

Preparation and infrared emissivity study of collagen-g-PMMA/ In_2O_3 nanocomposite

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Abstract

Collagen-g-PMMA copolymer and indium oxide nanoparticles were prepared by grafting copolymerization of methyl methacrylate onto collagen and sol–gel process separately, and collagen-g-PMMA/indium oxide nanocomposite was prepared by ultrasonic wave irradiation. Simultaneously two collagen/indium oxide nanocomposites were prepared by liquid–liquid dispersion and ultrasonic wave irradiation respectively in the interest of infrared emissivity investigation (8–14 μm). Three nanocomposites were characterized by SEM, TEM, IR spectroscopy, thermogravimetric analysis and infrared emissometer. SEM and TEM indicated that three nanocomposites were of different microstructures, and that collagen-g-PMMA copolymer and indium oxide nanoparticles self-assembled into homogeneously spherical aggregates of 600 nm in diameter, which is owing to, we proposed, the high activity of amphiphilic collagen-g-PMMA copolymer nanoparticles. It was found that two nanocomposites showed significantly lower infrared emissivity value than their components, but the rest one did not. Decrease mechanism of infrared emissivity value of nanocomposite was discussed based on microstructure. It was assumed that the decrease in infrared emissivity value of collagen-g-PMMA/indium oxide nanocomposite was attributed to strong interfacial interactions between collagen-g-PMMA and indium oxide.

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1. Introduction

Infrared low emissivity coating has always been playing an important role whether in civil or in military applications such as camouflaging military equipments or vehicles from infrared detection and the like [1–5]. In general, the coating is supposed to satisfy various requirements besides having infrared low emissivity. For example, in application to camouflage, the low emissivity coating should have good broadband compatibility, i.e., being effective in infrared as well as in radar, microwave or visible spectral range. In recent years, application of nanomaterials to low emissivity coating has attracted more and more attentions [3,6] due to unusual physicochemical and optoelectronic properties of nanomaterials [7]. Nanoscale indium oxide is commonly used material in low emissivity coating. In practical applications, the coating generally attains the

low emissivity by using nanocomposites based on indium oxide owing to high emissivity of the coating made of single nanoscale indium oxide. Much work has focused on incorporation of inorganic components into indium oxide [3,8]. However, few reports have dealt with the incorporation of organic components.

Collagen, a biopolymer, is a triple helix composed of three polypeptide chains. Owing to great number of dipoles and molecule-bound charges stored in collagen molecule, actually collagen is a bioelectret and has the properties of polarization, electrostatic attraction, etc. [9]. Furthermore, collagen molecule abounds in chemical elements having good affinity to metal oxide, such as oxygen, nitrogen [10], so collagen could be used to modify and stabilize metal oxide nanoparticles. In recent studies, Mirkin [11] showed that DNA strands that were analog to collagen could be attached to surfaces and applied in the directed assembly of nanoparticles. Native collagen, however, exists poor wet stability and mechanical property that will limit its practical applications. Noticeable improvements of such properties

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of collagen can be obtained through grafting copolymerization. Lipophilic polymethylmethacrylate (PMMA) shows good biocompatibility and has found large use in biomedical field particularly in strengthening of some biopolymer [12]. So, PMMA is suitable for grafting modification of collagen, with further consideration that PMMA, similar to collagen, is also a bioelectret material.

In this paper, we prepared collagen-g-PMMA/indium oxide nanocomposite by direct incorporation of preformed collagen-g-PMMA copolymer and indium oxide nanoparticles under the ultrasonic wave irradiation. The preformed collagen-g-PMMA copolymer and indium oxide were obtained using grafting copolymerization and sol–gel process respectively. Simultaneously, the preparation of two collagen/indium oxide nanocomposites was performed using ultrasonic wave irradiation and liquid–liquid dispersion separately in consideration of requirements of infrared emissivity study. On the basis of microstructure analysis of three nanocomposites, investigation on infrared emissivity of collagen-g-PMMA/indium oxide nanocomposite was carried out.

2. Experimental

2.1. Materials and characterization

Collagen (type I and III) was obtained from Taozheng Bioengineering Technology, Beijing, China. Indium metal ingots (99.999%) were bought from Chemical Reagent, Shanghai. All other chemicals and solvents were of analytical grade commercial materials. Methyl Methacrylate (MMA) was distilled in nitrogen under reduced pressure and used immediately. 2, 2'-Azo-bis-iso-butyronitrile (AIBN) was purified in absolute ethanol before use. IR spectra of the samples in the form of KBr pallets were recorded on a Nicolet Magna-IR 750 spectrometer (USA). The morphology of all the samples was confirmed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). SEM and TEM were performed on a Hitachi X-650 and Hitachi H-600, respectively. The amount of collagen in nanocomposite prepared by liquid–liquid dispersion was evaluated by thermogravimetric analysis (TGA). Thermogravimetric analysis was carried out on a TA Q600 (USA). Infrared emissivity value of powdery samples was measured using IRE-I Infrared emissometer of Shanghai Institute of Technological Physics, China.

2.2. Preparation of collagen-g-PMMA copolymer

Required collagen was dissolved in aqueous methanol solution (methanol: distilled water = 1:3, volumetric ratio), into which calculated MMA monomer was added followed by calculated initiator combination of Ammonium cerium nitrate (CAN) and AIBN (CAN: 0.5 mol/l in 1 N nitric solution, AIBN: 0.2 mol/l in methanol). The reaction was

carried out in nitrogen atmosphere at 50 °C for 3 h. The resultants were filtrated to get mixture of collagen-g-PMMA copolymer and PMMA homopolymer. The mixture was firstly extracted with acetone to remove homopolymer, subsequently was extracted with distilled water at 50 °C and then filtered. The collagen-g-PMMA copolymer was dried in air at 50 °C.

2.3. Preparation of indium oxide

One gram of indium metal ingots were thoroughly dissolved in 7 ml of concentrated nitric acid and diluted with distilled water to total volume of 100 ml, into which required amount of citric acid was added. Aqueous ammonia of 2 mol/l was added dropwise to the above solution in ambient temperature till indium hydroxide sol was obtained. The pH of solution was maintained in the range 5–6 at this stage. Then the solution was stirred at 50 °C for 2 h to ensure the complete precipitation. The precipitate was collected by filtration under vacuum, washed thoroughly by distilled water and dried in air. A white powdery solid obtained was grinded and calcined at 500 °C for 2 h to get the final indium oxide.

2.4. Preparation of nanocomposites

The first is the ultrasonic wave irradiation method. Collagen and indium oxide nanoparticles were mixed firstly at weight ratio of 3:1 and then dispersed in absolute ethanol, followed by stir for 4 h and irradiation with ultrasonic wave for 2 h. The collagen/indium oxide nanocomposite was filtered, washed thoroughly with absolute ethanol and dried in air at 50 °C. Collagen-g-PMMA/indium oxide nanocomposite was prepared by the same method described above. The weight ratio of two components was also 3:1.

The second is liquid–liquid dispersion method. One gram of collagen were dissolved in 50 ml of deionized water, into which 50 ml of acetone was added. After the collagen solution was stirred for 1 h, 0.6 g of indium oxide nanoparticles were added. And then stirring speed was fixed, temperature was elevated up to 323 K and retained for 6 h at a reduced pressure with an aspirator to evaporate and remove acetone. The collagen/indium oxide nanocom-

Table 1
Nanocomposite sample numbers

Composite no.	Preparation method	Organic component	Inorganic component
L-C-I	Liquid–liquid dispersion	Collagen	Indium oxide
U-C-I	Ultrasonic wave irradiation	Collagen	Indium oxide
U-Cg-I	Ultrasonic wave irradiation	Collagen-g-PMMA	Indium oxide

posite was filtered, washed with deionized water and dried in air at 50 °C.

Nonocomposites made by the two methods were defined by the following rule. The number of nanocomposites is denoted by three digits. From left to right, each digit denotes composition method, organic and inorganic component respectively. At the first digit, L stands for liquid–liquid dispersion and U stands for ultrasonic wave irradiation. At the second digit, C stands for collagen and Cg stands for collagen-g-PMMA copolymer. At the third digit, I stands for indium oxide.

Nanocomposite numbers were listed in Table 1.

3. Results and discussions

3.1. IR spectra

Upon exposure to liquid water or to aqueous solutions, the surfaces of metal oxide particles or films undergo a series of chemical reactions that are dictated to a large extent by the chemistry of the metal ions involved. These reactions involve surface hydroxylation and hydration (dissociative and non-dissociative water chemisorption), chemisorption of solutes and charge transfer reactions [13]. Owing to large surface-to-volume ratio of nanoparticle, numbers of indium ions exist on surface of hydrophilic indium oxide nanoparticles [14,15]. These indium ions show high activity and are in favor of hydration and hydroxylation. And substitution complexation and hydrogen bonding reactions could happen between hydroxyl groups formed or water molecule adsorbed on surface of indium oxide nanoparticles and collagen macromolecule. As shown in IR spectra (Fig. 1), composite L-C-I showed the characteristic absorption band around 1640 and 1540 cm^{-1} of the amide groups of the collagen [16], which was an evidence of adsorption of collagen on indium oxide. And, a rise in absorption over a wide interval of wave numbers smaller than 3500 cm^{-1} that was assigned to OH stretching band due to physically adsorbed water [17] is observed, indicating the formation of hydrogen bonds between adsorbed collagen and surface hydroxyl groups. Simultaneously, a red shift of adsorption band of amide from 1650 to 1640 cm^{-1} is indicative of substitution of C=O groups on collagen backbone for water molecules coordinated to unsaturated surface In^{3+} [18]. In addition, besides characteristic adsorption bands around 600, 564, 538 and 426 cm^{-1} of indium oxide [19], a new shoulder peak at 500 cm^{-1} which was assigned to bending vibrations of O–C=O appeared in composite L-C-I, which illustrated the bonding between the metal ion, indium (III) and the oxygen of carboxyl group in side chain of collagen [20].

3.2. Microstructure

Collagen is a hydrophilic macromolecule [21], so when collagen/indium oxide nanocomposite was prepared in ab-

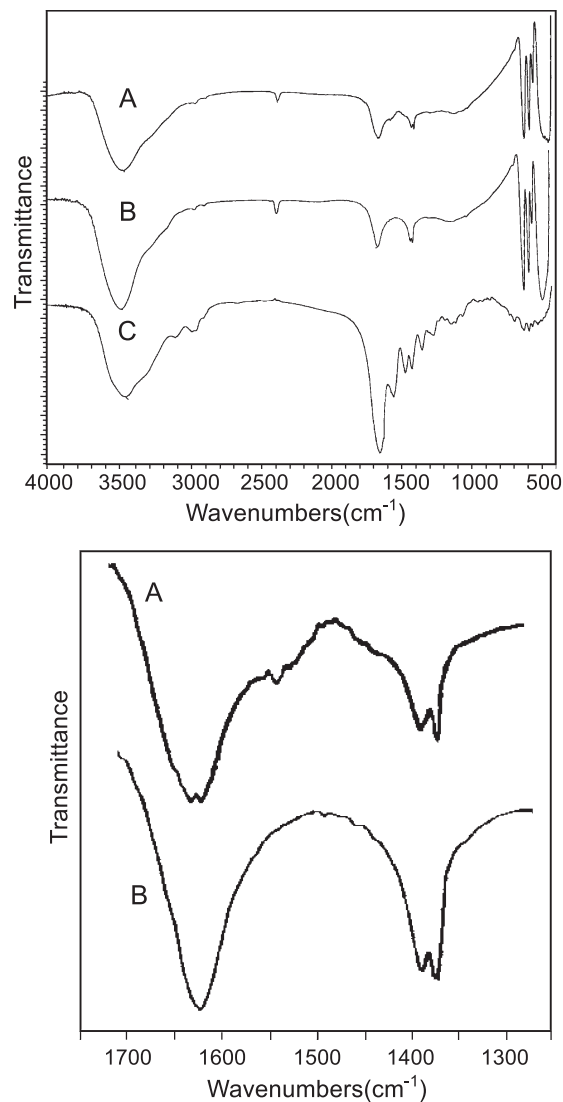


Fig. 1. IR spectra of (A) composite L-C-I, (B) indium oxide, (C) collagen.

solute ethanol and water separately, two different composite microstructures were obtained due to distinction in solvophilicity. The scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images shown in Figs. 2 and 3 illustrated the diversity of microstructures attained. As shown in Fig. 3f, grain size of indium oxide was 30–50 nm. However collagen/indium oxide nanocomposite L-C-I showed a broad range of aggregate size from 2 to 12 μm (Fig. 2c). Fig. 2d showed a local plan-view SEM of single aggregate, indicating that surface of composite L-C-I aggregate was wrapped by a layer of collagen on which some indium oxide nanoparticles were dispersed. Whereupon, we supposed that composite L-C-I had layer-by-layer structure, i.e., a layer of indium oxide followed by a layer of collagen, although it showed some irregularities in size and shape. For the locus of layer-by-layer structure, it was assumed that collagen appeared semi-flexible filaments and extended at liberty in aqueous solution, so collagen was capable of self-changing in conformation to adsorb on surface of indium

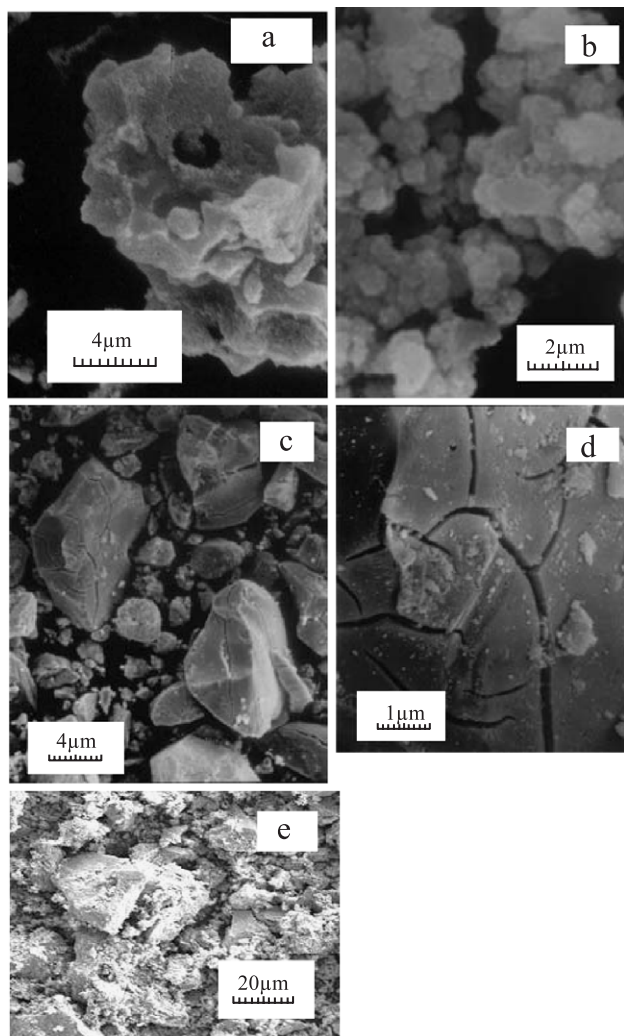


Fig. 2. SEM of (a) composite U-C-I, (b) composite U-C-g-I, (c–d) composite L-C-I, (e) pure indium oxide.

oxide [22]. Additionally, it is well known that hydroxyl groups on surface of indium oxide can absorb or dissociate protons to form positive and negative surface sites respectively [23], so strong electrostatic attraction also existed between indium oxide and collagen besides hydrogen bonding and surface complexation above-discussed in IR spectrum. Fig. 2a showed SEM image of composite U-C-I prepared in absolute ethanol. As expected, U-C-I showed shell-core structure owing to self-aggregation of collagen [24], in which the core was composed of collagen and indium oxide and in micrometer scale. Here we supposed that electrostatic attraction and hydrophilic–hydrophobic balance accounted for the formation of core [25]. Simultaneously, we could not deny the contributions of a very small amount of water in the reaction. In addition, it was hypothesized that the core-shell separation originated from different density of core and shell.

When collagen-g-PMMA copolymer nanoparticles were used, however, it is another case. Fig. 3b showed TEM image of collagen-g-PMMA copolymer obtained by graft-

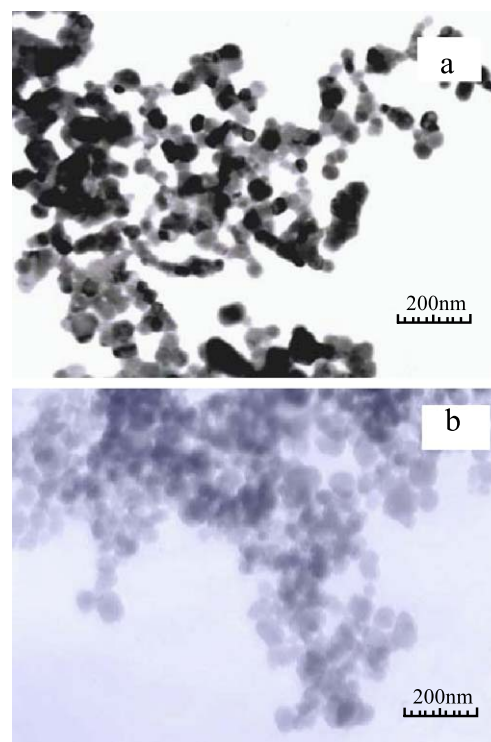


Fig. 3. TEM for (a) indium oxide, (b) collagen-g-MMA copolymer.

ing copolymerization, illustrating that the average grain size is in the range of 40–60 nm. And, as shown in Fig. 2b, nanocomposite U-C-g-I appeared quite different from L-C-I and U-C-I, which presented a homogeneous microstructure. Here collagen-g-PMMA copolymer and indium oxide nanoparticles organized into particle aggregates of about 600 nm in diameter. We proposed that this structure was attributed to self-assembly of nanoparticles. On one hand, more positive or negative charge-carried sites and pendant chemical groups existed on large surface of collagen-g-PMMA copolymer nanoparticles owing to nanosized effect [26], which boosted up interactions between two components, on the other hand, collagen became amphiphilic molecule due to introduction of PMMA side chain into collagen backbone. Therefore, collagen-g-PMMA copolymer nanoparticles could be used as building blocks to wrap indium oxide nanoparticles in order to self-organize into a stable hydrophobic structure [27] that was analogous to micelles in solution.

Table 2
IR emissivities of samples (ϵ_{TIR} at 8–14 μm)

Sample no.	Sample name	IR emissivity (ϵ_{TIR} at 8–14 μm)
1	Pure collagen	0.851
2	Pure indium oxide	0.913
3	Pure collagen-g-PMMA copolymer	0.896
4	Composite U-C-I	0.952
5	Composite L-C-I	0.610
6	Composite U-C-g-I	0.576

3.3. Infrared emissivity

The IR emissivity values at wavelength of 8–14 μm of all the samples were summarized in Table 2. Pure collagen, indium oxide and collagen-g-MMA copolymer had high emissivity values (0.851, 0.913 and 0.896, respectively). In contrast, composite L-C-I and U-Cg-I showed quite lower emissivity values (0.610 and 0.576, respectively) than its inorganic and organic components. Results of microstructure analysis showed that nanocomposite L-C-I and U-Cg-I had different structure. However, two structures shared a common point, i.e., organic and inorganic components exchanged interfacial interactions such as hydrogen bonds or electrostatic forces. These interfacial interactions altered vibration mode of molecules, atoms or pendant groups on interface between organic and inorganic components, which had direct influence on emissivity [4,28,29]. Namely, there existed a special interface layer that had different emissivity value from that of body of inorganic and organic components. Therefore, the decrease in emissivity values of both nanocomposites was most likely to be a direct consequence of the interfacial interactions.

Moreover, it was clear seen that composite U-C-I had higher emissivity value (0.952) than both of its components and composite L-C-I (0.610), although it consisted of the same organic and inorganic components as composite L-C-I. For indium oxide nanoparticles of 30–50 nm in diameter, the amount adsorbed for a close-packed monolayer of collagen molecules lying flat (“side-on” position) would be 15 mg/g In_2O_3 more or less [30]. So, the amount of collagen that exchanged interface interactions with indium oxide nanoparticles would be much less than the real collagen quantity for composite U-C-I in which the weight ratio of collagen to In_2O_3 is 3:1. And, superfluous collagen was self-assembled into large aggregates, i.e., collagen shell mentioned early, due to its poor solvophilicity. In consequence, no decrease in emissivity value of composite U-C-I was observed owing to negligible interface layer. TGA curve of composite L-C-I indicated that the amount of collagen that was incorporated onto indium oxide nanoparticles was about 16.6 mg/g In_2O_3 (see Fig. 4). Apparently, Close packed composite L-C-I had much larger ratio of interface layer to nanocomposite than composite U-C-I, and so, had more interface interactions and lower emissivity value. This further provided support for decrease mechanism of emissivity value depicted afore.

At the same time, it was found that composite U-Cg-I presented lower emissivity value than composite L-C-I. According to microstructure analysis, it was apparent that composite U-Cg-I is of larger contact interface than composite L-C-I on account of homogeneity of composite U-Cg-I and irregularities of composite L-C-I due to aggregation of indium oxide nanoparticles. Large contact interface implied that more molecules and atoms belonged to interface between two components, which signified more interface layer and more interface interactions. On the basis of

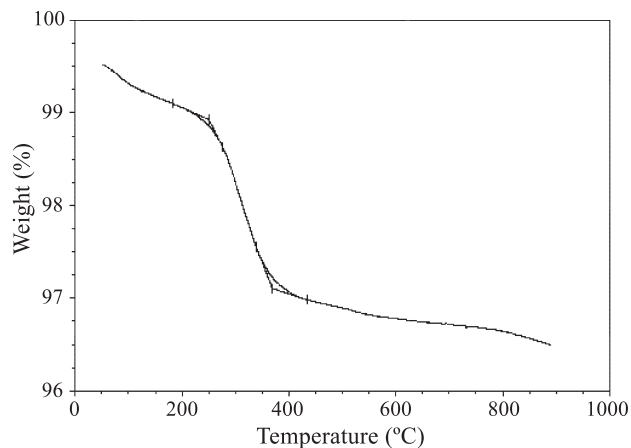


Fig. 4. Thermogravimetric analysis of composite L-C-I.

discussion above, interfacial interaction favored the decrease of emissivity value of nanocomposite. Therefore, we suggested that the lower emissivity value originated from more interface interactions of composite U-Cg-I.

4. Conclusions

Infrared emissivity at wavelength of 8–14 μm of two collagen/indium oxide and one collagen-g-PMMA/indium oxide nanocomposites was measured using IR emissometer. The emissivity of three samples examined was found to be different with values of 0.952, 0.576 and 0.610, respectively and interfacial interactions had great effect on emissivity of nanocomposite. Composite L-C-I and U-Cg-I showed lower emissivity values than that of their inorganic and organic components owing to interfacial interactions, but composite U-C-I showed a slightly higher emissivity value due to its poor interfacial interaction of integrated core and shell. In addition, amphiphilic collagen-g-PMMA copolymer nanoparticles facilitated the formation of orderly homogeneous structure of composite U-Cg-I due to its high activity, which resulted in increase of interfacial interactions between two components. Consequently, composite U-Cg-I had the lower emissivity value than that of composite L-C-I.

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