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Simulating biomineralization method for the synthesis of MS (M = Cd, Zn, and Cu)/Polyurethane nanocomposite

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Nanocomposite polyurethane/sulfides (CdS, ZnS, CuS) were successfully prepared via a simulating biomineralization method. Structural, morphological, and compositional studies of the materials were analyzed via Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), and differential scanning calorimetry (DSC). Formation mechanisms of MS nanoparticles in PU were studied. These methods provided a novel approach for the fabrication of nanocomposite films that may be applied to MS (M = Cd, Zn, and Cu) polyurethane field-assisted biosensors, photocatalysis, nonlinear optics, flat panel displays, and many other industrial processes.

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1. Introduction

Embedding II–VI semiconductor nanoparticles in a polymer matrix to form an inorganic/organic composites is expected not only to permit a wide-range selection of emitters and carrier transport materials but also to provide a new approach to construct high-performance electroluminescent efficient organic materials and inorganic semiconductors with high carrier density and low resistivity, which are the potential applications of this process [1]. In addition, the polymers are also expected to provide good mechanical, as well confer high kinetic, stability on nanometer-sized semiconductor particles [2].

In recent years, the fabrication of semiconductor nanoparticles in solid polymer matrixes has attracted increasing attention because the combination of semiconductor nanoparticle and polymer provides a simple route to stabilize and process the material by integrating the promising properties. Polymers are considered as a good choice for host materials because their physical properties can be designed, such as long-term stability and flexible processability. Interesting optical properties such as fluorescence, electroluminescence, and optical nonlinearity have already been observed in these composites.

Polyurethanes (PUs) are types of high-performance polymeric materials that have been widely used in the aerospace, electronics, and microelectronic industries because of their outstanding thermal and chemical stabilities as well as mechanical and electrical properties [3–5]. In recent years, the synthesis of polyurethane nanocomposite materials has been intensely studied because of their extraordinary properties and widespread potential applications [6,7].

In this paper, a method for the preparation of MS/PU nanocomposites in an aqueous system by simulating the bio-mineralization process was reported. Contrary to traditional chemical routes, the present method involves the use of thioacetamide (TAA) as the precursor of hydrogen sulfide ($CH_3CSNH_2 + 2H_2O \longrightarrow CH_3COOH + NH_4^+ + HS^-$, $M^{2+} + H_2S \longrightarrow MS + 2H^+$) in the reaction with sulfur and polyurethane /MS samples. We did not use H_2S as the sulfur ion source to avoid any toxicity effects. The formation of inorganic nanoparticles and the polymerization of monomers were simultaneously performed. and All processes were carried out in ambient conditions. The formation of inorganic nanoparticles and the polymerization of monomers were simultaneously performed.

2. Experimental section

2.1. Materials and instrument

Polyurethane (PU, $\overline{Mn}$ of 2860, an $\overline{Mw}$ of 4260) were synthesised). Zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 4H_2O$), cadmium nitrate tetrahydrate ($Cd(NO_3)_2 \cdot 4H_2O$), lead nitrate tetrahydrate ($Cu(NO_3)_2 \cdot 5H_2O$), acetic acid, thioacetamide (TAA, CH_3CSNH_2), and ethanol (CH_3CH_2OH) were analytical reagents with high grade quality and were all obtained from Shanghai Sanpu Chemical Co., Ltd. (China). These chemicals were used without further purification. Distilled water used in the experiment was double distilled without further purification.

Thermal analytical experiments were performed using a differential scanning calorimeter (DSC) with Analytik Jena AG Q100 operated in the conventional DSC mode at a heating rate of 10 ºC/min to determine simultaneously the correlation between temperature and weight loss in a nitrogen atmosphere. Scanning electron microscopy (SEM) was performed with a JSM-6380 microscope at an accelerating voltage of 200 KeV and a Hitachi Model H-800 transmission electron microscope (TEM) at an accelerating voltage of 200 KeV. The samples were coated with a thin layer of gold before measurement. Fluorescence measurements were performed at room temperature with a RF-5301PC fluorescence spectrometer (Shimadzu Instruments Inc, Japan).

2.2. Method of synthesis

2.2.1 Synthesis M^{2+}/PU

A 250 mL three-neck boiling flask was equipped with a mechanical stirrer and a nitrogen inlet. In the flask, 11.6 g of $H_2N(CH_2)_6NH_2$ was dissolved with 41.3 mL of dimethly carbonate, and 0.7 g of CH_3OH and M^{2+} was added. In normal temperature and pressure, the suspension was stirred using a mechanical stirrer for 8 h. Finally, the mixture of products was dried at room temperature. The products were dissolved into 3.5 mL of $HOCH_2CH_2OH$ in the 250 mL three-neck flask. The mixture was stirred vigorously in a nitrogen atmosphere at 160 °C for 1.5 h. by using $AlCl_3$ and epoxy resins as catalysts.

2.2.2 Preparation of MS/PU nanocomposite

First, 1.0043 g of polyurethane, which contain M^{2+}, was first diluted with DMF, and the pH=10 solution, which contain TAA（the concentration of TAA is 1×10^{-4}）, was added to the solution of polyurethane which contain M^{2+}, The mixture was then dispersed by ultrasonic vibration for 15 min, in order that the complete transformation between M^{2+} and S^{2-} to MS (Calculated from the mol of PU,the content of CdS,ZnS,CuS is 3.4% ,2.4%,2.3%) takes place in the reaction.The solid was dried in vacuum at room temperature for 6 h and was kept for further characterization.

3. Results and discussion

3.1 FTIR analysis MS/PU nanocomposite

The FTIR spectrum (Fig. 1) shows that the asymmetric stretching frequency of the O=C-O- band of the amidoformate group in PU is roughly located at 1261 cm^{-1}. The absorption peaks at 1253 cm^{-1} (ν C-O-C) and at 3350 and 1540 cm^{-1} (νN-H) indicate the existence of intermediate PU. After reacting with $Zn(NO_3)_2$, $Cd(NO_3)_2$, $Cu(NO_3)_2$, the bands at 2300 cm^{-1} became very different. However, the basic trend is consistent. The FTIR spectrum results indicate that the amido group of PU coordinated with M^{2+}. Monodisperse sulfides nanoparticles are generated because these M^{2+}/PU composites react with sulfurions and are released by the hydrolysis of thioacetamide.

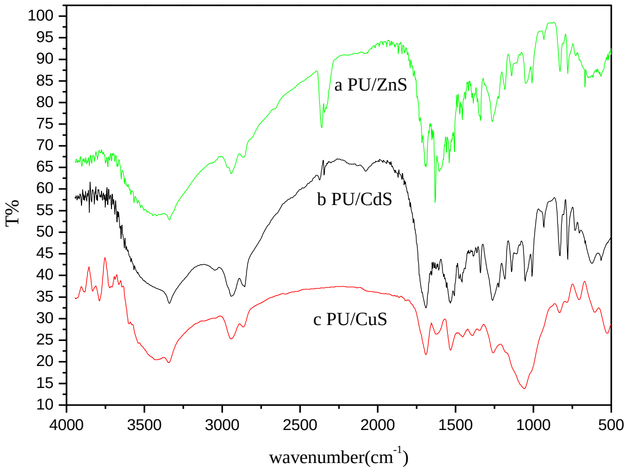

Fig. 1. FTIR spectra of the PU/MS.

3.2 UV/vis spectra

The synthesis of amido-coated MS nanocrystals involves the reaction between M and sulfur ions in the presence of amido group-containing ligands as organic ligands. The electron-deficient atoms of M on the surface of the semiconductor function as the binding sites to anchor organic ligands and to hinder further growth of crystal grains, which results in the formation of nanosized crystals. The mean size of the dispersed MS particles could be controlled by varying the initial amount of M deposition [8]. In our case, the preparation of CdS nanocrystals by cadmium chloride, TAA, and PU (as the ligand) was done at room temperature. The maximum absorption band of CdS nanocrystals occurs at 433 nm based on the UV/Vis spectra (Fig. 2). The absorption between 300 and 600 nm can be attributed to the embedded CdS nanoparticles. The UV/Vis on the set absorption of semiconductor nanoparticles is attributed to band-gap absorption and is relative to the bulk because of the quantum size confinement effect [9–11].

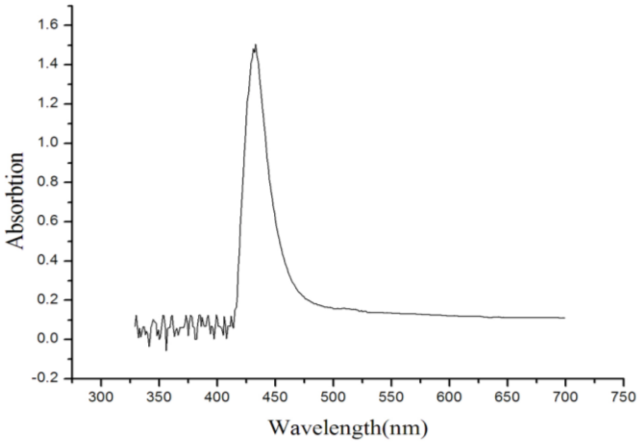

Fig. 2. UV spectra of the PU/CdS.

3.3 DSC

The DSC (Fig. 3) curve shows that the temperature of PU (Fig. 3a) endothermic peak at about 88.59 °C is attributed to the volatilization of residual water and organic solvent. The exothermic peak observed at 256 °C is related to the decomposition of the polymer. The DSC curve shows that the temperature of PU/CdS (Fig. 3b) endothermic peak at about 95.55 °C is attributed to the volatilization of residual water and organic solvent. The exothermic peak observed at 270 °C is related to the decomposition of the polymer. This result indicates a strong and uniform interaction between PU and nanoparticles [12]. Meanwhile, some several small exothermic peaks observed from 95.55 °C to 270 °C are due to the heat effect of the oxidation combustion of organic substances [13]. The DSC curve shows that the temperature of PU/ZnS (Fig. 3c) endothermic peak at about 98 °C is attributed to the volatilization of residual water and organic solvent. The exothermic peak observed at 258 °C is related to the decomposition of the polymer. The DSC curve shows that the temperature of PU/CuS (Fig. 3d) endothermic peak at about 110 °C is attributed to the volatilization of residual water and organic solvent. The exothermic peak observed at 263 °C is related to the decomposition of the polymer. The third temperature, which is attributed to the volatilization of residual water and organic solvent of PU endothermic peak, is at around 100 ℃. The decomposition of the polymer temperature of PU/MS is higher compared with PU. This result indicates a strong and uniform interaction between PU and the nanoparticles.

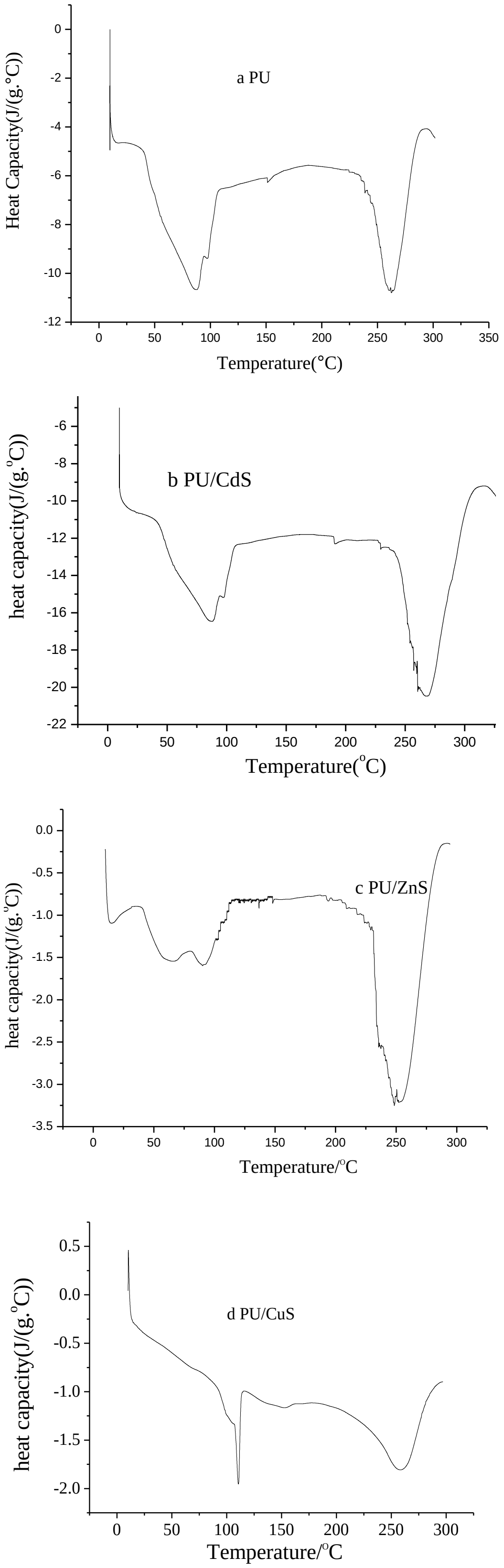

Fig. 3. DSC spectra of the PU ,PU/CdS, PU/ZnS, PU/CuS.

3.4 SEM of PU/CdS nanocomposite hybrids

Fig. 4 shows the SEM micrographs of the PU/CuS (Fig. 4a) and PU/CdS (Fig. 4b) nanocomposite films. The direct evidence of the formation of a nanocomposite was provided by the SEM investigation. In Fig. 4, the micrographs confirmed that the MS particles were well dispersed in the PU matrix. Polymer chains may be bridged by connecting to the same nanoparticle, and the multiplicity of such bridged chains and particles could lead to particle clustering [14]. The nanoparticles are dispersed in the PU matrix on a nanoscale, which indicates the formation of a nanocomposite to an extent.

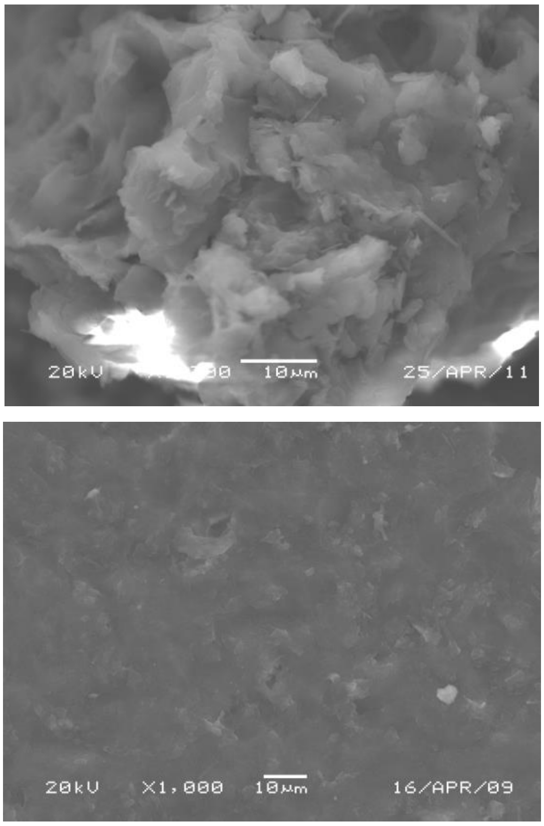

Fig. 4. The SEM micrographs of the PU/CuS (Fig. 4a), PU/CdS (Fig. 4b) nanocomposite films.

3.5 Formation mechanism of MS nanoparticles in PU

In MS nanoparticles growth, PU has an important function. TAA slowly decomposes in aqueous solution and homogeneously releases S^{2-} ions to produce the nanomaterials. Simultaneously, the MS nucleation and growth are well controlled because S^{2-} ions are supplied smoothly. All generated nanoparticles aggregate into PU. Fig. 5 describes the scheme of the formation of MS nanoparticles. When Upon addition, M^{2+} ions can coordinate with hydrophilic groups such as NH_2 in the PU chain. TAA slowly decomposes in aqueous solution and S^{2-} ions that are released from TAA first access the outer surface of PU then diffuse into the inner surface because of the hindrance between PU chains. Furthermore, S^{2-} ions first react with M^{2+} in the outer interface that covers the surface of PU film. Thus, the H_2S molecule has a hard time accessing the inner surface. Therefore, the dissolved ions can recrystallize into larger crystallites in the outer interface.

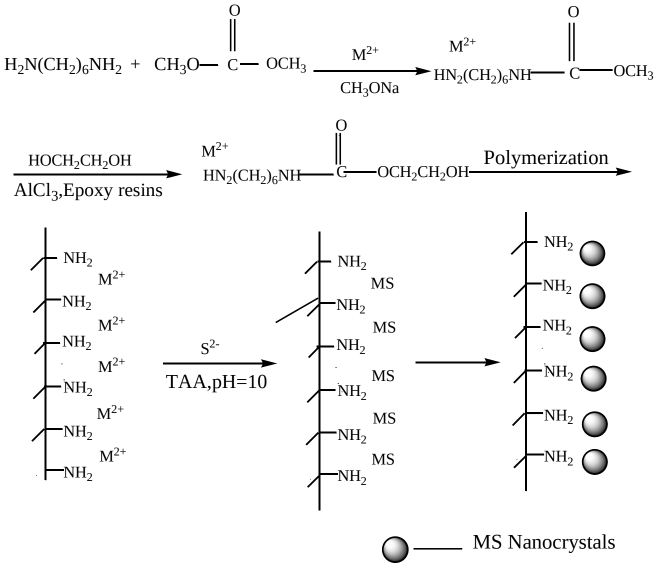

Fig. 5. The scheme of the formation of MS nanoparticals.

4. Conclusion

MS (M= Cd, Zn, and Cu) nanoparticles were fabricated via a simulating biomineralization method. Structural, morphological, and compositional studies of the materials were analyzed via Fourier transform infrared spectroscopy, scanning electron microscopy, and differential scanning calorimetry. Formation mechanisms of MS nanoparticles in PU were studied.The incorporation of MS (M=Cd, Zn, and Cu)/polyurethane as nanoparticles shows the stability and functionality of the tailored polymerix matrix. These methods have provided a novel approach for the fabrication of nanocomposite films, which may be applied to MS (M=Cd, Zn, and Cu) /polyurethane field-assisted biosensors, photocatalysis, nonlinear optics, flat panel displays, and many other industrial processes.

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