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$SiO_2/TiO_2/Ag$ multilayered microspheres: Preparation, characterization, and enhanced infrared radiation property

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ABSTRACT

$SiO_2/TiO_2/Ag$ core–shell multilayered microspheres were successfully synthesized by the combination of anatase of TiO_2 modification on the surfaces of SiO_2 spheres and subsequent Ag nanoparticles deposition and Ag shell growth with face-centered cubic (fcc) Ag. The composites were characterized by TEM, FT-IR, UV–vis, Raman spectroscopy and XRD, respectively. The infrared emissivity values during 8–14 μm wavelengths of the composites were measured. The results revealed that TiO_2 thin layers with the thickness of ~10 nm were coated onto the SiO_2 spheres of ~220 nm in diameter. The thickness of the TiO_2 layers was controlled by varying the amount of TBOT precursor. Homogeneous Ag nanoparticles of ~20 nm in size were successfully deposited by ultrasound on the surfaces of SiO_2/TiO_2 composites, followed by complete covering of Ag shell. The infrared emissivity value of the SiO_2/TiO_2 composites was decreased than that of pure SiO_2. Moreover, the introduction of the Ag brought the remarkably lower infrared emissivity value of the $SiO_2/TiO_2/Ag$ multilayered microspheres with the lowest value down to 0.424. Strong chemical effects in the interface of SiO_2/TiO_2 core–shell composites and high reflection performance of the metal Ag are two decisive factors for the improved infrared radiation performance of the $SiO_2/TiO_2/Ag$ multilayered microspheres.

1. Introduction

Recently, core–shell hybrid particles have attracted considerable attentions since the core could offer protection to the cores and introduce new properties to the hybrid structure [1]. There have been many potential applications of the core–shell hybrid particles in different fields, such as optoelectronics, optical devices, and catalysis et al. [2–5]. So far, the research of ordered core–shell structures has mainly focused on the deposition of organic, inorganic or metallic layers onto the surface of the specific core materials. These structures can adjust the composition and the assembly sequence of core and shell effectively, thus further modulate the properties of the composite material. A large number of binary core–shell composite materials has been widely investigated such as inorganic/inorganic [6,7], inorganic–metal [8], metal–metal [9,10], organic–inorganic nanocomposites [11] and so on. Among them, the materials of Au, Ag, SiO_2, TiO_2, and ZnO et al. are the most commonly used for the construction of the core–shell structure. To date, sono-chemical synthesis [12], surface functionalization deposition [13], surface sol–gel process [4,5], microemulsion reaction [14,15], and emulsion polymerization [16] have been applied to obtain the various core–shell structures of inorganic, metal, or organic coatings. Moreover, a small number of ternary core–shell composites have been designed and prepared such as $Fe_3O_4/Au/Ag$ [17], $Fe_3O_4/Ag/SiO_2$ [18], $Au/SiO_2/Ag$ [19], $SiO_2/Au/TiO_2$ [20] and $SiO_2/Ni/TiO_2$ [21]. In our previous work, $SiO_2/ZrO_2/Ag$ multicoated microspheres have also been prepared successfully [22]. These designed core–shell composites possess interesting optical and catalytic properties originated from special structure consist of metal and inorganic components alternately.

In this paper, we reported the preparation of $SiO_2/TiO_2/Ag$ "sandwich" core–shell composites via chemical deposition and seed-growth under ultrasonic irradiation. A thin TiO_2 layer was coated onto the SiO_2 spheres for the fabrication of SiO_2/TiO_2 core–shell composites. The Ag nanoparticles were further loaded on the SiO_2/TiO_2 substrate and acted as seeds for the growth of full Ag shell, resulting in the formation of $SiO_2/TiO_2/Ag$ composites. The structure and composition of core–shell multilayer structure were traced via Transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FT-IR), Ultraviolet and visible spectrophotometry (UV–vis), Raman spectroscopy and X-ray diffraction (XRD). The infrared emissivity during 8–14 μm wavelengths of the composites was measured, on which the

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influence of the coating composition of the coating layers were discussed.

2. Materials and methods

2.1. Materials

Tetraethoxysilane (TEOS, 99%) was obtained from Shanghai Chemical reagent Company and distilled under reduced pressure prior to use. Tetrabutyl titanate (TBOT), Silver nitrate ($AgNO_3$), Poly (vinylpyrrolidone) (PVP, K30, polymerization degree 360), *N*, *N*-Dimethylformamide (DMF), aqueous ammonia and formaldehyde, also from Shanghai Chemical reagent Company, were used as received without further purification. Ultrapure water was used in all preparations.

2.2. SiO_2 spheres preparation

Monodisperse silica spheres were synthesized by the well-known Stöber–Fink–Bohn method [23]. In a 100 mL flask, 50 mL absolute ethanol containing 1 M ammonia and 10 M H_2O was fully mixed for a few minutes using a magnetic stirrer, into which 0.28 M TEOS was added. The hydrolysis–condensation was started within 5 min after the addition of TEOS going with the present opalescence of the mixture. The reaction went on for 3 h maintaining at 25 °C. The final outcome was washed with water three times by centrifugation–ultrasonic dispersion process.

2.3. Preparation of SiO_2/TiO_2 core–shell composites

TiO_2 coatings on the surfaces of SiO_2 spheres were synthesized by the hydrolysis and condensation of TBOT precursor similar to the literature [24]. Typically, SiO_2 (0.1 wt%) were dispersed in 100 mL ethanol, followed by the addition of TBOT dropwise with the concentration of 0.01 M and 0.02 M in ethanol respectively. The same amount of water was added into the above mixture. The mixture was stirred and refluxed for 1.5 h to obtain $SiO_2/TiO_{2(1)}$ and $SiO_2/TiO_{2(2)}$ core–shell composites respectively. Subsequently, the resulting products were centrifugally separated and washed with ethanol and water. The samples were then calcined at 650 °C for 4 h.

2.4. Preparation of SiO_2/TiO_2/Ag multilayer microspheres

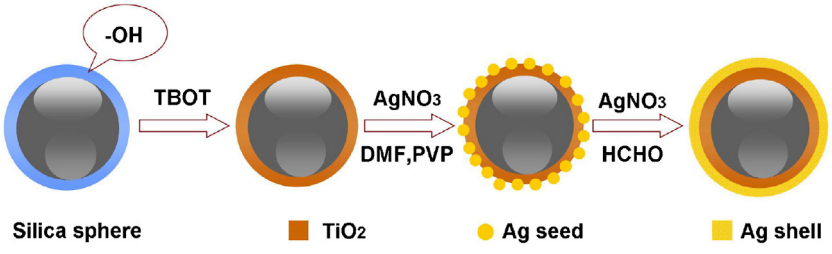
The preparation method of the SiO_2/TiO_2/Ag multilayer microspheres was similar to the procedure described in the previous work [22]. Precisely, the preparation process was divided into two steps: the initial deposition of Ag seeds on the surfaces of $SiO_2/TiO_{2(2)}$ core–shell composites and further growth of Ag shells. The typical procedure was processed as follows. 5 mL of $AgNO_3$ (0.8 mM) aqueous solution was added to a 45 mL PVP solution in DMF ((10)$AgNO_3$/(10)PVP(2) = 0.1), following the addition of silica sphere (0.02 wt%). The mixture was exposed to high-intensity ultrasound irradiation for 30 min. Ultrasound irradiation was accomplished with a high-intensity ultrasonic probe (Xinzhi Co., China, Ti-horn IX20 kHz IX800 W/cm^2) immersed directly in the reaction solution. When the reaction was finished, a dark brown precipitation was observed. The mixture was centrifugally separated from the suspension and ultrasonically washed with water. The above procedures were repeated two times in order to increase the density of silver seeds on the surface, which was signed as $SiO_2/TiO_2/Ag_{(sdx,\ x=1,2)}$. To further growth of a Ag shell, 10 mg of the seeded colloid particles aqueous solution (0.1 wt%) was mixed with 10 mL of a solution of $AgNO_3$ (1.5 mM), and then 25 μL of formaldehyde was added, immediately followed by 25 μL of concentrated ammonia. The above procedures were also repeated two times for the fabrication of $SiO_2/TiO_2/Ag_{(sh)}$.

2.5. Characterization

The samples were characterized by X-ray diffraction (XRD) using Cu K*a* radiation of $k = 1.54056$ Å operating at 40 kV and 30 mA with a Bruker D8 advanced diffractometer. The size and shape of the particles were observed under a transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM) (JEM-2100, Japan, with an accelerating voltage of 200 kV). For the TEM observation, the samples were ultrasonicated in ethanol to ensure that they were well dispersed, and then a drop of the dispersed sample was left to dry on a commercial, carbon-coated Cu grid. Fourier transformation infrared (FT-IR) spectra were obtained using a Thermo Nicolet 6700 spectrometer. The samples were prepared in the form of KBr pellets. UV–vis absorption spectra were measured with a SHIMADZU UV-2600 spectrophotometer, using a quartz cell with a 1 cm optical path length. Raman spectra were collected by a Raman spectrometer (SuperLabRam II, Dilor, France) using a He–Ne light-emitting diode laser ($\lambda = 632.8$ nm) at 5 mW. Infrared emissivity values of the samples were carried out on IRE-I Infrared emissivity measurement instrument of Shanghai Institute of Technology and Physics, China.

3. Results and discussion

The formation of SiO_2/TiO_2/Ag multilayer microspheres can present a good description for three steps as shown in Scheme 1. Firstly, the TiO_2 layers with tunable thickness by changing the amount of the TBOT precursor are modified on the SiO_2 spheres. The suitable ratio of TBOT precursor and water, to a great extent, affects the formation of uniform TiO_2 layers with no second-phase particles [24]. Subsequently, the Ag nanoparticles decorated SiO_2/TiO_2 multilayer composites are generated via the reduction of silver ions by DMF using PVP as protecting and complex agent under ultrasonic irradiation. PVP plays an important role in promoting the nucleation of the Ag nanoparticles in the reaction. Moreover, high ultrasonic power (800 W) also gives the Ag nanoparticles strong driving forces toward the SiO_2/TiO_2 surfaces at a high speed, resulting in the Ag seeds-modified surfaces. On the basis of the Ag seeds, complete Ag shell further grows on the surfaces of $SiO_2/TiO_2/Ag_{(sd)}$,



Scheme 1. Reaction scheme for the formation of SiO_2/TiO_2/Ag multilayer microsphere.