Journal of Solid State Chemistry 184 (2011) 2617–2622

Contents lists available at ScienceDirect

Journal of Solid State Chemistry

journal homepage: www.elsevier.com/locate/jssc

Preparation, characterization, and infrared emissivity property of optically active polyurethane/TiO_2/SiO_2 multilayered microspheres

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ARTICLE INFO

Article history:
Received 16 March 2011
Received in revised form
15 July 2011
Accepted 17 July 2011
Available online 27 July 2011

Keywords:
Optically active
TiO_2/SiO_2
Multilayered
Infrared emissivity

ABSTRACT

Optically active polyurethane/titania/silica (LPU/TiO_2/SiO_2) multilayered core–shell composite microspheres were prepared by the combination of titania deposition on the surface of silica spheres and subsequent polymer grafting. LPU/TiO_2/SiO_2 was characterized by FT-IR, UV–vis spectroscopy, X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), thermogravimetric analysis (TGA), SEM and TEM, and the infrared emissivity value (8–14 μm) was investigated in addition. The results indicated that titania and polyurethane had been successfully coated onto the surfaces of silica microspheres. LPU/TiO_2/SiO_2 exhibited clearly multilayered core–shell construction. The infrared emissivity values reduced along with the increase of covering layers thus proved that the interfacial interactions had direct influence on the infrared emissivity. Besides, LPU/TiO_2/SiO_2 multilayered microspheres based on the optically active polyurethane took advantages of the orderly secondary structure and strengthened interfacial synergistic actions. Consequently, it possessed the lowest infrared emissivity value.

1. Introduction

Stealthy technique aims at concealing the characteristic of the objective in order to evade from the detection. The infrared camouflage varies the infrared radiation features and brings down the detectable probability of the target. Controlling the temperature and infrared emissivity is the common method in the infrared stealthy technology [1,2]. The decrease of infrared emissivity becomes especially important on the occasion when the temperature could not be reduced [3,4]. Accordingly, a great number of new materials with low infrared emissivity have been prepared and investigated, such as metallic thin films, semiconducting materials, nanomaterials, and inorganic/organic composites [5–8]. Among them, the inorganic/organic composites composed of semiconducting nanomaterials and organic macromolecules especially have the potential for applications in low infrared emissivity coatings [9].

Core–shell construction particles with various morphologies and chemical compositions have become one of the most useful resources for functional materials [10–13], because of their unique properties (e.g., optical, electrical, catalytic, magnetic, and mechanical). In recent studies, V_2O3@C core–shell hybrid was prepared by Odani et al. [14], and used as the active mass in composite cathodes for rechargeable lithium ion batteries. Lv et al. [15] reported the synthesis of Fe_3O_4/SiO_2/Ag composite with core/shell/particles structure and its application in surface-enhanced Raman scattering. However, to the best of our knowledge, few previous reports have related to the exploitation of multilayered core–shell composite microspheres as the infrared stealth materials.

Optically activity macromolecules possess not only the advantages of any other polymers but also some unique characteristics [16–18], including ordered secondary structure, adjustable chiral parameter, and abundant inter-chain interaction as well. Many naturally and synthetic optically active polymers have been used as the chiral stationary phase (CSP) in high-performance liquid chromatography (HPLC), liquid crystals for display, catalysts for asymmetric synthesis and so on [19–21]. Amino acids are the most common chiral sources that have been widely used in the synthesis of optically active materials [22]. Polymers based on amino acid moieties are of interest due to their inherent biological compatibility and degradability, making them ideal candidates for a variety of biomaterial application [23]. Moreover, amino acid-based chiral polymers could have induced crystallinity with the ability to form higher ordered structures that exhibit enhanced properties [24,25]. In the present study, we focused on the preparation and infrared emissivity property of optically active polyurethane/titania/silica (LPU/TiO_2/SiO_2) multilayered core–shell composite microspheres. Inorganic/organic nanohybrids could combine the advantages of organic polymers and nanomaterials. Besides, possible interfacial interaction mechanism and the orderly secondary structure of the optically active polyurethane related to infrared emissivity of the composite were discussed.

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doi:10.1016/j.jssc.2011.07.027

2. Experimental

2.1. Materials

Tetraethoxysilane (TEOS, 99%) and 1-pentanol were purchased from Shanghai Chemical Reagent Company and distilled under reduced pressure prior to use. Triphosgene was obtained from Aldrich. Methyltrioctylammonium chloride (Aliquat®336) was produced by Acros Organics. Tetrabutyl titanate (TBOT), γ-methacryloxypropyl trimethoxysilane (KH550), L-tyrosine, thionyl chloride and other chemicals were all obtained from Shanghai Chemical Reagent company and used as-received. Deionized water was used for all the experiments.

2.2. Analysis and characterization

Melting point (mp) was determined by using an X-4 micromelting point apparatus. The optical rotations were measured on a WZZ-2S (2SS) digital automatic polarimeter at room temperature and the wavelength of sodium lamp was 589.44 nm. FT-IR spectra were recorded on a Bruker Tensor 27 FT-IR spectrometer at room temperature using KBr pellets. ^{1}H NMR spectra measurements were recorded on a Bruker AVANCE 300 NMR spectrometer. UV–vis spectra were recorded with a Shimadzu UV 3600 spectrometer using a 10 mm quartz cell at room temperature. X-ray diffraction (XRD) measurements were carried out on a Rigaku D/MAX-R with a copper target at 40 kV and 30 mA. The powder samples were spread on a sample holder, and the diffractograms were collected from 5° to 80° at the speed of 5°/min. X-ray photoelectron spectroscopy (XPS) tests were done on a Kratos Amicus (Britain) spectrometer at 12 kV and 180 W. Thermal analysis was conducted by using a TGA apparatus (TA Q-600, TA Instruments) at the heating rate of 10 K/min in a nitrogen atmosphere. TEM micrographs were obtained using a Hitachi H-600 microscope operating at 120 kV. Samples were prepared by placing the particle suspensions on a Cu grid (200 mesh; placed onto the filter paper to remove excess solvent) and allowing the solvent to evaporate at room temperature. SEM images were obtained on the LEO-1530VP microscope. Infrared emissivity values of the samples were investigated on the IRE-I Infrared Emissometer of Shanghai Institute of Technology and Physics, China.

2.3. Preparation of monodisperse SiO_2 microspheres

Amorphous SiO_2 nanoparticles were synthesized by the hydrolysis of TEOS with aqua ammonia according to the literature [26]. The obtained SiO_2 spheres were washed thoroughly with water and then dried under vacuum at room temperature.

2.4. Preparation of TiO_2/SiO_2 microspheres and A-TiO_2/SiO_2

Titania was coated on monodisperse SiO_2 spheres by using a similar procedure reported by Datye with the co-workers [27], the samples were then treated at 500 °C for 8 h. Two gram of TiO_2/SiO_2 microspheres were dispersed into 50 mL anhydrous ethanol with ultrasonication to obtain the suspension and 0.5 mL of KH550 was added later. The mixture was exposed to high-intensity ultrasound irradiation for 1 h at 25 °C. The resulting KH550-modified TiO_2/SiO_2 microspheres were collected by centrifuge and washed with ethanol and water to obtain A-TiO_2/SiO_2.

2.5. Monomer synthesis

2.5.1. HC1 salt

L-Tyrosine amyl ester hydrochloride was prepared as follows: to 1-pentanol (75 mL) at -5 °C, thionyl chloride (6.55 g, 0.055 mol) was dropped slowly in order to maintain the temperature under 0 °C. Then L-tyrosine (9.05 g, 0.05 mol) was added. The resulting mixture was stirred at 90 °C for 12 h. As the mixture cooled, the product was precipitated by the addition of diethyl ether (200 mL). The precipitate was collected, washed with diethyl ether (2×50 mL^2), and dried to give the off-white L-tyrosine amyl ester hydrochloride. Yield: 11.8 g (82%). Mp: 166–167 °C $[\alpha]_D^{25} = +6.5°$ (C=1 g/dL, methanol). ^{1}H NMR (300 MHz, DMSO-d$_6$): δ 0.85 (t, 3H, –CH_3), 1.19–1.23 (m, 4H, –CH_2–), 1.45–1.48 (m, 2H, –CH_2–), 2.90–3.06 (m, 2H, –PhCH_2–), 4.03 (t, 2H, –OCH_2–), 4.13 (t, 1H, $>$CH–), 6.69–7.02 (m, 4H, –C_6H_4–), 8.57 (s, 3H, –$N^+H_3Cl^-$), 9.45 (s, 1H, –OH). IR (ν/cm^{-1}): 3290 (O–H), 2954, 2933, 2870, 1739 (C=O), 1516, 1238, 842.

2.5.2. Isocyanate-phenol

Phosgene was obtained by the decomposition of triphosgene with Aliquat®336 according to the literature [28]. The phosgene that developed during the reaction was collected in CH_2Cl_2 and preserved below 0 °C. 1.45 g L-tyrosine amyl ester hydrochloride was added to the stirred solution of phosgene (5–10 g, 0.05–0.1 mol) in 50 mL CH_2Cl_2 which was kept at -5 °C. Then 50 mL of saturated aqueous sodium bicarbonate was dropped slowly within 10 min. The resultant mixture was stirred at 0–5 °C for an hour and then bubbled with nitrogen in order to remove the residual phosgene. The organic layer was collected, and the aqueous layer was extracted with three 5-mL portions of CH_2Cl_2. The combined organic layers were dried ($MgSO_4$), vacuum filtered, and concentrated to 20 mL to afford the colorless isocyanate of L-tyrosine amyl ester solution. The solution was used in the polymerization without further purification.

The spectroscopic data of isocyanate-phenol are as follows: ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.92 (t, 3H, –CH_3), 1.33 (m, 4H, –CH_2–), 1.68 (m, 2H, –CH_2–), 2.95–3.11 (m, 2H, –PhCH_2–), 4.19 (t, 2H, –OCH_2–), 4.21 (t, 1H, $>$CH–), 6.78–7.09 (m, 4H, –C_6H_4–). FT-IR (ν/cm^{-1}): 3418 (O–H), 2958, 2933, 2257 (–N=C=O), 1738 (C=O), 1516, 1217, 1000, 832, 575.

2.6. Preparation of LPU/TiO_2/SiO_2 multilayered microspheres

The prepolymerization of isocyanate of L-tyrosine amyl ester was carried out in situ with magnetic stirring under nitrogen at room temperature for 8 h by addition of triethylamine (3 mol%) as the catalyst. Then A-TiO_2/SiO_2 was dispersed into reactor and refluxed for 10 h. After cooling to room temperature, the mixture was centrifuged, thoroughly washed with diethyl ether and dried in vacuum to obtain LPU/TiO_2/SiO_2 multilayered microspheres. Fig. 1 shows the process of preparation.

3. Results and discussion

3.1. FT-IR and UV–vis spectra analysis

The FT-IR spectra of SiO_2, TiO_2/SiO_2, A-TiO_2/SiO_2, and LPU/TiO_2/SiO_2 multilayered microspheres are shown in Fig. 2. It clearly illustrates that all IR spectra show broad peaks corresponding to –OH at about 3430 cm^{-1}. Besides, every spectrum shows relatively strong peak at 1100 cm^{-1} which corresponds to the asymmetric stretching vibration mode of the Si–O–Si bridge of the siloxane link. In addition, strong intensity of the peaks in the broad range from 500 to 800 cm^{-1} corresponding to the symmetric stretching of the Ti–O–Ti group can be observed [29] after the deposition of titania on silica spheres. When the TiO_2/SiO_2 is modified by silane coupling agent, the peaks corresponding to methyl, methylene, and N–H groups of the KH550 are found at 2935, 2850, and 3400 cm^{-1} in Fig. 2c. As it can be seen in Fig. 2d, the characteristic absorptions at 1736 and 1711 cm^{-1} which assigned to the C=O groups of the amyl ester and carbamate have appeared after the grafting of LPU.