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Al_2O_3/SnO_2 Co-Nanoparticle Modified Grafted Collagen for Improving Thermal Stability and Infrared Emissivity

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Al_2O_3/SnO_2 co-nanoparticles were prepared with a modified sol-gel technique followed by a thermal treatment process. With these co-nanoparticles the grafted collagen-Al_2O_3/SnO_2 nanocomposites were obtained using a supersonic dispersion method. X-ray diffraction, FT-IR analysis, transmission electron microscopy, TGA/DTA and infrared emissivity test were performed to characterize the resulting nanoparticles and nanocomposites, respectively. The Al_2O_3/SnO_2 co-nanoparticles showed a narrow distribution of size between 20—40 nm and could be uniformly absorbed on the tri-helix scaffolds of the grafted collagen without any aggregation. The nanocomposites possessed better thermal stability and substantially lower infrared emissivity than the grafted collagen and Al_2O_3/SnO_2 co-nanoparticles with an increase of degradation temperature from 39 to 210 ℃ and a decrease of infrared emissivity from 0.850 of the grafted collagen and 0.708 of the Al_2O_3/SnO_2 co-nanoparticles to 0.424, which provided a potential application of the nanocomposites to areas such as photoelectronics.

Keywords grafted collagen, Al_2O_3/SnO_2, nanoparticle, nanocomposite, thermal stability, infrared emissivity

Introduction

Functionalized metal oxide nanoparticles are of great interest in terms of their potential applications to biomedical, electronic and optical materials.[1-3] The incorporation of metal oxide nanoparticles into organic matrices is a particularly interesting field in material engineering and the study of nanoparticle-matrix interaction.[4] These forming hybrid structures, which benefit from the flexibility and reactivity of tailored organic functional groups, the structural robustness and the chemical inertness of inorganic scaffold, have showed extensive applications to many areas, including electrocatalysis, electroanalysis, polymer science, protective coatings, surface analysis, electrosynthesis, molecular electronics, and so on.[5] Functionalized hybrids can now easily be prepared by using different methods such as cross-link method,[6] solid-state reaction,[7] grafting,[8-10] Langmuir-Blodgett (LB) techniques,[11] layer-by-layer self-assembly method,[12] sol-gel route,[13] controlled radical polymerization (CRP)[14] or one-step synthesis[15-17] process. Such an ever-evolving toolkit of methodologies provides the chemist with the ability to tailor materials that have suitable properties (both physical and chemical) for desired applications.

Collagen is one of the biopolymers most extensively used to construct functionalized hybrid structures.[18] Collagen molecule abounds in elements such as oxygen and nitrogen,[19] thus showing good affinity to metal oxide for stabilizing metal oxide nanoparticles away from their aggregation.[20] On the other hand, owing to a number of dipoles in the collagen molecule and the molecule-bound charges in its polypeptide chains, this protein possessed some distinctive properties such as polarization, electrostatic attraction and so on.[21] These characters supply choices to design valuable infrared stealthy materials by forming functionalized nanocomposites composed of this protein and metal oxide nanoparticles. However, native collagen has poor wet stability, mechanical property and high infrared emissivity, which restrict greatly its application to the field of infrared camouflage materials. Surface modification of natural materials by UV-induced graft copolymerization with either acrylamide or 2,2,3,3,4,4-heptafluorobutyl acrylate has been carried out to change surface hydrophilicity or hydrophobicity.[22] Noticeable improvement of the surface properties of the collagen has been obtained by radical copolymerization with some lipophilic materials such as methyl methacrylate (MMA).[23,24] The polymer of MMA (PMMA) obtained by using 2,2'-azobis(isobutyronitrile) as an initiator possesses good biocompatibility and has been used in

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biomedical field particularly in strengthening of some biopolymer.[23,25]

In this paper, we prepared a grafted collagen matrix with a graft copolymerization method and synthesized Al_2O_3/SnO_2 co-nanoparticles by a modified sol-gel technique followed by a thermal treatment process. The nanocomposites were obtained by direct incorporation of the Al_2O_3/SnO_2 co-nanoparticles into the grafted collagen matrix under ultrasonic wave irradiation. This structure possessed distinct thermal stability and low infrared emissivity resulting from the synergistic effect between its two components. The synthesis strategy was facile and would therefore be of general use in the functional nanoparticle-matrices.

Methods and materials

Preparation of Al_2O_3/SnO_2 co-nanoparticles

According to a typical preparation procedure, an amount of citrate acid corresponding to the stoichiometry of 1∶10∶20 for Al∶(Al+Sn)∶citrate was used as a solid precursor. After stoichiometric amounts of $SnCl_2$ and $AlCl_3$ were added to a 20 mg•mL^{-1} citrate acid solution with continuous stirring, the solution pH was adjusted to 7 with 1 mol•L^{-1} aq. NH_3. The solution was heated to 80 ℃ and maintained at this temperature for 2 h. The obtained solution was then dried in a vacuum cabinet. During this process, the solution pH was controlled in the range of 6—6.5 with 1 mol•L^{-1} aq. NH_3. The thermal decomposition of the bimetal xerogel was carried out after it was completely dried. The solid residue was heated to 450 ℃ in air at a heating rate of 10 ℃•min^{-1} and then annealed at this temperature for 24, 30 and 36 h under an air atmosphere to produce three powdery products marked as S_{24}, S_{30} and S_{36}, respectively.

Preparation of grafted collagen matrix

Collagen was purchased from Taozheng Bioengineering Technology Co Ltd (Beijing, China) without further purification. Methyl methacrylate (MMA) was chosen as a grafting monomer due to its effectiveness of resulting grafted copolymers and characteristic absorption peak in an IR region. Stabilized MMA was distilled under a reduced pressure in a nitrogen atmosphere and used immediately. The 1∶1 mixture of 0.01 mol•L^{-1} cerium ammonium nitrate (CAN, 99.9 wt%) in 1 mol•L^{-1} nitric acid and 0.01 mol•L^{-1} 2,2'-azobis(isobutyronitrile) (AIBN, 99.9 wt%) in methanol was used as polymerization initiator due to easy self-polymerization of MMA. CAN was used without further purification. AIBN was recrystallized from absolute alcohol prior to use.

The grafting process was carried out according to the report.[26] Briefly, required collagen powder was dissolved in 100 mL of water/methanol of 3∶1. The calculated amount of MMA monomer (0.5 mol/L) was added into the solution followed by the calculated initiator. The reaction was carried out at 50 ℃ in a nitrogen atmosphere for 2 h. The resultants were then separated by filtration, and the obtained product was washed with distilled water and extracted with acetone to remove the loosely bound homopolymer. This process was continued until no homopolymer could be found.

Preparation of grafted collagen-Al_2O_3/SnO_2 nanocomposite

Al_2O_3/SnO_2 co-nanoparticles and the grafted collagen were mixed at a weight ratio of 1∶3 and completely dispersed in ethanol by vigorous stirring for 4 h. After ultrasonic vibration for 4—6 h the grafted collagen-Al_2O_3/SnO_2 nanocomposite was obtained. After filtrated the final product was washed thoroughly with absolute ethanol and evaporated at room temperature to remove impurities and solvents.

Characterization

X-ray powder diffraction (XRD) characterization was performed on a Rigaku D/MAX-RB instrument using a copper target at 45 kV and 40 mA. Transmission electron micrographs (TEM) were obtained using a Hitachi H-600 instrument operated at 80 kV with a 35-micron objective. The FT-IR spectra were recoded on a Nicolet 5ZDX spectrometer in the 4000—400 cm^{-1} wavenumber range. The sample thermal analysis was conducted by using a TGA/DTA apparatus (TMDSC, TA Q-600, TA instrument) operated at a heating rate of 20 ℃/min, to determine simultaneously the reaction heat of materials and the correlation between temperature and weight lose. When the test began, the samples were heated to 100 ℃ and maintained at this temperature for 20 min to remove the thermal history. The temperature was finally increased to 900 ℃. The temperature and the mass of both the samples and the reference were monitored at all the time.

Infrared emissivity testing procedure was carried out as follows: phenolic-aldehyde acetal adhesive was used as an adhesion agent; dimethyl benzene was used to adjust the density of the adhesive with a proportion of 1∶2; composite powder samples were dispersed uniformly in mixed glue with a volume ratio of 25%—30%, the powder entrapping glue was brushed on a square polishing aluminum foil (60×60 mm^2). After the coated surface was set in air for 1 h and then exerted by a pressure of 0.1—0.2 MPa for 2 h the infrared emissivity of these coatings was recorded using an IR-I infrared emissivity measurement instrument (supplied by Shanghai Research Institute of Technology and Physics, China).

Results and discussion

FT-IR spectra

Figure 1 shows the FTIR spectra of the as-prepared samples. Different from Al_2O_3/SnO_2 xerogel (curve b), both the grafted collagen (curve a) and the composite of grafted collagen and Al_2O_3/SnO_2 xerogel (curve d) show

a peak at 1728 cm^{-1}, which results from the characteristic absorption of the amide group of the collagen.[23,27] The composite of the grafted collagen and Al_2O_3/SnO_2 co-nanoparticles (curve e) shows the characteristic absorption of hydroxyl groups on the co-nanoparticle surface (curve c) at around 1670 cm^{-1} and a violet shift of the characteristic absorption peak of amide groups in the grafted collagen from 1728 cm^{-1} to 1756 cm^{-1}. The shift of 28 cm^{-1} results from the formation of hydrogen bond in the nanocomposites.[25] The hydrogen bonding interaction between the Al_2O_3/SnO_2 co-nanoparticles and the grafted collagen also leads to violet shifts of some FTIR bands of the grafted collagen, for example, the absorption peaks at 554 and 1110 cm^{-1} were shifted to 639 and 1167 cm^{-1}, respectively.

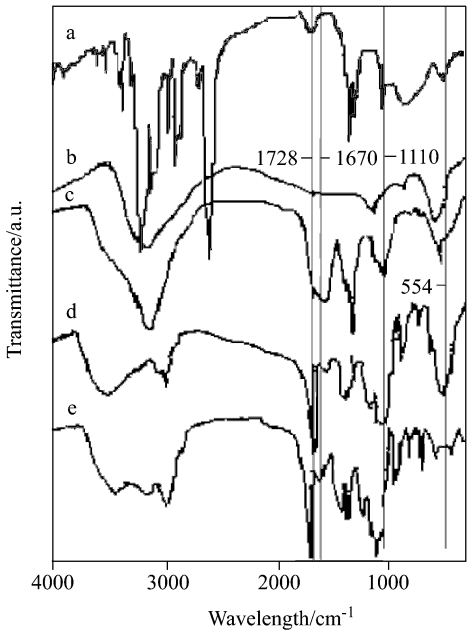

Figure 1 FTIR spectra of (a) grafted collagen, (b) Al_2O_3/SnO_2 xerogel, (c) Al_2O_3/SnO_2 nanoparticles, (d) composite of grafted collagen and Al_2O_3/SnO_2 xerogel, (e) nanocomposite of grafted collagen and Al_2O_3/SnO_2 nanoparticles.

XRD analysis

The collagen is a biomacromolecule, and both collagen and grafted collagen can not show the crystal structure. Thus the grafted collagen did not change the crystal structure of Al_2O_3/SnO_2 co-nanoparticles, and the crystal form of Al_2O_3/SnO_2 co-nanoparticles in the composite could be examined by an XRD pattern. Both XRD patterns of Al_2O_3/SnO_2 xerogel and Al_2O_3/SnO_2 co-nanoparticles showed the same 2θ values of peak positions (curves a and b in Figure 2). This proved that no change of crystal parameters occurred in the process of the heat treatment. The pattern of Al_2O_3/SnO_2 co-nanoparticles dispersed in a grafted collagen matrix, however, showed some different peaks (curve c) and some decrease in peak intensity corresponding to the Al_2O_3/SnO_2 co-nanoparticles. The peaks at 2θ values of 17.2° and 19.8° corresponded to the particle size d (referred to the crystal surface distance) of 0.24 and 0.134 nm, respectively, proposing a layer structure of the co-nanoparticles.[28] The peak at 2θ value of 31.7° was attributed to the d value of 0.44 nm, where the d value corresponded to the spacing between the polymer chains. The emergence of these novel diffraction peaks supplied indirect evidence for the interaction of Al_2O_3/SnO_2 nanoparticles and the grafted collagen matrix discussed above.

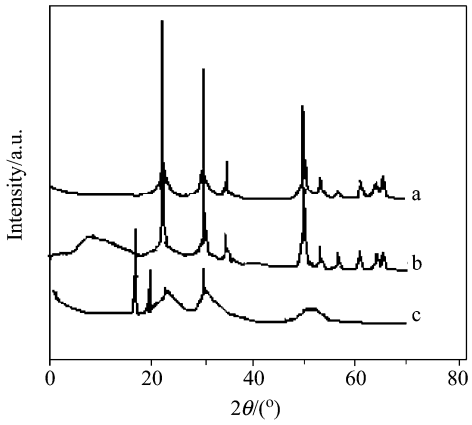

Figure 2 XRD patterns of (a) Al_2O_3/SnO_2 xerogel, (b) Al_2O_3/SnO_2 nanoparticles and (c) Al_2O_3/SnO_2 nanoparticles dispersed in grafted collagen matrix.

TEM micrographs

Some morphological differences among Al_2O_3/SnO_2 xerogel, co-nanoparticles and nanocomposites (grafted collagen-S_{24}) could be observed in Figure 3. The Al_2O_3/SnO_2 xerogel showed amorphous conglomeration morphology. In contrast, Al_2O_3/SnO_2 co-nanoparticles formed after heat treatment of the xerogel displayed well-distributed granule-shaped nanocrystals with the size of 20—40 nm. A distinct adsorption structure could be seen from the TEM of the nanocomposites. Most of the co-nanoparticles were touched with other neighbors and wrapped by grafted polymer chains. This morphology might give another proof to verify the strong interaction between two components on a microscale.

Thermal analysis

The changes of Al_2O_3/SnO_2 samples during heating at temperatures ranging from room temperature to 900 ℃ in air at a rate of 20 ℃•min^{-1} could be examined by a thermal analysis. The TGA patterns of typical grafted collagen-Al_2O_3/SnO_2 composites are shown in Figure 4. The TGA curve indicated the weight of the grafted collagen-xerogel gradually decreased in the temperature range from 200 to 600 ℃. However the weight loss of the grafted collagen-Al_2O_3/SnO_2 composites was very fast, which only occurred in the range of 210—420 ℃ with a dramatic decrease from 360 to 400 ℃. Furthermore the weight variations of the grafted collagen-S_{24} and S_{30} were much larger than that of the grafted collagen-xerogel. The original degradation temperature of

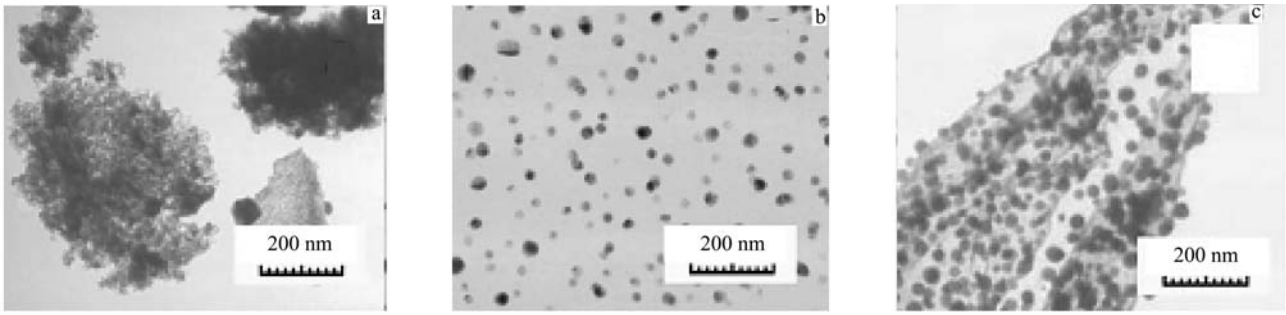

Figure 3 TEM micrographs of (a) Al_2O_3/SnO_2 xerogel, (b) Al_2O_3/SnO_2 nanoparticles and (c) grafted collagen-S_{24} nanocomposites.

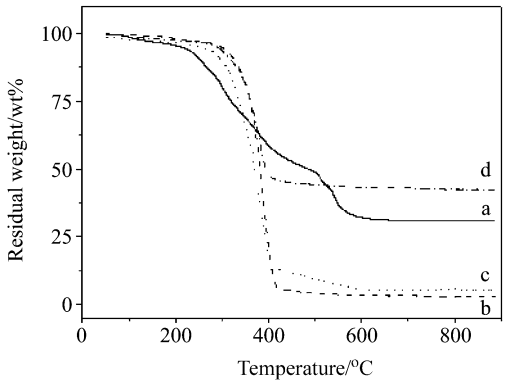

Figure 4 TGA curves of (a) grafted collagen-xerogel, (b) grafted collagen-S_{24}, (c) grafted collagen-S_{30} and (d) grafted collagen-S_{36} samples.

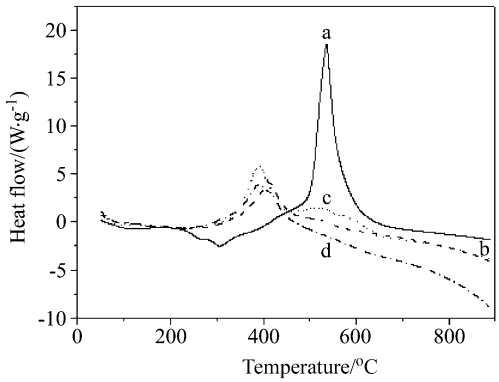

Figure 5 DTA curves of (a) grafted collagen-xerogel, (b) grafted collagen-S_{24}, (c) grafted collagen-S_{30} and (d) grafted collagen-S_{36} samples.

collagen was only 39 ℃.[29] Thus the grafted collagen-Al_2O_3/SnO_2 composites possessed good thermal stability. The different changes upon temperature increase indicated the interactions between the grafted collagen-co-nanoparticles and their structures were different from those of the grafted collagen-xerogel, which improved the thermal stability of the grafted collagen. In contrast, the interactions between Al_2O_3/SnO_2 xerogel and the grafted collagen matrix were weak. This conclusion coincided with the FTIR results.

The DTA signal of the grafted collagen-xerogel presented two weak endothermic peaks at 270 and 310 ℃, respectively, which associated with the decomposition of the biopolymers. These two peaks did not existed in grafted collagen-S_{24}, S_{30} and S_{36} samples, which was also due to the hydrogen bonding interaction. The single exothermic peaks in 360—450 ℃ occurring in the grafted collagen-S_{24}, S_{30} and S_{36} curves were attributed to the breaking of hydrogen bonding between the two components. Different from the nanocomposites, the weak interactions between the Al_2O_3/SnO_2 xerogel and the grafted collagen matrix produced an exothermic peak in 510—600 ℃, which was attributed to the decomposition of residual gels.

Infrared emissivity testing

The infrared emissvity testing data were given in Table 1, where it was observed that the infrared emissivity

Table 1 Infrared emissvity (wavenumber: 8—14 μm) of the different samples

Sample	Infrared emissivity	Sample	Infrared emissivity
collagen	0.850	S_{36}	0.747
grafted collagen	0.898	grafted collagen-Al_2O_3/SnO_2 xerogel	0.590
Al_2O_3/SnO_2 xerogel	0.649	grafted collagen-S_{24}	0.424
S_{24}	0.708	grafted collagen-S_{30}	0.451
S_{30}	0.723	grafted collagen-S_{36}	0.462

(8—14 μm) of the nanocomposites was much lower than those of the two components (grafted collagen-S_{24}: 0.424, grafted collagen: 0.898, S_{24}: 0.708). As known, there were two main modes of heat transfer (infrared energy) through a fibrous insulator: (1) the heat conduction through the gas filling the space between the fibers, and (2) the heat transferred by thermal radiation that was emitted, absorbed, and scattered by the fibers.[30] Conventional polymer materials contained many microscale pores, which hampered the heat transfer within the material, but in the grafted collagen-Al_2O_3/SnO_2 composites, the space containing air in these pores could be replaced by the metal oxide co-nanoparticles. The metal oxide possessed good heat conductivity, so the heat transfer process could be reinforced greatly in

above two modes. Thus the whole material possessed lower emissivity than the two components alone. This character was also assigned to the strong synergistic effect between the grafted collagen-Al_2O_3/SnO_2 nanoparticles.[23]

Conclusion

A novel nanocomposite was prepared by immobilizing Al_2O_3/SnO_2 co-nanoparticles on the tri-helix scaffolds of a grafted collagen matrix with the hydrogen bonding interaction. This hydrogen bond between the grafted collagen and the Al_2O_3/SnO_2 co-nanoparticles can improve the thermal stability of the nanocomposites. Besides, the nanocomposite possesses much lower infrared emissivity value than its two components, which could also be attributed to the Al_2O_3/SiO_2 co-particle-matrix hydrogen bonding interaction. This nanocomposite may act as a good candidate material for nanosensors and nanoelectronics.

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