

Bio-Inspired Fabrication of Lotus Leaf Like Membranes as Fluorescent Sensing Materials

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Abstract: A fluorescent organic small molecule, hexaphenylsilole (HPS), has been used as a sensing material, while a HPS/polymethyl methacrylate composite film with a lotus leaf like structure is prepared by a simple electrospin method. The film shows high stability and excellent sensitivity for the metal ions Fe^{3+} and Hg^{2+} , respectively. The special surface morphology containing micro-/nanocomposite structure is attributed to the exhibition of these unusual properties.

Keywords: fluorescence • luminescence • membranes • nanostructures • sensors

Introduction

Fluorescent sensors are an indispensable tool for monitoring metal ions in real time and real space at a molecular level without the requirement of special instrumentation. Such sensors have found application in many fields, such as medical diagnostics, environmental control, living cells, and elec-

tronics.^[1–3] Although many solid-state (thin film) fluorescent chemosensory devices are generally reported, most systems have a limited solid-state application arising from the lack of reproducible spectroscopic features.^[4–7] Hence, the development of optical detectors exhibiting good reproducibility will facilitate the wider utilization of sensors. Herein, micro-/nanocomposite films with hydrophobic properties are introduced as fluorescent detectors. The films are shown to exhibit an enhanced reproducibility which plays an important role for prolonging the life span of fluorescent sensors in the future.

The electrospinning technique^[8–10] has been found to be a unique and cost-effective approach for fabricating large-surface-area membranes for a variety of sensor applications to improve performance.^[11–13] Pyrene-derived nanofibrous membranes have been successfully prepared as highly sensitive optical sensors for metal ions (Fe^{3+} and Hg^{2+}).^[11] Considering that a small organic molecule of hexaphenylsilole (HPS) shows a special “aggregation-induced emission” (AIE) effect in the solid state,^[14–17] it was chosen as a fluorescent detector in this work. The micro-/nanocomposite membranes, which are similar to the lotus leaf surface, were prepared by the electrospinning method after the addition of polymethyl methacrylate (PMMA). The HPS/PMMA composite film shows not only excellent sensitivities for Fe^{3+} ions, but also highly reproducible fluorescent properties. All these advantages can be attributed to the lotus leaf like structure displaying both large specific surface area and hydrophobic characteristics. The latter may lead to a self-cleaning effect on the surface, therefore enhancing the reproducibility of the fluorescent sensor.

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Results and Discussion

Firstly, HPS (1 wt%) and PMMA (15 wt%) dissolved in a dimethylformamide (DMF) solution were electrospun to obtain HPS/PMMA films on glass slides. The as-prepared membranes are uniform and exhibit good adhesion and structural stability. The scanning electron microscope (SEM) images of the HPS/PMMA micro-/nanocomposite film are shown in Figure 1. A web of many sub-micrometer-sized

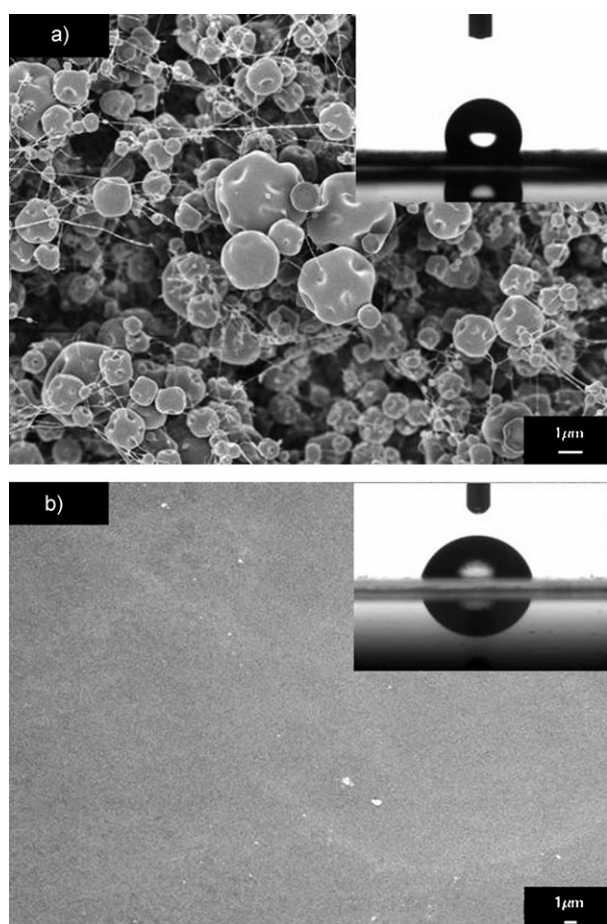


Figure 1. a) SEM image of electrospun film; insert: Photograph of water droplet shape on the electrospun film with a CA of $(115 \pm 2.6)^\circ$; b) SEM image of the smooth films; insert: Photograph of water droplet shape on the smooth film with a CA of $(74 \pm 1.2)^\circ$.

spheres with nanofibers over the whole substrate can be observed in Figure 1a. It shows that in the hierarchical structure there are many “nanopores”, as well as many nanoscale protuberances covering each sub-microsphere. The diameters of the sub-microspheres, nanopores, and nanofibers are about 0.5–2.0 μm, 300–100 nm, and 20–30 nm, respectively. The formation of these structures would most likely be caused by the insufficiently fast stretching during the whipping and bending process of the jet during the spraying process. These special structures on the film are similar to those on the lotus leaf surface. The water contact angle (CA) on

an HPS/PMMA micro-/nanocomposite film is about $115 \pm 2.8^\circ$ (the shape of a pure water droplet of about 2 μL in volume is given as the inset in Figure 1a), demonstrating its hydrophobicity. For comparison, the SEM image of a smooth HPS/PMMA film obtained by spin coating is shown in Figure 1b. It can be seen clearly that the smooth film is featureless since the polymer molecules are kinetically trapped in a disordered state during the spin-coating process. This smooth HPS/PMMA film is hydrophilic with a CA of about $74 \pm 1.5^\circ$ (insert in Figure 1b). The change of the wettability causes the HPS/PMMA micro-/nanocomposite film to show very good stability as an optical detector for metal ions arising from its surface hydrophobicity.

The HPS/PMMA micro-/nanocomposite film in solution can be used to detect several metal ions such as Ni^{2+} , Ag^+ , Sn^{4+} , Ca^{2+} , Fe^{3+} , K^+ , Zn^{2+} , Hg^{2+} , Cd^{2+} , Fe^{2+} , Cr^{3+} , Cu^{2+} , and Pb^{2+} . Only additions of Fe^{3+} and Hg^{2+} have a significant quenching effect on the fluorescence intensity, where a higher sensitivity for Fe^{3+} compared to Hg^{2+} is observed. The reproducibility of the detector's fluorescence was investigated by observing the reversible luminescence transition of the lotus leaf like films versus the number of 10 mM Fe^{3+} solution/water cycles starting from water. Interestingly, the lotus leaf like HPS/PMMA composite films demonstrated reversible luminescence switching. Figure 2 clearly shows that upon 370 nm light excitation, the lotus leaf like HPS/

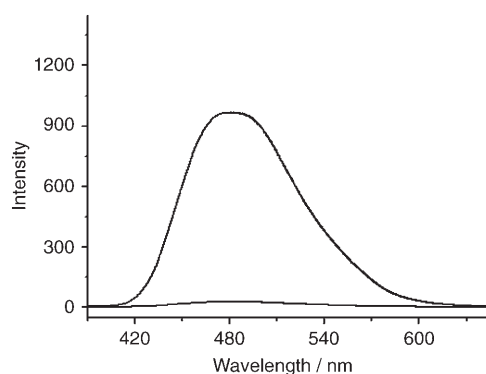


Figure 2. Fluorescence emission spectra of HPS/PMMA composite films in pure water (bright state) and in a 10 mM Fe^{3+} solution (dark state) upon 370 nm light excitation.

PMMA composite films in pure water exhibit a strong blue green emission with a maximum at 481 nm and a relative intensity of 943, while the film in 10 mM Fe^{3+} solution emitted weakly with a relative intensity of 37. The light emission is reversibly switched between bright and dark states by changing the immersion between pure water and the 10 mM Fe^{3+} solution without any sign of degradation after 10 repeating cycles (Figure 3a). By comparison, for the smooth HPS/PMMA films, (Figure 3b) the fluorescence intensity decreases to 70% of the original intensity after the first cycle and continues to decrease with an increasing number of repeating cycles. After 10 repeating cycles, the fluorescence decreases to 25% of the original intensity, confirming

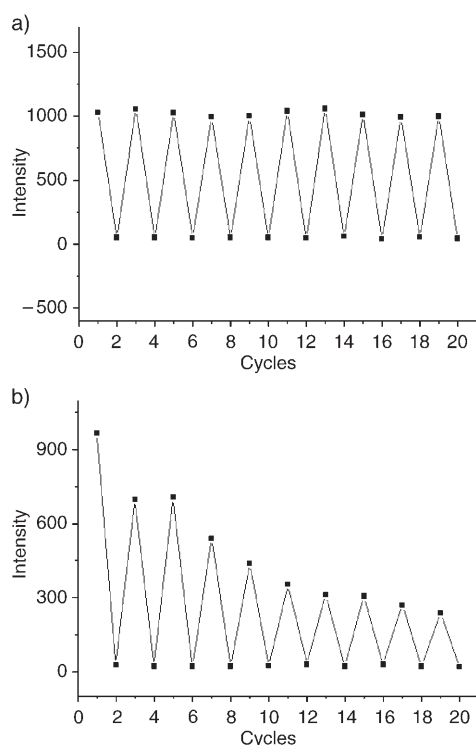


Figure 3. Repeated switching between dark and bright states of the emission of the as-prepared films against the number of 10 mM Fe^{3+} solution-water cycles starting from water; a) electrospun film. b) smooth film.

the good stability and reproducibility of the lotus leaf like HPS film. Considering the effect of surface wettability, similar to the surface of the self-cleaning lotus leaf, the HPS/PMMA micro-/nanocomposite structure film is hydrophobic, exhibiting a water contact angle of $115 \pm 2.8^\circ$. After it is taken out from the Fe^{3+} solution, the Fe^{3+} ions can be washed away very easily arising from the hydrophobic property of the surface, and hence accounts for the reproducible ability to sense the presence of metal ions. However, the smooth surface of HPS/PMMA is hydrophilic, and the water contact angle is $74 \pm 1.5^\circ$. The Fe^{3+} ions may stay on the surface of the smooth film after it is taken out from the Fe^{3+} solution and rinsed, which subsequently leads to a reduction in luminescence following each cycle.

Figure 4a shows the change in fluorescence spectra as a function of the concentration of ferric ion. It was observed that the fluorescence intensity decreases with increasing Fe^{3+} concentration. This decrease in fluorescence intensity arises from the quenching of the HPS indicator by Fe^{3+} ions, and the extent of quenching depends on the amount of Fe^{3+} ion present. Similar behavior was also observed for Hg^{2+} ions (Figure 4b).

Theoretically, the quantitative measure of fluorescence quenching is described by the Stern–Volmer constant, K_{sv} [as shown in Eq. (1)].^[18,19]

$$I_0/I = 1 + K_{sv}[Q] \quad (1)$$

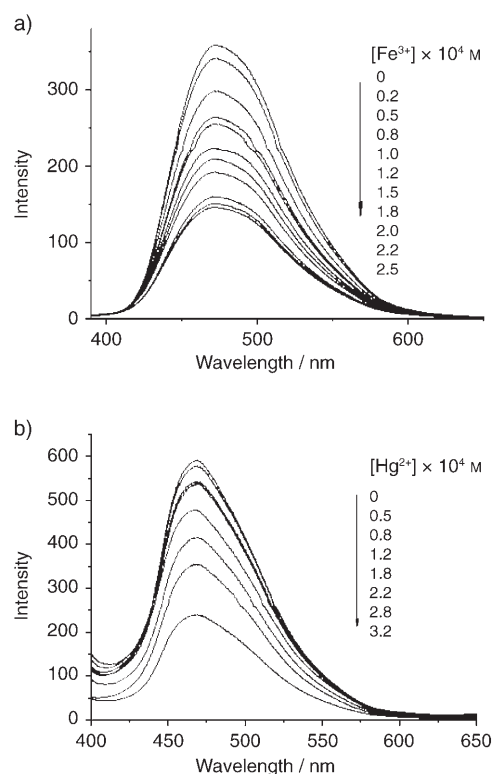


Figure 4. Fluorescence emission spectra of the electrospun sensing film with different concentrations of metal ions. a) Fe^{3+} ; b) Hg^{2+} .

I_0 and I are the intensities of fluorescence in the absence and the presence of the quencher, respectively. The value of I_0/I is proportional to the concentration of the quencher, $[Q]$. When all other variables are maintained constant, the higher the K_{sv} value, the lower the concentration of quencher required to quench the fluorescence.

The data obtained by performing a Stern–Volmer analysis for the lotus leaf like and smooth HPS/PMMA films are shown in Figure 5. For quencher concentrations in the range of 10^{-4} to 10^{-5} M, linear plots of I_0/I versus concentration of quencher are obtained, confirming a Stern–Volmer relationship. Stern–Volmer constants (K_{sv}) of the lotus leaf like HPS/PMMA films, calculated from the slopes of the plots, were found to be $6.21 \times 10^3 \text{ M}^{-1}$ and $1.27 \times 10^3 \text{ M}^{-1}$ for Fe^{3+} and Hg^{2+} , respectively, while K_{sv} of the smooth films is $2.48 \times 10^3 \text{ M}^{-1}$ and $0.6 \times 10^2 \text{ M}^{-1}$ for Fe^{3+} and Hg^{2+} , respectively. The values of the lotus leaf like films are 2 to 3 times greater than those of the smooth films.

The quenching efficiency can be defined by K_{sv} as in Equation (2)^[18,19]

$$K_{sv} = k_2\tau_1 \quad (2)$$

where τ_1 is the luminescence decay time of the fluorophore in the absence of the quencher ($1/k_1$), and k_2 is the bimolecular quenching rate constant. Therefore, there are two factors that influence the sensitivity of the quenching process. One is the luminescence decay time (τ_1) of the fluorophores.

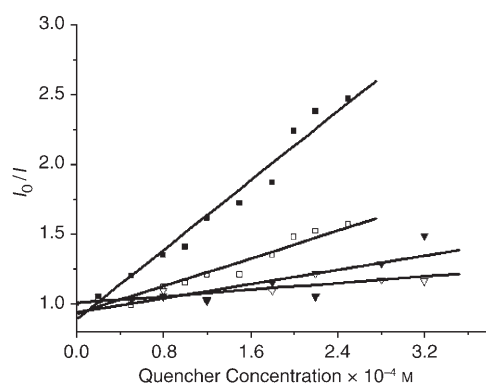


Figure 5. Stern–Volmer plots of two kinds of films as a function of different quencher concentrations (■ lotus-leaf-like structure film for Fe^{3+} , □ smooth film for Fe^{3+} , ▼ lotus-leaf-like structure film for Hg^{2+} , ▽ smooth film for Hg^{2+}).

The longer the value of τ_1 , the larger the K_{sv} value, which results in a higher sensitivity. The other involves controlling the quencher diffusion and separation rate of the fluorophores by changing the microstructural properties of the sensing film. The quencher diffusion and separation rate is related to the surface morphology. The lotus leaf like structure films with both large specific surface area and hydrophobic properties are propitious to the quencher diffusion and separation, and therefore increase the bimolecular quenching rate constant k_2 . Accordingly, the significant enhancement of the sensitivities of the sensors mentioned above is attributed to the higher surface area of the micro/nano-hierarchical structure membranes, which is beneficial for quencher diffusion and separation.

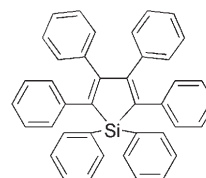
The selection of Fe^{3+} and Hg^{2+} by the HPS film can be well understood. Fe^{3+} , Hg^{2+} , and Ag^+ have a higher standard electrode potential (Fe^{3+} 0.77 V, Hg^{2+} 0.85 V, Ag^+ 0.8 V) than other ions (Ni^{2+} -0.25 V, Sn^{4+} 0.15 V, Ca^{2+} -2.87 V, Mg^{2+} -2.36 V, K^+ -2.93 V, Zn^{2+} -0.76 V, Cd^{2+} -0.4 V, Fe^{2+} -0.44 V, Cr^{3+} -0.41 V, Cu^{2+} 0.34 V, Pb^{2+} -0.13 V). Evidently, these three ions are electron-deficient metal cations, and may quench the fluorescence of electron-rich molecules such as HPS. However, the steric hindrance should be considered as an additional factor. Although the distance between two adjacently chromophoric silole cores is far from the normal π - π interaction distance (ca. 3–4 Å), the twisted arrangements of the peripheral aromatic rings^[20] leads to large steric hindrance. Thus, only the cation with a smaller diameter can get across the hindrance and interact with HPS to quench its fluorescence. In this case, the diameters of Fe^{3+} , Hg^{2+} , and Ag^+ are 1.1, 2.0, and 2.3 Å, respectively. Owing to this size effect of metal cations, Fe^{3+} and Hg^{2+} can interact with HPS molecules to different degrees, and lead to different sensitivities of the HPS films. Ag^+ can not penetrate through the steric hindrance freely to approach the HPS molecules, and therefore is unable to quench the fluorescence of the HPS film.

Conclusions

We have successfully developed a lotus leaf like structure HPS/PMMA composite film with fluorescence-responsive detection of Fe^{3+} and Hg^{2+} using the electrospinning technique. If compared to smooth films, lotus leaf like structure HPS/PMMA composite films are hydrophobic, which does not only enhance sensitivity, but also the reproducible stability of the sensors. This may give rise to new perspectives in practical applications. Furthermore, this study suggests that HPS and other siloles have a promising future in sensitive detection. The present findings should open the way for the development of sensitive detection of organic small molecules.

Experimental Section

Sample Preparation: 1,1,2,3,4,5-hexaphenylsilole (HPS) was synthesized according to the literature,^[21,22] and its chemical structure is shown in Scheme 1. Polymethyl methacrylate (1.77 g) and HPS (0.119 g) were



Scheme 1. Chemical structure of 1,1,2,3,4,5-hexaphenylsilole (HPS).

added to DMF (10 g) with stirring at room temperature for 12 h to form a solution of 15 wt% PMMA and 1 wt% HPS. The electrospinning solution was loaded into a 2-mL hypodermic syringe perpendicular to a 0.5-mm-diameter stainless steel needle. The positive electrode of a high-voltage power supply was placed onto the tip of the needle. The negative electrode was connected to a metallic collector wrapped in aluminum foil, which served as the counterelectrode. The working distance (WD) between the tip and collector was 14 cm. A voltage of 17 kV was applied, and composite films were collected on the cleaned glass substrates placed on the surface of the aluminum foil. For comparison, smooth films were fabricated by spin coating onto the freshly cleaned substrates at 1000 rpm for 15 s. Water was purified using a Milli-Q purification system (Millipore Corp., Bedford, MA) with a resistivity of 18 MΩ cm.

Sample Characterization: Morphology of the films was investigated using a JEOL JSM-6700F SEM at 3.0 kV. UV/Vis absorption spectra were recorded on a UV-3100. The fluorescence spectra were measured by a Hitachi F-4500 fluorescence spectrophotometer. CAs were measured on a Dataphysics OCA20 CA system at ambient temperature. The average CA value was obtained by measuring more than five different positions for the same sample.

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