the other hand, the as-prepared sample shows a good photocatalysis performance on rhodamine-B under irradiation of UV light. In addition, this approach could be extended to synthesize other metal oxides with hollow nanostructures. In particular, the as-synthesized TiO_2 hollow nanospheres will be of great importance due to their potential applications in photocatalysis, drug delivery, separations and cell targeting, *etc*.

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