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Preparation, characterization, and infrared emissivity property of optically active polyurethane/TiO₂/SiO₂ multilayered microspheres

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ABSTRACT

Optically active polyurethane/titania/silica (LPU/TiO₂/SiO₂) multilayered core–shell composite microspheres were prepared by the combination of titania deposition on the surface of silica spheres and subsequent polymer grafting. LPU/TiO₂/SiO₂ 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 μ m) was investigated in addition. The results indicated that titania and polyurethane had been successfully coated onto the surfaces of silica microspheres. LPU/TiO₂/SiO₂ 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/TiO₂/SiO₂ 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.

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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 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, V₂O3@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 Fe₃O₄/SiO₂/Ag composite with core/shell/particles structure and its application in surfaceenhanced 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 acidbased 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/TiO₂/SiO₂) 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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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. ¹H 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 SiO₂ 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 TiO₂/SiO₂ microspheres and A-TiO₂/SiO₂

Titania was coated on monodisperse SiO₂ 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 TiO₂/SiO₂ 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 TiO₂/SiO₂ microspheres were collected by centrifuge and washed with ethanol and water to obtain A-TiO₂/SiO₂.

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 mL²), and dried to give the off-white L-tyrosine amyl ester hydrochloride. Yield: 11.8 g (82%). Mp: 166–167 °C $[\alpha]_D^{25} = +6.5^{\circ}$ (C=1 g/dL, methanol). ¹H NMR (300 MHz, DMSO-d₆): δ 0.85 (t, 3H, –CH₃), 1.19–1.23 (m, 4H, –CH₂–), 1.45–1.48 (m, 2H, –CH₂–), 2.90–3.06 (m, 2H, –PhCH₂–), 4.03 (t, 2H, –OCH₂–), 4.13 (t, 1H, > CH–), 6.69–7.02 (m, 4H, –C₆H₄–), 8.57 (s, 3H, –N⁺H₃Cl⁻), 9.45 (s, 1H, –OH). IR (v/cm⁻¹): 3290 (O–H), 2954, 2933, 2870, 1739 (C=0), 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 CH₂Cl₂ 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 CH₂Cl₂ 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 CH₂Cl₂. The combined organic layers were dried (MgSO₄), 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: ¹H NMR (300 MHz, CDCl₃): δ 0.92 (t, 3H, -CH₃), 1.33 (m, 4H, -CH₂-), 1.68 (m, 2H, -CH₂-), 2.95-3.11 (m, 2H, -PhCH₂-), 4.19 (t, 2H, -OCH₂-), 4.21 (t, 1H, > CH-), 6.78-7.09 (m, 4H, -C₆H₄-). 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/TiO₂/SiO₂ 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-TiO₂/SiO₂ 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/TiO₂/SiO₂ 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 SiO₂, TiO₂/SiO₂, A-TiO₂/SiO₂, and LPU/TiO₂/SiO₂ 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 TiO₂/SiO₂ 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.



Fig. 1. The scheme of preparation of LPU/TiO₂/SiO₂.



Fig. 2. FT-IR spectra of (a) $SiO_2,$ (b) $TiO_2-SiO_2,$ (c) A-Ti $O_2-SiO_2,$ and (d) LPU-Ti $O_2-SiO_2.$

Fig. 3 shows the UV–vis spectra of the silica colloids before and after the wrapping. No distinct peak is observed for bare silica (Fig. 3a). While after the deposition of titania, intense absorptions (Fig. 3b) appear due to the strong scattering effect of the composite nanoparticles [30]. As shown in the spectra of LPU/TiO₂/SiO₂, the peak at 235 nm and a broad absorption at about 265 nm emerge, which correspond to the π – π * transition of the aromatic rings and n– π * transition of carbonyl groups in the macromolecular chain. These results indicate that the grafting reaction has taken place as expected.

3.2. XRD analysis

The XRD patterns of SiO₂, TiO₂/SiO₂ calcined at 500 °C and LPU/ TiO₂/SiO₂ microspheres are shown in Fig. 4. SiO₂ displays a very broad hump centered at 2θ =22°, originating from the amorphous phase of silica colloid. After the deposition of titania and thermal treatment at 500 °C, XRD pattern of TiO₂/SiO₂ in Fig. 4b exhibits other peaks at 2θ =25°, 38°, 48°, 55°, 63°, and 69° compared to that



Fig. 3. UV-vis absorption spectra of (a) bare silica spheres, (b) TiO₂-SiO₂ coreshell composites, and (c) LPU-TiO₂-SiO₂ multicoated microspheres.

of pure SiO₂, which correspond to the primary diffractions of (1 0 1), (0 0 4), (2 0 0), (2 1 1), (2 0 4), and (2 2 0) crystalline planes in the anatase structure of titania [31]. For the LPU/TiO₂/SiO₂ microspheres, besides the diffraction peaks of TiO₂/SiO₂, the diffractogram displays partially crystalline area at about 21° which could be assigned to the presence of hard segment in the polyurethane such as benzene rings. The result further demonstrates that the grafting of optically active LPU just occurs on the surface of TiO₂/SiO₂ without destroying the crystalline structure of it.

3.3. Morphological analysis

SEM images of the samples under the same scale are shown in Fig. 5. As it can be seen, the silica microspheres show slippery surface and a narrow range of particle size distribution. With the deposition of titania, the diameter of the spheres increase. Some insular aggregates emerge and the surfaces of spheres become rough evidently as revealed in Fig. 5b and c. The surface uniformity is improved after grafting with the polyurethane (Fig. 5d), a wrap of

the organic polymer on the surface of TiO_2/SiO_2 particles could be supposed consequently.

The LPU/TiO₂/SiO₂ multilayered microspheres could be visualized by transmission electron microscopy (TEM) as illustrated in Fig. 6. The pure silica particles shown in Fig. 6a are spherical in shape and the average diameter is about 820 nm. Observed from Fig. 6b, a thin coating of heterogeneous surface is obtained after the deposition of titania, and this is further confirmed by the heat treatment of the composite. As shown in Fig. 6c, it is obvious that a core-shell structure with amorphous silica core and a layer of crystalline titania is completely enriched. The shell appears to be uniform with the thickness of 25 nm or so. Moreover, the



Fig. 4. XRD spectra of (a) SiO₂, (b) TiO₂-SiO₂, and (c) LPU-TiO₂-SiO₂.

corresponding electron diffraction pattern (the inset in Fig. 6c) also shows a typical diffraction pattern of highly crystallized titania, which is consistent with the XRD result concluded earlier. The presence of the grafted optically active polyurethane on the TiO_2/SiO_2 could be clearly illustrated by the light appearance round the surface of the composite sphere as announced in Fig. 6d.

3.4. XPS analysis

X-ray photoelectron spectroscopy (XPS) studies are carried out on the pure SiO₂, TiO₂/SiO₂, and LPU/TiO₂/SiO₂ microspheres to verify the formation of the multilayered structure since the analysis depth of XPS is only several nanometers [32]. As can be seen in Fig. 7a, the surface of bare SiO₂ is composed of O (537 eV) and Si (158 eV and 107 eV) elements, the appearance of C (289 eV) could be attributed to the carbon dioxide in the atmosphere. After the disposition of titania, the XPS spectrum has been changed, the peaks corresponding to Ti (461 and 568 eV) element are found instead of silicon (Fig. 7b), which indicate that the surface of SiO₂ is completely covered by titania. As shown in the spectrum of LPU/TiO₂/SiO₂, the titanium peaks disappear, while the peaks corresponding to C (287 eV) and O (535 eV) elements strengthen along with the emergence of N (402 eV) peak.

Moreover, the thermogravimetric analysis (TGA) is used and presented in Fig. 8. The main weight loss starting at 250 °C is assigned to the thermal decomposition of optically active polyurethane. The amount of LPU grafted onto the TiO_2/SiO_2 is about 0.18 g/g inorganics. All of the results confirm that LPU is grafted onto the surface of TiO_2/SiO_2 spheres, and the composite possesses multi-layered construction.



Fig. 5. SEM micrographs of (a) SiO₂, (b) TiO₂(amorphous)-SiO₂, (c) TiO₂(anatase)-SiO₂, and (d) LPU-TiO₂(anatase)-SiO₂.



Fig. 6. TEM micrographs of (a) SiO₂, (b) TiO₂(amorphous)-SiO₂, (c) TiO₂(anatase)-SiO₂, and (d) LPU-TiO₂(anatase)-SiO₂.





Fig. 8. TGA curve of LPU–TiO₂–SiO₂ composite.

Fig. 7. XPS spectra of (a) $SiO_2,$ (b) $TiO_2-SiO_2,$ and (c) $LPU-TiO_2-SiO_2$ multicoated microspheres.

3.5. The infrared emissivity properties

The infrared emissivity values of the samples at wavelength of $8-14 \,\mu\text{m}$ are investigated and listed in Table 1. It is well known that the infrared radiation property of the substance is closely related to the composition, structure, the form of the chemical

bonds, and so on [33-35]. The bare SiO₂ has high infrared emissivity value of 0.782. Core/shell structural TiO₂/SiO₂ nanoparticles before and after the thermal treatment show the values of 0.721 and 0.685, respectively. The strong chemical effects occur between the SiO₂ and TiO₂ nanoparticles, which change the vibration mode of molecules, atoms, or pendant groups lying on the interface and lead to the special effect of the incidence wave [36]. The interfacial interactions dissociate and weaken the

Table 1

Infrared emissivity values of samples.

Samples	Infrared emissivity (ϵ_{TIR} at 8–14 $\mu\text{m})$
SiO ₂	0.782
TiO _{2(amorphous)} /SiO ₂	0.721
TiO _{2(anatase})/SiO ₂	0.685
LPU/TiO ₂ /SiO ₂	0.553

infrared emissivity of the material [37–39]. Moreover, TiO₂/SiO₂ spheres with the anatase titania possess lower infrared emissivity value than the amorphous one due to the well crystallinity. After the grafting of optically active polyurethane, the infrared emissivity value of LPU/TiO₂/SiO₂ multilayered core-shell composite microspheres is reduced to 0.553. It is well known that organic polymers have high infrared emissivity values due to their high unsaturated groups in the structure. The orderly secondary structure of macromolecular chain could lead to the formation of massive intermolecular interactions easily, which reduce the index of hydrogen deficiency and the unsaturated degree. Consequently, optically active polymer is favored to the reduction of infrared emissivity due to the orderly secondary structure and more intermolecular interactions [40,41]. Meanwhile, the synergistic effect on the interface is reinforced by the coupling agent between the grafted organics and inorganics, and thus resulted in low infrared emissivity.

4. Conclusions

It is demonstrated that the LPU/TiO₂/SiO₂ multilayered coreshell composite microspheres were obtained by the titania deposition on the surface of silica spheres and subsequent polymer grafting. TiO₂/SiO₂ particles had lower infrared emissivity value than bare SiO₂ as a result of the interfacial interactions. In addition, the crystalline of TiO₂ also affected the infrared emissivity properties of the composite. TiO₂ coating with anatase crystalline owned the lower infrared emissivity value than with the amorphous one. After the grafting of optically active polyurethane on the surface of TiO₂/SiO₂, the infrared emissivity value of the multilayered core–shell composite microspheres was evidently decreased to 0.553. Orderly secondary structure and strengthened interfacial synergistic action both accounted for the remarkable decrease in infrared emissivity value of the composite.

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