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Optically active polyurethane@indium tin oxide nanocomposite: Preparation, characterization and study of infrared emissivity

Yong Yang^a, Yuming Zhou^{a,*}, Jianhua Ge^a, Xiaoming Yang^b

^a School of Chemistry and Chemical Engineering, Southeast University, Jiangsu Optoelectronic Functional Materials and Engineering Laboratory, Nanjing 211189, PR China ^b Suzhou Sidike New Material Technology Co., Ltd., Suzhou 215400, PR China

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ABSTRACT

Optically active polyurethane@indium tin oxide and racemic polyurethane@indium tin oxide nanocomposites (LPU@ITO and RPU@ITO) were prepared by grafting the organics onto the surfaces of modified ITO nanoparticles. LPU@ITO and RPU@ITO composites based on the chiral and racemic tyrosine were characterized by FT-IR, UV-vis spectroscopy, X-ray diffraction (XRD), SEM, TEM, and thermogravimetric analysis (TGA), and the infrared emissivity values (8–14 μ m) were investigated in addition. The results indicated that the polyurethanes had been successfully grafted onto the surfaces of ITO without destroying the crystalline structure. Both composites possessed the lower infrared emissivity values than the bare ITO nanoparticles, which indicated that the interfacial interaction had great effect on the infrared emissivity. Furthermore, LPU@ITO based on the optically active polyurethane had the virtue of regular secondary structure and more interfacial synergistic actions between organics and inorganics, thus it exhibited lower infrared emissivity value than RPU@ITO based on the racemic polyurethane.

1. Introduction

In the last decades, an intense attention has been arisen to investigations dealing with optically active macromolecules for their unique characteristics, such as orderly secondary structure, adjustable chiral parameter, and abundant inter-chain interaction [1,2]. Optically active polymers derived from amino acids are of interest due to their inherent biological compatibility and degradability, which make them ideal candidates for a variety of biomaterial applications [3,4]. Moreover, amino acid-based chiral polymers could have induced crystallinity with the ability to form higher ordered structures that exhibit enhanced properties. The polymethionine membrane and its oxidized membrane show high oxygen permeability [5]. Poly(c-alkyl a-glutamic acid)s are used as surface treatment reagents of artificial leathers, and examined as liquid crystalline materials, piezoelectric materials, and LB films [6,7]. Peptides consisting of L-leucine, L-alanine, and L-lysine show an artificial enzymatic behavior in the decarboxylation of oxaloacetate [8].

Recently, special interest has focused on the functionalized metal oxide nanoparticles in terms of their potential applications to biomedical, catalytic, and optical materials [9–12]. Indium tin oxide (ITO) is a doped degenerate semiconductor material with the properties of high conductivity and transparency under visible light, intense

reflectivity for infrared, favorable chemical stability and so forth. It is widely used in photoelectric material, display technique, construction engineer, etc. [13–17]. However, to the best of our knowledge, ITO is mainly applied with the thin-film form and few reports have related to the pulverous ITO grafted with optically active polymers.

Controlling the temperature and infrared emissivity of the object are both of the common methods in infrared camouflage [18,19]. The decrease of infrared emissivity becomes especially important on the occasion of that the temperature could not be reduced [20]. Among most of the Infrared low-emissive materials, organic/inorganic composites especially have the potential for applications by means of combining the structure tunability of organics and the robustness and chemical inertness of inorganics. In the present study, optically active polyurethane@indium tin oxide (LPU@ITO) and racemic polyurethane@indium tin oxide (RPU@ITO) nanocomposites based on tyrosine were prepared after the surface modification of ITO nanoparticles. On the basis of microstructure analysis of the nanocomposites, the effect of macromolecular conformations and the interfacial interactions between organics and inorganics on the properties of infrared emissivity were discussed.

2. Experimental

2.1. Materials

Metal indium (\geq 99%) was obtained from Shanghai Long Jin Metal Material Limited Company. SnCl₄·5H₂O (analytical reagent)

^{*} Corresponding author. Tel.: +86 25 52090617; fax: +86 25 52090617. *E-mail address:* ymzhou@seu.edu.cn (Y. Zhou).

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was produced by Shanghai No. 4 Reagent & H.V. Chemical Limited Company. L-Tyrosine, DL-tyrosine, triethylamine, hydrochloric acid (analytical reagent), and ammonia water (25%) were all purchased from Shanghai Chemical Reagent Company and used as received without further purification. Methyltrioctylammonium chloride (Aliquat[®]336) was produced by Acros Organics. Triphosgene and γ -aminopropyltriethoxysilane (KH550) were obtained from Aldrich. Thionyl chloride, 1-hexanol and other solvents were all obtained from Shanghai Chemical Reagent Company and distilled by the standard methods. Deionized water was used for all 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 and ¹³C NMR spectra measurements were recorded on a Bruker AVANCE 300 MHz NMR spectrometer. Chemical shifts were reported in ppm. 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. Thermal analysis experiments were performed using a TGA apparatus operated in the conventional TGA mode (TA Q-600, TA Instruments) at the heating rate of 10 K/min in a nitrogen atmosphere, and the sample size was about 50 mg. 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 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 ITO and A-ITO

ITO nanoparticles with the In:Sn atomic ratio as 90:10 were prepared by chemical co-precipitation process and calcinated at 600 according to the literature [21]. 2 g of ITO nanoparticles were dispersed into 50 mL anhydrous ethanol with ultra-sonic to obtain the suspension, 0.5 mL of KH550 was then added. The mixture was exposed to high-intensity ultrasound irradiation for 1 h at 25 °C and refluxed for 4 h. The resulting KH550-modified ITO nanoparticles were separated by centrifuge and washed with ethanol and deionized water to obtain A-ITO.

2.4. Monomer synthesis

2.4.1. HC1 salts

L-Tyrosine hexyl ester hydrochloride was prepared as follows: to 1-hexanol (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 95 °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 ether (2× 50 mL) and dried to give the white powdery L-tyrosine hexyl ester hydrochloride. Yield: 13.4 g (89%). Mp: 162–164 °C. [α]_D²⁵ = +7.6° (*C* = 1 g/dL, methanol). ¹H NMR (300 MHz, DMSO-d₆): δ 0.82–0.8 (t, *J* = 6.48 Hz, 3H, -CH₃), 1.20–1.25 (m, 6H, -CH₂–), 1.43–1.47 (m, 2H, -CH₂–), 2.89–3.10 (m, 2H, -PhCH₂–), 4.00–4.05 (t, *J* = 6.42 Hz, 2H, -OCH₂–), 4.10–4.14 (t, *J* = 6.99 Hz, 1H, CH–), 6.68–7.01 (m, 4H, -C₆H₄–), 8.55 (s, 3H, -N⁺H₃Cl⁻), 9.41 (s, 1H, -OH). FT-IR (ν/cm^{-1}): 3297 (O–H), 2953, 2869, 1738 (C=O), 1516, 1230, 843.

DL-Tyrosine hexyl ester hydrochloride was prepared in the similar way using DL-tyrosine instead of L-tyrosine. White solid. Yield: 14.3 g (95%). Mp: 176–179 °C. $[\alpha]_D^{25} = 0^\circ$ (*C* = 1 g/dL, methanol). Its ¹H NMR, IR data are similar to L-tyrosine hexyl ester hydrochloride and thus omitted.

2.4.2. Isocyanate-phenols

Phosgene was obtained by decomposition of triphosgene with Aliquat[®]336 according to the literature [22]. The phosgene that developed during the reaction was collected in CH₂Cl₂ and preserved below 0 °C. 1.51 g L-tyrosine hexyl 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 hexyl ester solution. The solution was used in the polymerization without further isolation. The isocyanate of DL-tyrosine hexyl ester was prepared in the similar way using DL-tyrosine hexyl ester hydrochloride instead of L-tyrosine hexyl ester hydrochloride.

The spectroscopic data of isocyanate–phenol are as follows (take isocyanate of L-tyrosine hexyl ester for example). ¹H NMR (300 MHz, CDCl₃): δ 0.84–0.88 (t, *J* = 6.15 Hz, 3H, –CH₃), 1.27 (m, 6H, –CH₂–), 1.58–1.60 (m, 2H, –CH₂–), 2.91–2.93 (m, 2H, –PhCH₂–), 4.09–4.13 (t, *J* = 6.54 Hz, 2H, –OCH₂–), 4.38 (m, 1H, CH–), 6.67–6.96 (m, 4H, –C₆H₄–). ¹³C NMR (75 MHz, CDCl₃): δ 13.9, 22.5, 25.4, 28.4, 31.3, 39.1, 58.8, 66.7, 115.5, 127.5 (N=C=O), 130.6, 154.9 (C–OH), 170.8 (C=O). FT-IR (ν /cm⁻¹): 3419 (O–H), 2957, 2932, 2259 (– N=C=O), 1738 (C=O), 1516, 1004, 834.

2.5. Preparation of LPU@ITO and RPU@ITO composites

The prepolymerization of isocyanate of L-tyrosine hexyl ester was carried out in the CH_2Cl_2 solution with magnetic stirring under nitrogen at room temperature for 8 h by addition of triethylamine (3 mol%) as the catalyst. Then A-ITO 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@ITO composite. Fig. 1 shows the scheme of the process of preparation and the RPU@ITO composite was prepared in a similar way.

3. Results and discussion

3.1. FT-IR and UV-vis spectra analysis

Fig. 2 shows the FT-IR spectra of ITO, A-ITO, LPU@ITO, and RPU@ITO composites. For the bare ITO, three peaks at 498, 568, and 603 cm⁻¹ are assigned to the phonon vibrations of In–O bonds and are characteristic of cubic In_2O_3 [23]. Except the band at 3405 cm⁻¹ belonging to hydroxyl groups on the surface of ITO, there is no absorption between 750 and 3500 cm⁻¹ because of the intense reflection effect of ITO against infrared. After the surface modification of ITO under ultrasonic radiation, the peaks of methyl, methylene, and N–H group of KH550 are found at 2850 cm⁻¹, 2935 cm⁻¹, and 3415 cm⁻¹, respectively. As it can



Fig. 1. Scheme of preparation of LPU@ITO composite.

be seen in Fig. 2c and d, the characteristic absorptions corresponding to the C=O groups of hexyl ester and carbamate have appeared at 1736 cm^{-1} and 1711 cm^{-1} after the grafting by LPU and RPU.

The UV-vis spectra of ITO before and after being grafted by polyurethanes are displayed in Fig. 3. No absorption is observed for the pure nanoparticles because of the strong scattering process from ITO. As shown in the spectra of RPU@ITO and LPU@ITO composites, the bands corresponding to the π - π * transition of the aromatic rings and n- π * transition of carbonyl groups, in the macromolecular chain, have appeared around 235 nm and 265 nm, respectively. Both of the spectroscopic analyses indicate that the grafting reactions have taken place as expected.

3.2. XRD analysis

The crystalline structure analyses of ITO, RPU@ITO, and LPU@ITO composites are also carried out in order to verify the

formation of organic–inorganic composite. As shown in Fig. 4, the characteristic peaks at $2\theta = 21.5$, 30.5, 35.4, 51.0, and 60.7° correspond to the primary diffractions of $(2 \ 1 \ 1)$, $(2 \ 2 \ 2)$, $(4 \ 0 \ 0)$, $(4 \ 4 \ 0)$, and $(6 \ 2 \ 2)$ crystalline planes in cubic bixbyite structure of the \ln_2O_3 . No phases corresponding to tin or to other tin compounds were detected indicating that the tin atoms were doped substitutionally in the \ln_2O_3 lattice [24,25]. For the composites, besides the crystalline peaks of ITO, the diffractograms display partially crystalline areas at about 21° which could be assigned to the presence of hard segment in the polyurethane such as benzene rings. The diffraction patterns of ITO in the composites are coincident with the bare ITO nanoparticles, which suggest that no change of crystal parameters occurred during the process of grafting and the reactions just take place on the surface of ITO.

3.3. Morphological analysis

SEM images of ITO, RPU@ITO, and LPU@ITO composites are shown in Fig. 5. As can be seen in Fig. 5a, the ITO nanoparticles





Fig. 2. FT-IR spectra of: (a) ITO, (b) A-ITO, (c) RPU@ITO, and (d) LPU@ITO composites.



Fig. 4. XRD patterns of: (a) ITO, (b) RPU@ITO, and (c) LPU@ITO composites.

show spherical shape with a narrow range of grain size distribution, and the average diameter of them is 60 nm or so. It can be clearly observed that the nanoparticles have some agglomerations. As expected, in Fig. 5b and c, the spheres universally present some increase in size and shape, which indicate that the ITO is thoroughly wrapped by organics. Furthermore, it should be noted that, the RPU@ITO presents larger aggregates than LPU@ITO due to the grafting over more ITO nanoparticles.

Fig. 6 shows the TEM photographs of ITO before and after being grafted by polyurethanes. As shown in Fig. 6a, ITO exhibits globular structure and some of them assemble into larger aggregates. The sectional area electron diffraction pattern (Fig. 6a, inset) shows a typical polycrystalline composition of ITO with no preferred orientation that corresponds to the XRD analysis. After the organification with polyurethanes, RPU@ITO and LPU@ITO nanocomposites (Fig. 6b and c) show a distinct layer of amorphous surroundings with the thickness about 10 nm. It is noteworthy that the dispersion degree of ITO has been maintained in the main for LPU@ITO compared with the nanoparticles prior to grafting. The extent of aggregation becomes more serious for RPU@ITO though the ultrasonic dispersion is adopted during both of the reactions. This demonstrates that optically active polyurethane with orderly secondary structure possesses the advantage of less steric hindrance which contributes to the uniform wrapping. On the contrary, racemic polymer with the random coiled molecular chain assembles the nanoparticles and leads to the package involving a number of ITO nanoparticles. In addition, we could conclude that organic polymers have been successfully grafted onto the surfaces of ITO.

3.4. Thermal stability analysis

The thermogravimetric analysis (TGA) was employed for determining the amount of organics grafted onto ITO. The weight loss curves of ITO, RPU@ITO, and LPU@ITO composites are presented in Fig. 7. The slight weight loss in Fig. 7a is assigned to the release of moisture adsorbed and structure water for the bare ITO. In curves b and c, the main weight losses starting at about 200 °C are assigned to the thermal decomposition of polymers. The amounts of polyurethanes grafted onto the ITO are about 0.26 g/g



Fig. 5. SEM micrographs of: (a) ITO, (b) RPU@ITO, and (c) LPU@ITO composites.



Fig. 6. TEM micrographs of: (a) ITO, (b) RPU@ITO, and (c) LPU@ITO composites.

and 0.32 g/g inorganics for RPU@ITO and LPU@ITO, respectively. It is worth noting that the weight loss of LPU@ITO derived from chiral tyrosine is larger than that of RPU@ITO derived from racemic tyrosine, and this may result from the different chain conformations. Optically active LPU with regular macromolecular structure facilitates the dispersion and grafting of ITO, which correspond to the morphological analyses above.

3.5. The infrared emissivity analysis

Several of inorganic materials especially semiconductive nanoparticles have been used in reducing infrared emissivity of the object, and ITO is of great value among them [26,27]. The



Fig. 7. TGA curves of: (a) ITO, (b) RPU@ITO, and (c) LPU@ITO composites.

infrared emissivity values of the samples at wavelength of 8-14 µm are investigated and listed in Table 1. The pure ITO nanoparticles have relative higher infrared emissivity value of 0.701. After being grafted with polymers, the infrared emissivity values of RPU@ITO and LPU@ITO composites are reduced to 0.596 and 0.512, respectively. This suggests that the synergistic effect between the grafted polyurethanes and ITO nanoparticles plays an important role in the decreasing of infrared emissivity. The interfacial interactions reinforced by the coupling agent alter the vibration mode of molecules, atoms or pendant groups on the interface between organic and inorganic components, which had direct influence on infrared emissivity [28,29]. Moreover, LPU@ITO composite based on the optically active polyurethane exhibits lower infrared emissivity value than RPU@ITO which base on the racemic polyurethane. On one hand, LPU@ITO with the wrapping of optically active polyurethane possesses the larger grafting amount of organics. This implies more interfacial lavers and interfacial interactions. On the other hand, 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 [30]. Therefore, the

Table 1		
Infrared	emissivity values of samples.	

Samples	Infrared emissivity (ϵ_{TIR} at 8–14 $\mu m)$
ITO	0.701
RPU@ITO	0.596
LPU@ITO	0.512

infrared emissivity value of LPU@ITO is lower than that of RPU@ITO.

4. Conclusions

LPU@ITO and RPU@ITO nanocomposites were prepared after the surface modification of ITO nanoparticles by silane coupling agent, and the infrared emissivity values at wavelength of 8– 14 μ m were investigated. LPU@ITO and RPU@ITO showed lower infrared emissivity values than bare ITO nanoparticles by virtue of the interfacial synergistic actions between organics and inorganics. LPU@ITO composite based on the optically active polyurethane possessed stronger interfacial interactions than RPU@ITO by means of the less steric hindrance and more interfacial layers. In addition, the orderly secondary structure of organics would easily lead to the formation of intermolecular interactions. Both of them resulted in the decrease of infrared emissivity. Consequently, LPU@ITO exhibited an infrared emissivity value down to 0.512 that is lower than RPU@ITO.

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