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# Facile synthesis of silica–titania core–shell microsphere and their optical transmission spectra

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ABSTRACT

$SiO_2$–$TiO_2$ core–shell microspheres are prepared by the liquid-phase deposition method, in which anatase $TiO_2$ are shells and $SiO_2$ sphere as cores. The positions of the transmittance peak of the water suspension for $SiO_2$–$TiO_2$ core–shell microspheres are moving toward the long wave number. The red-shift is maybe caused by the variation in the $TiO_2$ shell thickness.



## 1. Introduction

In recent years, the preparation and study of core–shell spheres with uniform structures have attracted substantial interest because of their physicochemical properties. The isolation of the core from the surroundings can be used to create materials with fundamentally different properties to those of the bare microspheres. For example, the coating may be used to passivate the core chemically, [1] as a size-selective membrane to control catalytic processes at the core surface, [2] as the photocatalyst for treating wastewater, [3,4] or it may be used as a sandwich structure to modify its optical properties. [5–7] Core–shell particles have been synthesized using metals, semiconductors, metal oxides, alloys, dyes, biomolecules, etc. as the core or shell. Among the various types of core–shell particles, $SiO_2$ and $TiO_2$ either as core or shell have attracted considerable attention. Primarily this is because silica includes easy and controlled formation, possibility of functionalization by a variety of organic or inorganic molecules, [8] $TiO_2$ possess low absorption in the visible and near infrared regions and relatively high refractive index [9].

Silica spheres encapsulated in titania have been investigated as photocatalysts and photonic devices [3,10–13]. For example, Li et al. [3] synthesized $SiO_2$–$TiO_2$ core–shell microsphere by using the liquid-phase deposition (LPD) method, this photocatalyst can be easily separated from the reaction medium by sedimentation. But, this work doesn't focus on the changes of $TiO_2$ shell thickness and the related optical properties of $SiO_2$–$TiO_2$ core–shell sphere. Subsequently, Nakamura et al. [11] prepared closed-packed titania-coated silica spheres using a layer-by-layer (LBL) templating method and studied the optical properties of those colloidal crystalline arrays. Liu et al. [12] synthesized silica–titania composite submicrospheres through the hydrolysis of titanium alkoxide, the transmission spectra of assembly of $TiO_2$/$SiO_2$ complex spheres was investigated. Among these literatures, researchers are more concerned about photonic properties of the solid silica–titania order structure; there are few researches to indicate the optical properties of $SiO_2$–$TiO_2$ core–shell microsphere suspension.

In this work, we report facile synthesis of $TiO_2$ shell on the $SiO_2$ core by the liquid-phase deposition under moderate condition and find their special optical transmission spectra in the aqueous solution. The effect of the shell thickness on the optical transmission spectra was investigated.

## 2. Experimental

$SiO_2$ cores prepared using the ammonia-catalyzed Stöber method is very uniform with smooth surfaces [14]. $SiO_2$–$TiO_2$ core–shell microspheres were prepared according to the previously reported method [3,15] with some modifications. The surface of $SiO_2$ microspheres was established by the adsorption of polyelectrolytes using the layer-by-layer (LbL) technique. 20 mL of a PAH solution containing 1 g/L of PAH (poly allylamine hydrochloride) was added to 30 mL of a colloidal suspension containing 0.2 g of silica spheres under magnetic stirring for 1 h. Then, the microspheres were collected by centrifugation followed by washing using deionized water three times to remove residual PAH. The 0.2 g above products was dispersed in 20 mL of

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deionized water. A given amount of $(NH_4)_2TiF_6$ (0.1 mol/L) solution and 4 mL $H_3BO_3$ (0.6 mol/L) were added to the above solution followed by ultrasonication for 4 h. The white precipitate was centrifuged, washed with deionized water for four times and then dried in a vacuum oven at 60 °C. 0.002 g above-mentioned sample dispersed in 20 ml aqueous solution and was sealed in a glass vessel for optical observation and measurement. X-ray diffraction (XRD) patterns were obtained with a Bruker D8 Advance/Discover diffractometer, using CuK$\alpha$ radiation. The SEM and TEM images were carried out with the field-emission scanning electron microscopy (FE-SEM, HITACHI S-4800) and transmission electron microscope (FEI Tecnai G2 F20). UV–visible transmittance spectra were characterized with UV/Vis/NIR Spectrometer (Perkin-Elmer, Lambda 950).

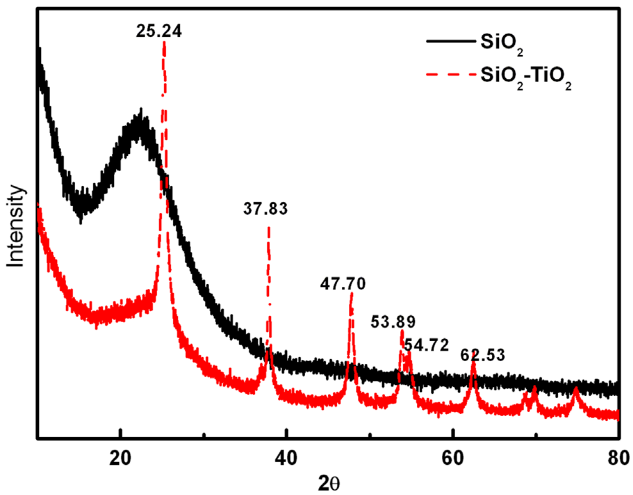


**Fig. 1.** PAGE \# "'Page: '#"" XRD patterns of $SiO_2$ and $SiO_2$–$TiO_2$ core–shell microspheres. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)

## 3. Results and discussion

XRD patterns of $SiO_2$ microspheres and $SiO_2$–$TiO_2$ core–shell microspheres are shown in Fig. 1. An intense broad peak is attributable to the amorphous silica core (black curve) [16]. The diffraction peaks for $SiO_2$–$TiO_2$ core–shell microspheres can be readily indexed to that of the anatase phase (red curve) of $TiO_2$ structure (PDF ICDD. 21-1272).

The morphology and structure of $SiO_2$–$TiO_2$ core–shell microspheres are explored by scanning electron microscopy (SEM), transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM). As is seen from Fig. 2a, the silica spheres synthesized in this work possessed a uniform size and smooth surface. The mean diameter of $SiO_2$ microspheres was about 1360 nm. With the assistance of a layer of PHA, uniform titania shells were obtained on the surface of $SiO_2$ microspheres (see Fig. 2b), the diameter of $SiO_2$-$TiO_2$ core-shell microspheres was increased, which is almost consistent with the TEM image (see Fig. 2c). As clearly seen from Fig. 2d, the $TiO_2$

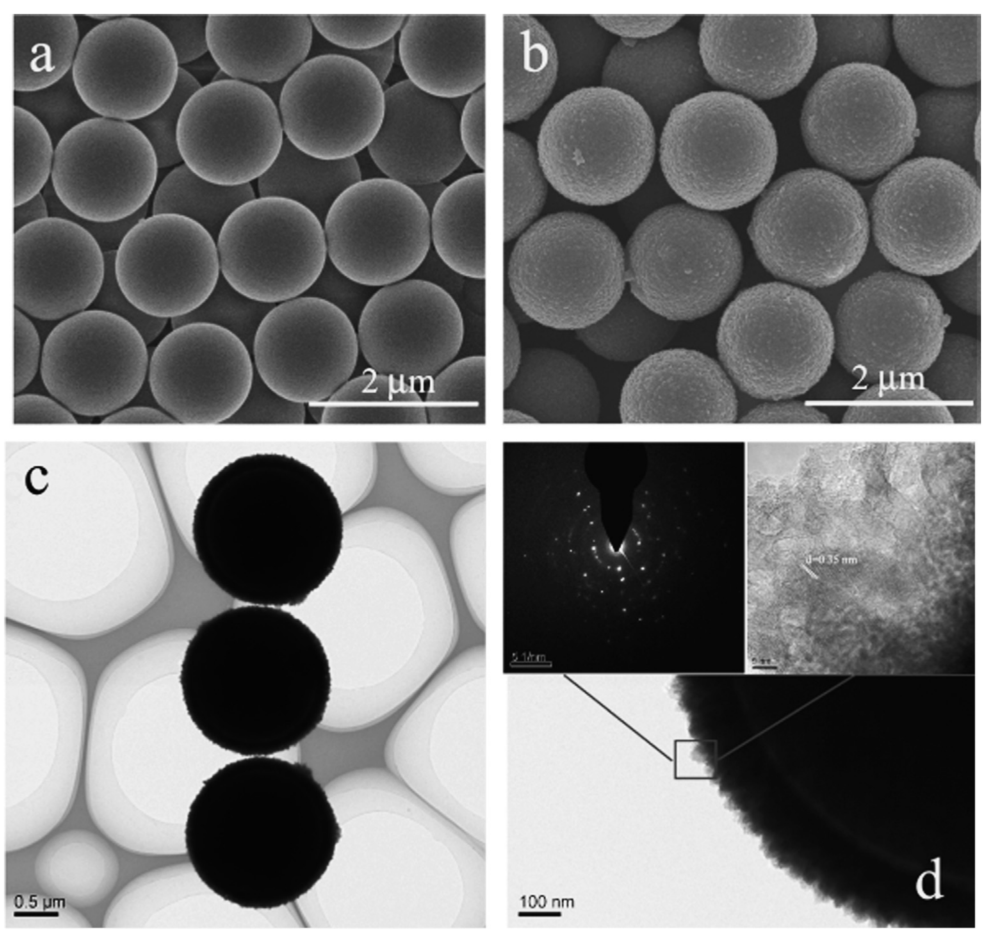


**Fig. 2.** (a) SEM of $SiO_2$ microspheres, (b) SEM of $SiO_2$–$TiO_2$ core–shell microspheres, (c) TEM of $SiO_2$–$TiO_2$ core–shell microspheres, and (d) HRTEM of $SiO_2$–$TiO_2$ core–shell microspheres. The insets show a local image of the shell's SAED image and HRTEM image within the frame of (d).