

应用于热控的壳厚可控核壳结构 $\text{SiO}_2@\text{TiO}_2$ 颗粒制备

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摘要: 利用 Stöber 方法合成了平均粒径在 800 nm, 球形度、单分散性良好的 SiO_2 微球, 再将其作为制备核壳结构 $\text{SiO}_2@\text{TiO}_2$ 颗粒的内核。利用钛酸四丁酯水解反应, 在 SiO_2 内核上包覆制备了壳厚在 30~100 nm 的 TiO_2 壳层, TiO_2 壳层厚度可根据水解反应中钛酸四丁酯的量调控。将制得的 $\text{SiO}_2@\text{TiO}_2$ 核壳结构颗粒在 550 °C 煅烧 1 h, 氧化钛壳层的晶型转变为锐钛矿相, 晶型转变为锐钛矿相的 TiO_2 更适合作为填料应用于近红外反射涂层。本文合成厚度可控 $\text{SiO}_2@\text{TiO}_2$ 微球的方法是一种改进的溶胶凝胶方法, 即在溶胶凝胶方法的基础上增加水热合成工艺。另外, 本合成方法工艺简单, 无表面活性剂或者耦合剂的引入。

关键词: 水热合成; 核壳粒子; 溶胶-凝胶

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Synthesis of $\text{SiO}_2@\text{TiO}_2$ Core-Shell Particles with Controlled Shell Thickness for Thermal Management Applications

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Abstract: Titania coating on silica core particles was performed from monodisperse silica spheres with mean diameter of 800 nm using tetrabutyl titanate by Stöber method. The thickness of the titania coating layer was varied from 30 nm to 100 nm depending on the concentration of tetrabutyl titanate. After calcining the core-shell particles in air at 550 °C for 1 h, anatase titania coating layer was obtained suitable for scattering near infrared radiation. The preparation route is a modification of sol-gel method, i.e. a hydrothermal process is also involved. Additionally, it is a simple route without an added coupling agent or surfactant.

Key words: hydrothermal synthesis; core-shell particles; sol-gel process

0 Introduction

Pigmented coatings with high reflectivity against solar irradiation can be used to control unwanted thermal heating that occurs as materials absorb sunlight such as heat in building, battleship hulls, satellite panels, spacecraft^[1-4].

Currently titanium dioxide is the most used commercial pigment in thermal infrared reflecting coatings because it efficiently scatters infrared light due

to high refractive index. In addition, the light scattering ability of $\text{SiO}_2@\text{TiO}_2$ core-shell particles is stronger than solid or hollow spherical titania particles^[5]. An optimized pigment can attain maximum diffuse solar reflectance and reduce the pigment volume concentration required. Furthermore, for environmental reasons it is also desirable to minimize the amount of titania in the pigment.

Near-infrared radiation (700~2 500 nm) accounts for about 50% of the energy in solar irradiance

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spectrum (300~2 500 nm), so pigments that can strongly scatter near-infrared radiation are needed for infrared reflective coatings^[6]. The optimum diameter range of core-shell particles should be 0.6~0.8 μm and the optimal shell thickness should be 50~100 nm to maximize solar reflectance in the near infrared region^[5].

Over the past few decades, extensive research efforts have been devoted to the designed and controlled preparation of core-shell materials due to their unique structure-induced magnetic, optical, mechanical, thermal, electrical, catalytic properties^[7]. There are also numerous reports on $\text{SiO}_2/\text{TiO}_2$ core-shell particles by impregnation, precipitation, and sol-gel methods^[8-12]. However, most of these studies have been focused on the applications of catalysts, adsorbents and electrodes. Mostly, particle size is less than 300 nm and the thickness of the titania coatings layer is varied from 5~50 nm, which is not designed for thermal applications^[13-14]. It is useful and needed that production of $\text{SiO}_2/\text{TiO}_2$ particles is oriented towards development of heat-insulating coatings. Furthermore, hydrothermal process is introduced to synthesize fine core-shell particles and increase shell thickness, which could eliminate second-phase titania produced in hydrolysis and condensation reactions of tetrabutyl titanate (TBOT).

1 Experimental

The chemicals used for the synthesis: tetraethoxy silane (TEOS, A.R.), tetrabutyl titanate (TBOT, A.R.), isopropyl alcohol (A.R.), anhydrous ethanol, nitric acid and aqueous ammonia were obtained from Beijing Chemical Reagent Corporation (Beijing, China). All the chemicals were used as received without further purification.

1.1 Fabrication of silica cores

Mono-dispersed spherical SiO_2 particles were prepared as core particles using Stöber method^[13]. In a typical procedure for fabricating silica particles, 6.6 mL of aqueous ammonia (36wt%) was added into a mixture containing 40 mL of isopropyl alcohol and 2.7 mL of deionized water, and all the reactants were stirred for 5 minutes. 2.23 mL TEOS was added into another mixture

solution containing 48.5 mL of isopropyl alcohol, and all the reactants were stirred for 5 min. Then the two solutions were mixed and the full solution was stirred at 25 $^{\circ}\text{C}$ for 10 h. Finally, the solution was centrifuged to obtain silica particles.

1.2 Titania coating

In a typical synthesis process, 2 g of SiO_2 particles was dispersed in a mixture solution containing 25 mL of anhydrous alcohol and 0.25 mL of TBOT, and the mixture was stirred for 5 min. 0.2 mL of nitric acid was added into another mixture solution containing 25 mL of anhydrous alcohol and 10 mL of deionized water. Then the second solution was added dropwise to the first one and the full solution was stirred at 25 $^{\circ}\text{C}$ for 2 h. Finally, a direct hydrothermal treatment of the mixed solution yielded fine core-shell spheres at 180 $^{\circ}\text{C}$ for 24 h. The thickness of titania shell can be from 30 nm to 100 nm by changing the amount of TBOT from 0.25 mL to 1 mL. After hydrothermal reaction, the particles were centrifuged, and then washed with distilled water and anhydrous alcohol for five times. The washed precipitates were dried at 90 $^{\circ}\text{C}$ for 10 h and finally were calcined in air at 550 $^{\circ}\text{C}$ for 1 h.

The formation and morphology of the as-prepared SiO_2 and $\text{SiO}_2/\text{TiO}_2$ particles were investigated by scanning electron microscope (SEM) (S-4800, operated at 5 kV), transmission electron microscopy (TEM) (JEM-2100F, operated at 160 kV), and X-ray diffraction patterns were recorded on a Dmax-3B Advance X-ray diffractometer equipped with graphite monochromatized $\text{Cu K}\alpha$ radiation ($\lambda=0.15418\text{ nm}$) from 10 $^{\circ}$ to 80 $^{\circ}$ degrees (2θ) with a voltage of 40 kV and a current of 40 mA.

2 Results and discussion

Many factors affect the sol-gel process: pH value, temperature, molar ratio of alkoxide to water, and solvents. However, solvents affect the diameter of silica spheres^[15]. In detail, atom array, molecular flexibility, surface tension, and viscosity of solvents affect the sphere diameter. In this study, isopropyl alcohol was selected as solvent for its long carbon chain to obtain large silica particles. As shown in Fig.1, spherical silica

particles with size about 800 nm of narrow distribution, high monodispersity and non-agglomeration are synthesized using Stöber method at 25 °C.

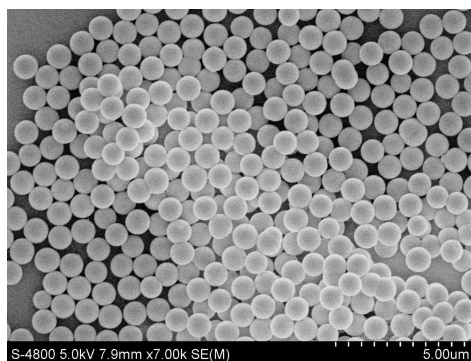


Fig.1 SEM image of silica spherical particles of about 800 nm synthesized using Stöber method at 25 °C

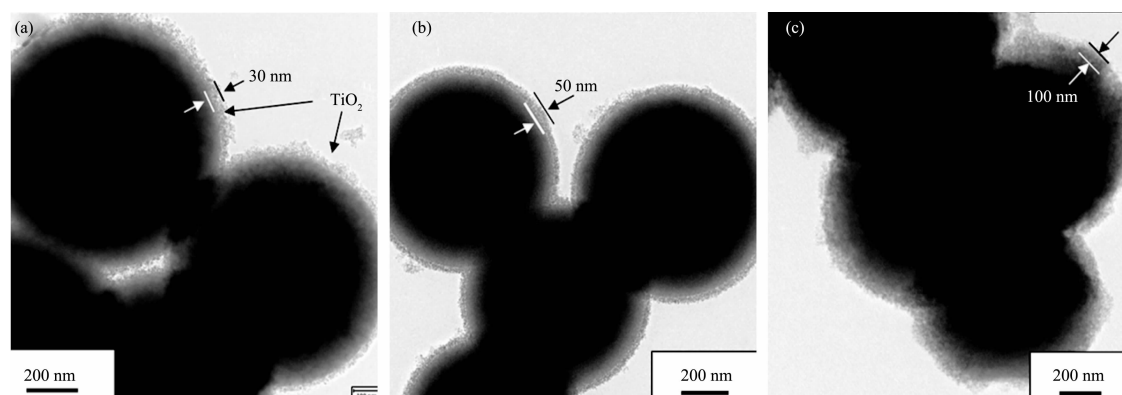
At the beginning of hydrolysis and condensation reactions of TEOS with an alkali catalyst, a large number of small silica crystal nucleuses are formed quickly. As reaction goes on, both the concentration of TEOS and the number of small silica crystal nucleuses decrease. When the concentration of TEOS is decreased below the critical nucleation concentration, new crystal nucleus cannot be generated. Hydrolysis and condensation reactions of residual TEOS occur on the surface of primary crystal nucleus resulting in 800 nm of the silica spheres at the end of the reaction.

At the beginning of the reaction, the diameter of spheres is increased. However, as the spheres' diameter becomes large enough, a decrease in the curvature of the spheres brings down the driving force and surface diffusion coefficient. Finally, the growth of the spheres

becomes very slow and the diameter reaches 800 nm suitable for infrared reflective coatings. Then these particles were used as core particles to synthesize core-shell structural particles.

According to the sol-gel process, TiO_2 is generated by the hydrolysis and condensation of TBOT, and then deposits on the surface of the SiO_2 spheres to form a shell layer. The production of a uniform shape of core-shell particles is directly dictated by the TiO_2 nano-particle generation and its deposition on the core particles (Fig.2 (a), (b), and (c)). That is, when the generation rate of TiO_2 nano-particles by the sol-gel process is below the deposition rate of TiO_2 particles on the core particles, all the TiO_2 particles are consumed to form the shell layer. The results badly call for careful control of the generation rate of TiO_2 nano-particles by adjusting the reaction conditions for the hydrolysis and condensation, including the concentrations of TBOT and H_2O , and reaction temperature in the sol-gel process. Since TBOT is a precursor, the generation of TiO_2 nano-particles is expected to be promoted with increasing the concentration of TBOT, thus thickening the shell layer.

In order to increase the thickness of the titania layer, we increased the concentration of the precursor. Some authors suggested that concentrations of TBOT in excess of $0.025 \text{ mol} \cdot \text{L}^{-1}$ would result in aggregation of the coated particles^[11]. However, in our work, no aggregation of the core particles was observed because hydrolysis rate of TBOT was controlled and



(a) TEM image for core-shell particles prepared at 0.25 mL of TBOT, (b) TEM image for core-shell particles prepared at 0.5 mL of TBOT, and (c) TEM image for core-shell particles prepared at 1 mL of TBOT

Fig.2 TEM images for $\text{SiO}_2/\text{TiO}_2$ core-shell particles prepared under various reaction conditions

hydrothermal process was introduced.

Uniform core-shell particles are produced and the thickness of titania shell is varied from 30 nm to 100 nm depending on the amount of TBOT (Fig.2 (a), (b), and (c)). Up to the amount of TBOT of 1 mL, the layer thickness of the core-shell particles is increased to 100 nm (Fig.2(c)). The amount of TBOT is controlled during reaction process, so the generation of titania crystal nucleuses is controlled without causing aggregation of the core particles. The smoothness of the coating shown here leads us to believe that the process involves controlled hydrolysis of the TBOT followed by heterogeneous nucleation of the hydrous titanium oxide on the silica sphere.

The generation of TiO_2 particles is facilitated when increasing the temperature. At 25 $^{\circ}\text{C}$, the deposition of TiO_2 particles seems to be enough to consume the generated TiO_2 particles.

Hydrothermal process is introduced to consume second-phase titania particles. Hydrothermally obtained powders could be produced with a different microstructure, morphology and phase composition by varying parameters such as temperature, pressure, duration of process, concentration of chemical species. Moreover, hydrothermal process provides a high temperature and high pressure environment. Mass transfer rate is so high in hydrothermal process that the second-phase titania particles can be consumed easily. In this study, the as prepared titania coating is

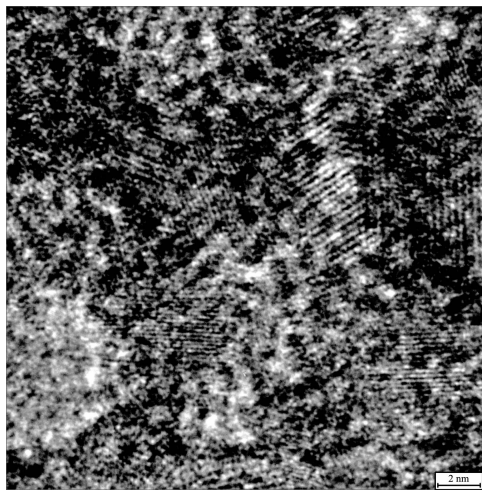


Fig.3 Titania crystals on the surface of the silica core particles

amorphous. When the sample is heated to 550 $^{\circ}\text{C}$ in air, the titania is crystallized to form the anatase phase. Within the titania layer, the anatase crystallites are randomly oriented (Fig.3).

XRD patterns of SiO_2 particles and $\text{SiO}_2@\text{TiO}_2$ core-shell particles after calcination at 550 $^{\circ}\text{C}$ for 1 h are shown in Fig.4. XRD patterns of all the $\text{SiO}_2@\text{TiO}_2$ core-shell particles with various shell thickness show clear anatase diffractions corresponding to the planes (101), (004), and (200) at $2\theta=25.3^{\circ}$, 37.8° and 48.1° , respectively. With increase in shell thickness, the FWHM (full width at half maximum) of anatase peaks decrease, indicating larger crystallite sizes.

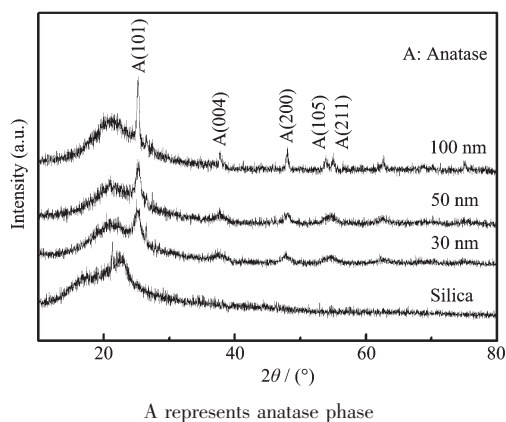


Fig.4 XRD patterns for SiO_2 amorphous particles and $\text{SiO}_2@\text{TiO}_2$ core-shell particles of different shell thickness after calcination at 550 $^{\circ}\text{C}$ for 1 h

3 Conclusions

Selecting isopropyl alcohol as solvent, controlling of tetraethoxy silane (TEOS) concentration and solution pH value, silica spheres of about 800 nm were synthesized by sol-gel method and used as core spheres to fabricate core-shell particles. Tetrabutyl titanate can be utilized to produce thick and uniform titania coatings with various shell thickness on monodispersed silica spheres while maintaining high monodispersity and low aggregation. Low temperature, dropwise feeding of reactants, and hydrothermal process are main means to obtain high monodispersity and low aggregation core-shell particles. TEM images indicate that the thickness of titania coating layer is varied from 30 nm to 100 nm, and the crystal structure is anatase from the XRD results.

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