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Biomimetic Method Synthesis of HgS/Polyurethane Composite Film and Its Sensing Properties to Ba^{2+}

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Polyurethane-conjugated HgS nanocrystals with tunable sizes prepared by using biomimetic method. The obtained HgS nanoparticles with good dispersibility were characterized by Fourier transform infrared. Scanning electron microscopy are used to envisage the binding of nanoparticles with functional groups. The polyurethane molecules can control nucleation and growth of HgS crystals by binding on the surface of nanocrystals to stabilize nanoparticles. Quantum confinement effect of polyurethane-conjugated HgS nanocrystals was confirmed by UV-Vis spectra. The nanoparticles exhibit a well-defined emission feature at about 291 nm. The fluorescence results reveal that the PU/HgS nanoparticles film is sensitive to Ba^{2+}, and a small amount of Ba^{2+} makes the emissions increase rapidly. The emission is hardly affected by other common ions in water. The nanocomposite film is possible to become a special sensor material for Ba^{2+}.

Key words: Polyurethane, HgS nanoparticals, Fluorescence sensor

I. INTRODUCTION

There has been a growing need for developing highly sensitive and selective probes for the detection of metal ions with their toxic effect in the environment. Some fluorescence probes have been successful in detection of significant metal ions, but some metal specific probes were still short in the market.

Quantsum dot (QD)-based sensors of detection have attracted extensive interest for the special optical component QDs [1−3]. Many methods such as sonochemical method [4], everse micelles [5], sol-gel processing [6], chemical bath deposition [7], microwave irradiation [8], hydrothermal and solvothermal routes [9, 10] *etc.* were used to synthesize II-VI semiconductors nanocrystals. However, due to the disadvantage of traditional methods such as high synthetic temperature and pressure, toxic organic solvents, a simple and environmental friendly synthetic route is a key research challenge.

HgS is the most important semiconductor possessing excellent optical property in the infrared region [11−14]. It has been widely used in photoelectric conversion devices, electrostatic image materials and ultrasonic transducers *etc.* [15, 16]. There was few reports on HgS nanocrystals owing to the difficulties in handling the materials during synthesis and the toxicity of mercury. A new and efficient preparation method of HgS semiconductor is still one of the most challenging issues. Biomimetic synthesis became a hot topic in last decade [17, 18]. Wang and their workers prepared HgS nanoparticals in the chitosan matrices [19]. Yang and co-workers have reported the biomimetic synthesis of HgS nanocrystals using proteins as matrices [20, 21]. Herein, we used polyurethane as template to synthesize HgS nanoparticles through biomimetic method and studied the interaction of HgS nanoparticles. Its structure was characterized using FTIR, UV-Vis, SEM, *etc.* The synthesis procedure was a one-step method using non-toxic and low cost materials. In addition, polyurethane-conjugated HgS nanocrystals were more stable than other QDs solution. The fluorescence properties of the composites were studied and the fluorescence emission of the film was very sensitive to the presence of Ba^{2+} in the aqueous phase. What's more, its response to the salts is also fully reversible. Therefore the development of this sensor is simple for the detection of the Ba^{2+}.

II. EXPERIMENTS

A. Materials and characterizations

Mercury chloride ($HgCl_2$) and thioacetamide (TAA) were of analytical grade. All the reagents were used as received without any further purification. Water was used after purification through double distillation.

Fourier transform infrared (FTIR) spectroscopy was conducted with a Nicolet Nexus 670 spectrometer. Scanning electron microscopy (SEM) was performed with a JSM-6380 microscope at an accelerating voltage of 200 kV. The samples were coated with a thin

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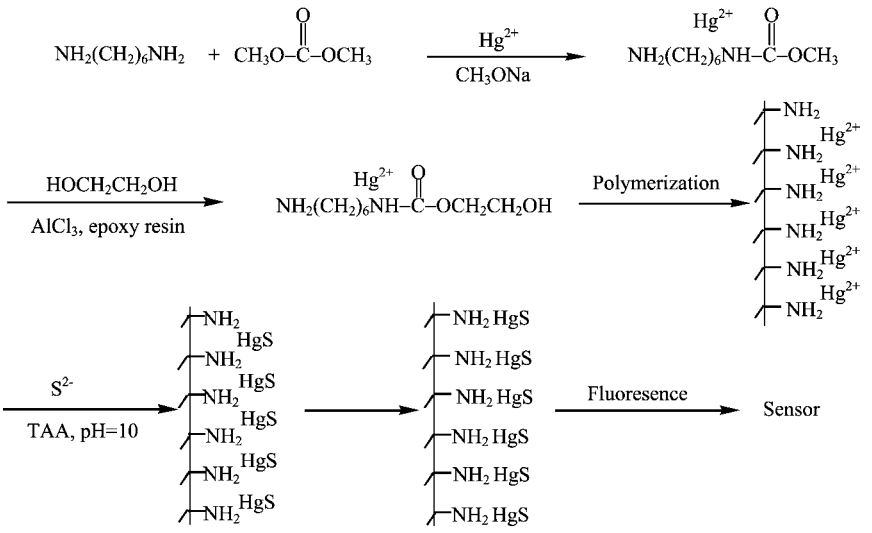

FIG. 1 Schematic of PU/HgS nanocomposite film.

layer of gold before measurement. Fluorescence measurements were performed at room temperature with an RF-5301PC fluorescence spectrometer (Shimadzu Instruments, Inc., Japan).

B. Experiments

PU/HgS nanocomposite film was prepared [22]. The overall synthetic procedure is presented in Fig.1. A three-neck 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 into 41.3 mL dimethyl carbonate, and CH_3OH (0.7 g) and $HgCl_2$ were added in it. The suspension was stirred for 8 h under normal temperature and pressure. The products were dried and dissolved into 3.5 mL $OHCH_2CH_2OH$ in the 250 mL three-neck flask. Then it was stirred vigorously under nitrogen atmosphere at 160 °C for 1.5 h with $AlCl_3$ and epoxy resins as catalytic agent. Then, 1.0043 g of the product was diluted in DMF. The compound slides on the activation of the plates. After drying, the film was immersed for 24 h in fresh TAA (0.1 mmol/L) solution with pH=10. The solid was dried in vacuum at room temperature and immersed for 24 h in fresh TAA (0.1 mmol/L) solution with pH=10 again for five times. The PU/HgS nanocomposite film were gotten using polyurethane as template to synthesize HgS nanoparticles by simulating biomineralization process. The synthetic route without toxic organic solvents is simple, environmental friendly.

C. Selective test of the PU/HgS nanocomposite film

The prepared PU/HgS film was installed in a quartz cell with about 2.5 mL redistilled water. The cell was mounted into the fluorescence spectrometer in a fixed position to ensure the detection of fluorescence emission intensity without interference from the excitation light source. Various cations solutions such as Ba^{2+}, Pb^{2+}, Ca^{2+}, ... with the same concentration were introduced into the cell one after another. After each measurement, the film was washed with redistilled water until its fluorescence intensity reached the initial blank value and the fluorescence emission intensity was used for analytical determination.

D. Detection of Ba^{2+}

The signal output value was calculated according to the relative fluorescence intensity I/I_0, *i.e.* the fluorescence intensities of the PU/HgS-based sensor system at 444 nm in the presence of Ba^{2+} I was compared with that without Ba^{2+} I_0. The experiment conditions were optimized by relative fluorescence intensity at 444 nm after adding 100 nmol/L Ba^{2+} into the sensor system. To study the relationship between relative fluorescence intensity and the amount of Ba^{2+}, different concentrations of Ba^{2+} were added to the assay solution and the fluorescence spectra were recorded. In the experiment, the film was allowed to adhere to one inner side of a quartz cell with a volume of ca. 3.5 cm^3. Then, 2.5 mL of solvent was added into the cell. Finally, the spectra were recorded when the fluorescence intensity became stable after the injection of Ba^{2+} solution into the cell. The reversibility of the film to Ba^{2+} was examined using a standard method. The film was exposed to an aqueous solution of the analyte, and then the maximum emission intensity of the film was recorded. This was followed by adding proper amount of Ba^{2+} to the solution. Finally, the emission intensity of the film was measured 5 times every 6 min. After the measurements,

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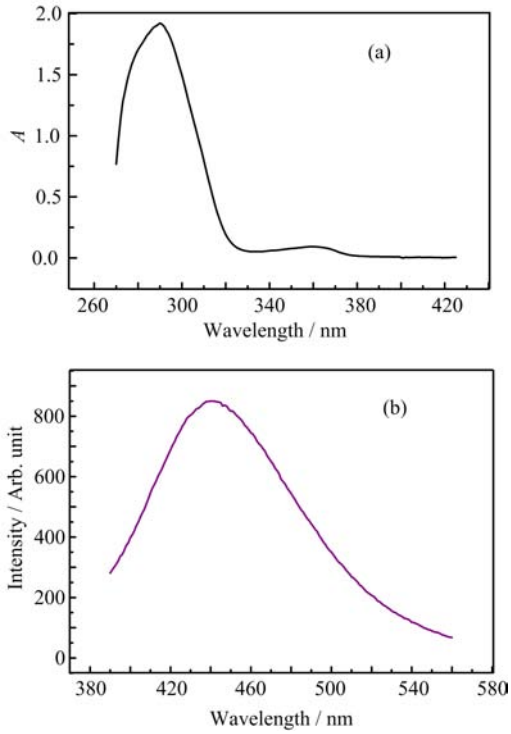

FIG. 2 (a) UV-Vis spectrum and (b) fluorescence emission spectrum of the PU/HgS nanocomposite film.

the film was washed with redistilled water several times. The measurement was repeated 5 times with the same concentration of the analyte. To test the reversibility of the film sensor for Ba^{2+}, the film was alternatively exposed.

III. RESULTS AND DISCUSSION

A. Optical properties of HgS nanocrystals

UV-Vis absorption spectra have been proven to be very sensitive to the formation of nanoparticles [23]. Both the position and the intensity of absorption are related to the size of semiconductor particles [24]. The UV-Vis spectrum of PU/HgS nanocomposite film is determined with excitation wavelength of 291 nm (Fig.2(a)). The fluorescence emission spectrum of the PU/HgS nanocomposite film at about 444 nm is shown in Fig.2(b).

B. FTIR investigation on the PU/HgS nanocomposite film

FTIR spectroscopy measurements were performed to study the structural changes of polyurethane in the PU/HgS nanocomposite film. The FTIR spectra of pure polyurethane, the intermediate of polyurethane, and HgS-polyurethane are shown in Fig.3. The peaks

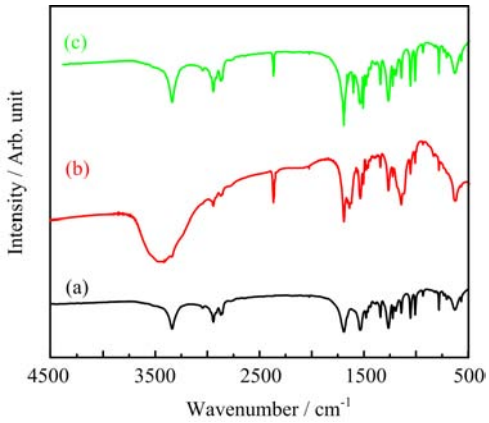

FIG. 3 FTIR spectral data of (a) PU, (b) intermediate, and (c) PU/HgS film.

of pure polyurethane at 3434, 1649, and 1530 cm^{-1} are assigned to the stretching vibration of OH, amide I (mainly C−O stretching vibrations), and amide II (the coupling of bending vibrations of NH), respectively. From Fig.3, the difference between amide II of pure polyurethane and PU/HgS is obvious, suggesting that there might be coordination interaction between HgS and NH group of polyurethane, which may play an important role in the formation of nanoparticles. These results confirm that polyurethane molecules are attached to the nanoparticles surface in the separated samples through binding sites NH_2 groups for Hg^{2+}.

C. SEM image of PU/HgS nanocomposite film

Figure 4 represents a typical SEM image of the nanostructured PU/HgS, illustrating morphology of the film with a nanoparticle size of about 66 nm, uniformly distributed across the film. Due to the chain structure of polyurethane, it was not possible to establish nanostructure with smaller particle size distribution. However, from the obtained results it can be concluded that many small bundles in the nanostructured PU/HgS films were clear-cut on the surface of the composite films, which indicated that HgS was biosynthesized in the film matrix with unique three-dimensional structure of molecules. The polymer chains might have been bridged by connection to the same nanoparticle, and the multiplicity of such bridged chains and particles could lead to particle clusters.

D. Fluorescence investigation on the PU/HgS nanocomposite film

The selectivity of the PU/HgS nanocomposite film to common anions was studied, and the fluorescence intensities were monitored after mixing common anions with the PU/HgS nanocomposite film. The results are

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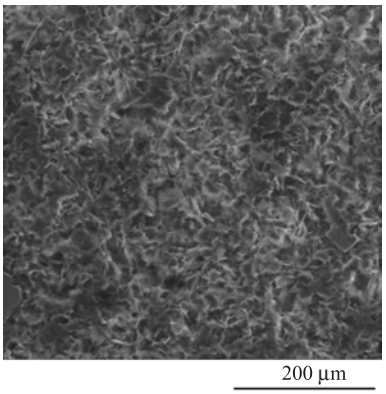

FIG. 4 SEM of PU/HgS film.

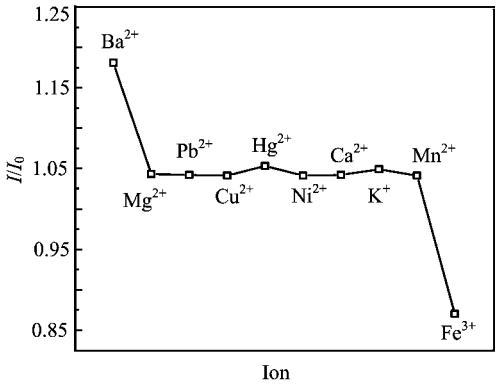

FIG. 5 Selectivity of PU/HgS film to common anions.

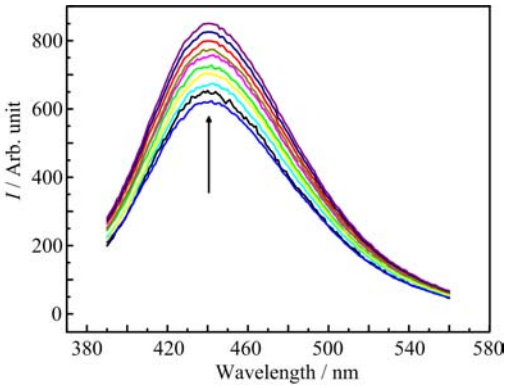

FIG. 6 The fluorescence property of PU/HgS film in various concentrations of Ba^{2+} from 0, 39.8, 79.36, 118.58, 157.48, 196.07, 234.37, 272.37, 310.1, to 347.1 μmoL/L as arrow shows.

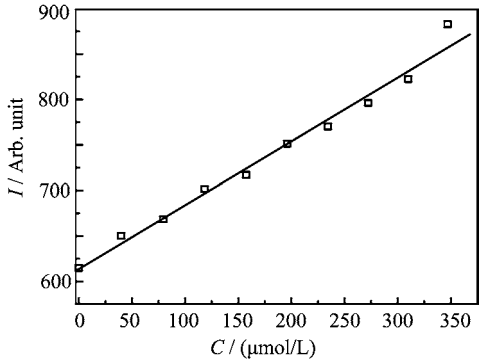

FIG. 7 Dependence of the fluorescence intensity of the PU/HgS film on concentration of Ba^{2+}.

illustrated in Fig.5. All inorganic anions do not show a significant fluorescence change except Ba^{2+}. The result implies that Ba^{2+} can provide significant interactions with the PU/HgS nanocomposite film surface.

The fluorescence intensity of PU/HgS nanocomposite film can be enhanced gradually by Ba^{2+}. Figure 6 shows the fluorescence emission spectra of the film as a function of Ba^{2+} concentration C increased from 0 to 347.1 μmol/L. Clearly, the emission of the film was enhanced significantly with increasing barium ions concentration. It is obvious that the fluorescence was enhanced efficiently, which is the fluorescence intensity in the presence and absence of Ba^{2+}, gets stronger gradually with increasing the concentration of Ba^{2+} until the concentration reaches 347.1 μmol/L. When the concentration of Ba^{2+} exceeds 347.1 μmol/L, the fluorescence is enhanced in disorder. According to the above analysis, 347.1 μmol/L is chosen as the optimum Ba^{2+} concentration. And the minimal detection limit of the Ba^{2+} based on polyurethane-conjugated HgS nanocrystals is 0.12 μmol/L.

Figure 7 shows the dependence of the fluorescence intensity (λ_{ex}=291 nm, λ_{em}=444 nm) of the PU/HgS film on barium ions concentration. The correlation is represented by Eq.(1):

$$I = 7.057C + 614.53, \qquad R^2 = 0.9835 \tag{1}$$

where I is the fluorescence intensity, C is Ba^{2+} concentration, R^2 is the correlation coefficient of the dependence.

The reversibility of the film to barium ions was examined using a standard method. The film was exposed to an alcohol solution, the maximum emission intensity of the film was recorded, and an appropriate amount of barium ions was added to the solution. Finally, the emission intensity of the film was measured every 3 min for five times. The film was then washed with water several times. The measurement was repeated five times with the same concentration of Ba^{2+}. The results are shown in Fig.8. It shows that the emission of the film can be fully restored.

IV. CONCLUSION

In this work, the synthesis of PU/HgS nanocomposite film was carried out. The obtained HgS nanoparticles with good dispersibility have been characterized by

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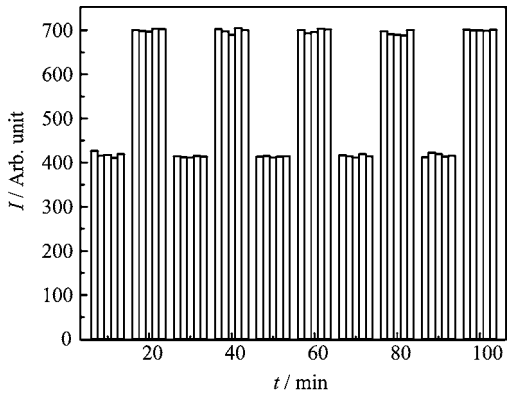

FIG. 8 Reversibility of the film sensor for Ba^{2+}.

FTIR. SEM shows the binding of nanoparticles with functional groups. The polyurethane molecules can control nucleation and growth of HgS crystals by binding on the surface of nanocrystals to stabilize nanoparticles. It is interesting to note that the synthetic PU/HgS nanocomposite films with high stability and high luminescence quantum yield in solution are very suitable for fluorescence sensing and detection. The fluorescence results reveal that the PU/HgS nanoparticles film are sensitive to Ba^{2+}, the nanocomposite film is possible to become a special sensor materials for Ba^{2+}.

V. ACKNOWLEDGMENTS

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