

# Synthesis, characterization, and fluorescence sensor property of polyurethane / CuS nanocomposites

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Polyurethane/CuS nanocomposite films were prepared via simulating biomineralization method in the presence of polyurethane obtained through in situ polymerization. These films were investigated by using Fourier transform infrared spectra, dynamical mechanical analysis, and scanning electron microscopy. The fluorescence emission of the nanocomposite films is sensitive to the presence of benzaldehyde. These films have a strong fluorescence emission quenching with the increasing benzaldehyde concentration. The common anions and cations in organic reagent have no effect on the determination of benzaldehyde.

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## 1. Introduction

Nanocrystalline semiconductors have been attracting considerable research interest because of their distinct properties. The nanomaterials can be different from those of their corresponding bulk materials [1–2]. Their properties are strongly dependent on size, shape, and surface properties. When a metal sulfide is deposited on a polymer substrate that is flexible and transparent, the resulting polymer-coated metal sulfide will be useful for electronic and optical device applications [3–5]. Among the metal sulfides, copper sulfides are important materials because of their technological applications. Copper sulfides are interesting because of their complex structure and valence state, which result in some distinct properties [6–7]. Green CuS is particularly interesting because of its metal-like electrical conductivity in liquid helium temperature [8]. Many techniques have been employed to prepare CuS in various polymers. Mizogami et al. [4] prepared poly(acrylonitrile)-coated CuS via the sputtering method. Grijalva and his co-workers [9] prepared amorphous and crystalline CuS and deposited them on different polymer substrates, such as poly(ethylene), poly(ethylene terephthalate), and 6-nylon through immersion. These films are formed in the reaction mixture of  $\text{Cu}^{2+}$  and thiourea in alkaline solution.

In the present investigation, we aim to gain understanding of the structure of the nanocomposites in various stages of their formation. A model system of polyurethane and copper sulfide was used in this study. Its structure was probed using Fourier transform infrared spectra (FTIR), Uv-vis, scanning electron microscopy

(SEM), and differential scanning calorimeter (DSC). The fluorescence properties of the composites were studied to monitor the pollutant in the environment as an indicator.

## 2. Experimental

### 2.1. Materials

All materials were of analytical reagent grade, commercially available, and used without purification.

### 2.2. Characterizations

FTIR spectroscopy was performed with a NICOLET-NEXUS670 spectrometer. The samples were ground with KBr crystals and pressed into a flake for IR measurement. Thermal analysis experiments were performed using a DSC operated in the conventional DSC mode at a heating rate of 10 °C/min to determine the correlation of temperature and weight loss in a nitrogen atmosphere simultaneously. SEM was conducted with a JSM-6380 microscope at an accelerating voltage of 200 kV. The samples were coated with a thin layer of gold before measurement. Fluorescence measurements were performed carried out at room temperature with a RF-5301PC fluorescence spectrometer (Shimadzu Instruments Inc, Japan).

### 2.3. Activation of quartz plates

A clean quartz plate (0.9 cm × 3 cm) was placed into a

concentrated  $\text{H}_2\text{SO}_4$  solution containing 5 wt%  $\text{K}_2\text{CrO}_4$ . The solution was heated to  $100\text{ }^\circ\text{C}$  and maintained at this temperature for 10 min. The plate was removed from the solution and rinsed with water. After the treatment, the plate was covered with a smooth, thin layer of water and free of dust and other impurities. The oxidizing treatment should be repeated when the plate did not pass the test. The activated quartz plate was dried at  $100\text{ }^\circ\text{C}$  in a dust-free oven for 1 h, cooled to room temperature, and kept in a desiccator.

#### 2.4. Synthesis of PUs that contain $\text{Cu}^{2+}$

A 250 mL three-neck boiling flask was equipped with a mechanical stirrer and a nitrogen inlet. In the flask, 11.6 g of  $\text{H}_2\text{N}(\text{CH}_2)_6\text{NH}_2$  was dissolved into 41.3 mL of dimethyl carbonate. Subsequently,  $\text{CH}_3\text{OH}$  (0.7 g) and  $\text{CuCl}_2$  were added. Under normal temperature and pressure, the suspension was stirred with 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  $\text{OHCH}_2\text{CH}_2\text{OH}$  in a 250 mL three-neck flask. With a catalyzer of  $\text{AlCl}_3$  and epoxy resins, the mixture was stirred vigorously under a nitrogen atmosphere at  $160\text{ }^\circ\text{C}$  for 1.5 h. Polyurethanes (Pus) were obtained afterward.

#### 2.5. Preparation of the PU/CuS nanocomposite films

About 1.0043 g of PU was diluted in DMF, and the TAA solution (pH 10) was added into this solution. The mixture was ultrasonicated for 15 min. The compound slide on the activation of the plates was used in a series of controllable experiments. The solid was dried in vacuum at room temperature. The synthesis of CuS/PU nanocomposite hybrids is shown in Fig. 1.

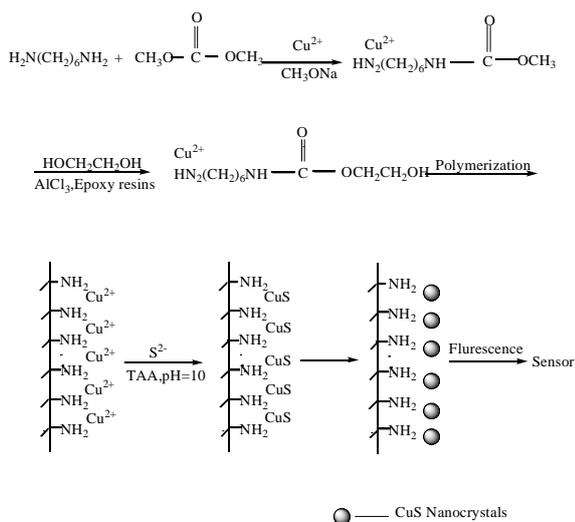


Fig.1. The synthesis scheme of PU/CuS film

#### 2.6. Sensing and reversibility of film response to benzaldehyde

In the experiment, the film was allowed to adhere on

one inner side of a quartz cell with a volume of ca.  $3.5\text{ cm}^3$ . Afterward, solvent with a volume of  $2.5\text{ cm}^3$  was added into the cell. Finally, the spectra were recorded when the fluorescence intensity became stable after the injection of benzaldehyde solution into the cell. The reversibility of the film to benzaldehyde was examined using a standard method. The film was exposed to an aqueous solution of the analyte, and the maximum emission intensity of the film was recorded. Subsequently, proper amount of benzaldehyde was added to the solution. Finally, the emission intensity of the film was measured for five times in every 6 min. After the measurements, the film was washed with pure water several times. The measurement was repeated for five times with the same analyte concentration. To test the reversibility of the film sensor for benzaldehyde, the film was alternatively exposed.

### 3. Results and discussion

CuS synthesis involves the reaction between copper and sulfur ions. The copper ions on the surface of the semiconductor serve as the binding sites to anchor organic ligands and hinder further growth of crystal grains, which results in the formation of nanosized crystals. In our case, CuS nanocrystals were prepared in only 15 min at room temperature.

#### 3.1. Spectral data

According to the FTIR spectra of the pure PU (a), PU/CuS (b), and a PU (c) intermediate (Fig. 2), strong absorption peaks at  $1690\text{ cm}^{-1}$  ( $\nu\text{ C}=\text{O}$ ) show that abundant hydroxyl groups are tethered on the surface of CuS nanocrystals. The absorption peaks at  $1253$  ( $\nu\text{ C}-\text{O}-\text{C}$ ),  $3350$ , and  $1540\text{ cm}^{-1}$  ( $\nu\text{ N}-\text{H}$ ) indicate the existence of the PU (c) intermediate. However, the carbonyl group of PU is shown in the region of  $2940$  and  $2860\text{ cm}^{-1}$  [10]. In the case of the spectrum of PU/CuS, where the characteristic peaks of pure PU and CuS are still maintained, (OH) stretching and bending bands are observed at  $3423$ ,  $1657$ ,  $1410$ , and  $1200\text{ cm}^{-1}$  in pure CuS. Therefore, PU structure is affected with the presence of CuS.

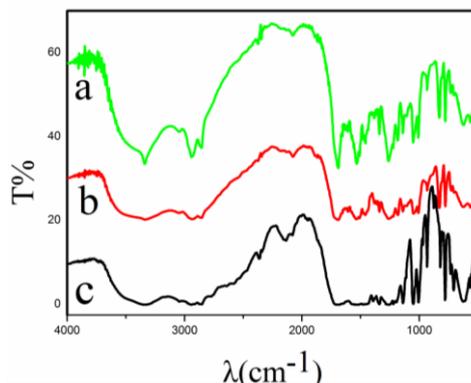


Fig. 2. The FTIR of PU and PU/CuS (a, PU/CuS film; b, PU film; c, Intermediate of PU)

### 3.2. Thermal properties

The DSC curve (Fig. 3) shows that the temperature of the PU/CuS endothermic peak at about 108 °C is the volatilization temperature of residual water and organic solvent. The exothermic peak observed at 258 °C is related to the decomposition of the polymer. Obviously, this result indicates a strong and uniform interaction between PU [10] and nanoparticles. This behavior was already observed with different PU composites and reflects the glass transition of the appended PU chains (i.e., less mobile than free ones), without any substantial contribution from macromolecules [11]. Furthermore, the small exothermic peaks observed at 108–258 °C are caused by the heat effect of the oxidation combustion of organic substances. This result also indicates a strong and uniform interaction between PU and nanoparticles. This feature also agrees with the previous SEM measurements.

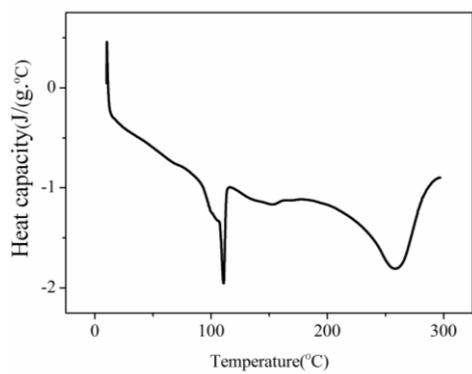


Fig. 3. The DSC of PU/CuS

### 3.3. SEM characterization of PU/CuS nanoparticle films

Fig. 4 shows the typical SEM image of PU/CuS nanoparticle films. The sizes of the nanoparticles are uniform. Polymer chains may also be bridged via connecting to the same nanoparticle, and a multiplicity of such bridged chains and particles could lead to particle clustering. The nanoparticles are dispersed in the PU matrix on a nanoscale, which indicates the formation of a nanocomposite.

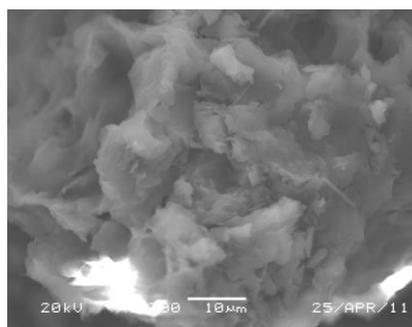


Fig. 4. The SEM of PU/CuS

### 3.4. Sensing properties of the present film to benzaldehyde

Fig. 5 shows the fluorescence emission spectra ( $\lambda_{ex}=313$  nm,  $\lambda_{em}=407$  nm) of the film as a function of benzaldehyde concentrations ( $C_{(benzaldehyde)}/g \cdot mL^{-1}$ ): 0.00,  $2.049 \times 10^{-3}$ ,  $4.23 \times 10^{-3}$ ,  $6.4935 \times 10^{-3}$ ,  $8.6987 \times 10^{-3}$ ,  $1.0972 \times 10^{-3}$ ,  $1.2671 \times 10^{-3}$ ,  $1.4194 \times 10^{-3}$ , and  $1.8 \times 10^{-2}$  g·mL<sup>-1</sup>. Clearly, the emission of the films increases significantly with an increase in benzaldehyde concentration from 0 g·mL to  $1.8 \times 10^{-2}$  g·mL. The correlation equation (Fig. 6) is as follows:

$$I = -7.5844c + 327.89 \quad (R^2 = 0.9893) \quad (1)$$

Generally, the process can last until 12 h.

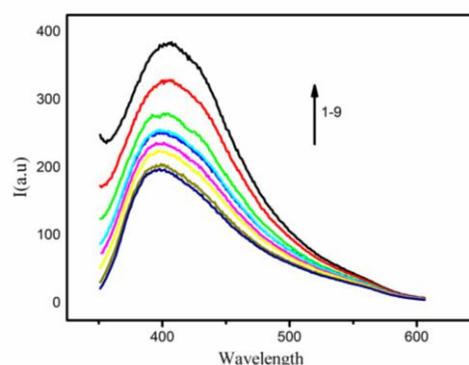


Fig. 5. The sensing properties of PU/CuS film ( $C_{(benzaldehyde)}/g \cdot mL^{-1}$ ): 0.00,  $2.049 \times 10^{-3}$ ,  $4.23 \times 10^{-3}$ ,  $6.4935 \times 10^{-3}$ ,  $8.6987 \times 10^{-3}$ ,  $1.0972 \times 10^{-3}$ ,  $1.2671 \times 10^{-3}$ ,  $1.4194 \times 10^{-3}$ , and  $1.8 \times 10^{-2}$  g·mL<sup>-1</sup>

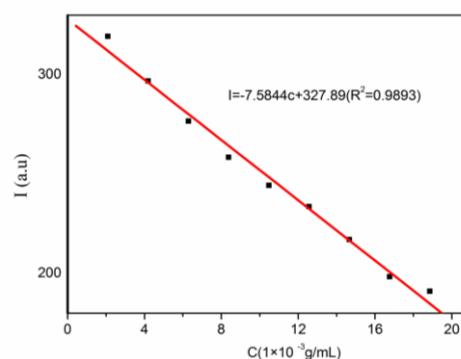


Fig. 6. The dependence of the fluorescence intensity of the PU/CuS film on the concentration of benzaldehyde ( $C_{(benzaldehyde)}/g \cdot mL^{-1}$ ): 0.00,  $2.049 \times 10^{-3}$ ,  $4.23 \times 10^{-3}$ ,  $6.4935 \times 10^{-3}$ ,  $8.6987 \times 10^{-3}$ ,  $1.0972 \times 10^{-3}$ ,  $1.2671 \times 10^{-3}$ ,  $1.4194 \times 10^{-3}$ , and  $1.8 \times 10^{-2}$  g·mL<sup>-1</sup>

### 3.5. Reversibility of the film response to benzaldehyde

The results are shown in Fig. 7. The response of the film to the same benzaldehyde concentrations is fully

reversible. Furthermore, the time needed to reach equilibrium in the response is less than 5 min, which is a rather fast response. To test the reversibility of the film sensor to benzaldehyde, the film was alternatively exposed to a solution of benzaldehyde and pure water, and the corresponding fluorescence emission was measured. After each measurement of the salt solution, the film was washed with pure water several times. The results show that the emission of the film could be fully restored (Fig. 7).

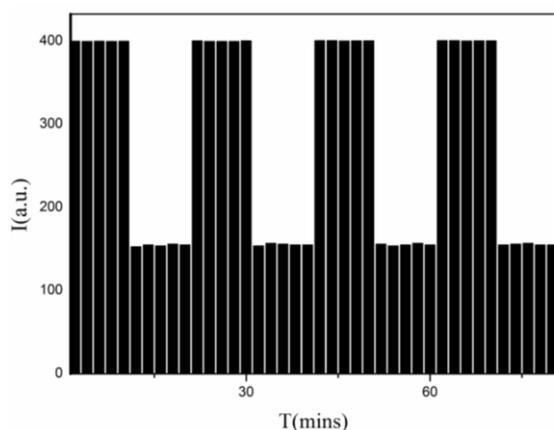


Fig. 7. The reversibility of PU/CuS

#### 4. Conclusion

A new film sensor for benzaldehyde was developed via simulating a biomineralization process synthesizing CuS nanoparticles into PU. The fluorescence emission of the film is sensitive to the presence of benzaldehyde in liquid phase. Benzaldehyde is efficient and sensitive to the emission of the film, which was ascribed to the hindrance effect induced by CuS particles. To the best of our knowledge, this paper is the first to report that the film sensor is sensitive to benzaldehyde and that the detection limit is  $6.290 \times 10^{-3}$  mol/L. Considering the sensitivity, reversibility, and fast response of the present film in the detection of benzaldehyde, the film may have potential

uses in the monitoring of benzaldehyde.

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