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Colorimetric and fluorescent nanofibrous film as a chemosensor for Hg^{2+} in aqueous solution prepared by electrospinning and host–guest interaction†

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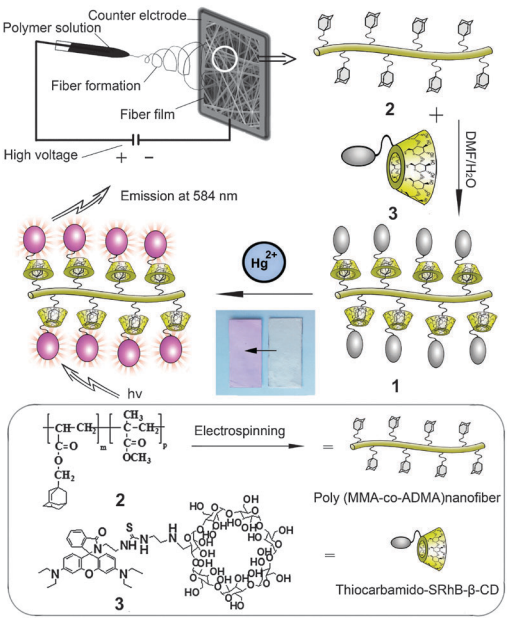
A fluorescent sensing film for Hg^{2+} ions was fabricated by host–guest interaction and electrospinning. When the nanofibrous film was put into a solution of Hg^{2+} ions, it gave rise to orange fluorescence, causing a clear color change from white to pink-red.

Mercury is a highly toxic element in ecosystems. Mercury-induced toxicity can cause a number of severe adverse effects on human health.[1] Highly selective and sensitive chemosensors for Hg^{2+} are hence demanded.[2]

Fluorescence techniques have become powerful tools for sensing and imaging of trace amounts of metal ions because of their simplicity, sensitivity, and real-time monitoring with fast response time.[3] Rhodamines are dyes extensively employed in fluorogenic-labeling and fluorescent chemosensors owing to their high absorption coefficient, high fluorescence quantum yield and long-wavelength absorption and emission. By virtue of these fascinating properties, excellent examples of rhodamine-based turn-on fluorescent Hg^{2+} sensors have been reported.[4,5] However, their application in related analytical techniques in the homogeneous phase is not suitable for the separation, removal and enrichment of target species.[6]

Nowadays, the electrospinning technique has been found to be a unique and cost-effective approach to fabricate membranes with large surface areas for fluorescent sensor application. It is expected that this large available surface area has the potential to provide unusually high sensitivity and fast response time in sensing application.[7–10] However, these films prepared by covering and doping or other physical methods suffer from issues such as fluorophore leaking, thickness control, and inner-layer analyte diffusion.[11–14] The use of supramolecular interactions (*i.e.*, host–guest interactions) is an attractive alternative to physical adsorption methods as these interactions can be easily tuned by the appropriate selection of geometrically complementary host and guest molecules, such as β-cyclodextrin (β-CD) (host) and adamantane (guest) (Scheme 1).

In this work, we have successfully developed a novel fluorescent sensing system (Scheme 1), in which the rhodamine–cyclodextrin



Scheme 1 Chemical and schematic illustration for the preparation of nanofibrous film fluorescent sensors for Hg^{2+} ions.

fluorophore moiety **3** is loaded on the cross-linked adamantane-functionalized nanofiber **2** surface *via* host–guest interaction. One major advantage of this method is that guest molecules grafted on the surfaces result in a fluorescent receptor with minimal changes in surface properties such as hydrophilicity and charge. In addition, since the immobilization occurs by inclusion complex formation, the functionalized surfaces can be readily synthesized and characterized. Fluorescent receptor immobilization then takes place by self-assembly on the surfaces without additional need for chemical conjugation and reagents added. The response of these fluorescent sensing films fabricated in a self-assembling way is significantly faster due to the direct exposure of fluorophore moieties, avoiding, at least in principle, the inner-layer diffusion problem encountered by cyclodextrin-based physically fabricated sensing films.

The detailed procedures for the synthesis of inclusion complex nanofibrous film **1** can be found in S3–S7 (ESI†). To confirm that the fluorophore moiety **3** was successfully loaded on the surface of nanofibrous film **2**, FTIR was investigated. Fig. 1 exhibits the

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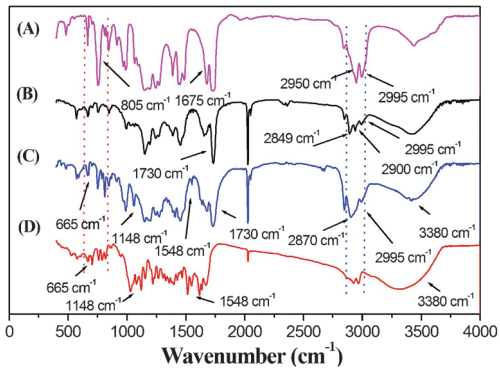

Fig. 1 FT-IR spectra of pure MMA (A), nanofibrous film **2** (B), nanofibrous film **1** (C) and fluorophore moieties **3** (D).

FTIR spectra of pure MMA (A), nanofibrous film **2** (B), nanofibrous film **1** (C) and fluorophore moiety **3** (D). The spectrum of nanofiber **2** (B) differs considerably from that of pure MMA (A) in a range of 2800–2900 cm^{-1}. Fig. 1 (B) exhibits bands at 2900 cm^{-1} and 2849 cm^{-1}, which are attributed to methylene asymmetric C–H stretching and methylene symmetric C–H stretching from the adamantine molecule. In particular, two distinct bands measured at 805 cm^{-1} and 1675 cm^{-1} for monomer MMA have disappeared in the sample of nanofibrous film **2**. These bands are ascribed to the bending vibration of ═C–H out-of-plane and C═C vibrations from the allyl group in MMA. Therefore, we confirmed that adamantane was successfully introduced into nanofibrous film **2**. In addition, FTIR measurement shows that the characteristic bands of free moiety **3** at 3379–3389 cm^{-1} (NH stretching), 1730 cm^{-1} (aromatic C═O stretching), 1548 cm^{-1} (secondary amide N–N bending), 1360–1250 cm^{-1} (aromatic C–N stretching), 1200–1050 cm^{-1} (C═S stretching), 1148 cm^{-1} (aliphatic C–N stretching) and 700–665 cm^{-1}(secondary amide N–H wagging) are exhibited in spectra of nanofibrous film **1** (C). These bands, however, are not present in nanofibrous **2** (B). The present FTIR data indicate that the attachment of fluorophore moiety **3** to the surface of nanofibrous film has indeed taken place *via* host–guest interaction. Notably, the inclusion of adamantine in a β-CD cavity shifts methylene stretching vibration to higher frequency *i.e.* from 2849 to 2870 cm^{-1} during the formation of the thiocarbamido-SRhB-β-CD/poly (MMA-*co*-ADMA) complex (Fig. 1(C)). The frequency shift was explained by the breakdown of the intermolecular hydrogen bonding associated with these molecules and the establishment of stronger binding in the complex system.[15]

A set of typical SEM images of nanofibrous film **2** are shown in Fig. 2(a). It can be seen that the film is composed of numerous, randomly oriented nanofibers. The surface of nanofiber **2** doesn't show any serious cracks or degradation. Fiber surface after self-assembly of fluorophore moiety **3** shows slight fiber adhesion, and fibers become thick and curved (Fig. 2(b)). The average diameter of nanofibers **2** is 495 nm. After loading fluorophore moiety **3** on the surface of nanofiber **2**, the nanofibrous film becomes conglutinate, coarsened, tortuous slightly, and the average diameter of nanofiber **1** is 520 nm. Moreover, the BET surface areas of the nanofibers produced with and without fluorophore moiety **3** were measured to be 3.1893 and 2.9505 $m^2\ g^{-1}$ respectively. This network structure of electrospun film provides a surface area-to-volume ratio roughly 1 to 2 orders of magnitude higher than that of known continuous thin films.[16] This unique porous structure could greatly accelerate the targets to diffuse close to the sensing elements and increase the complexation efficiency.

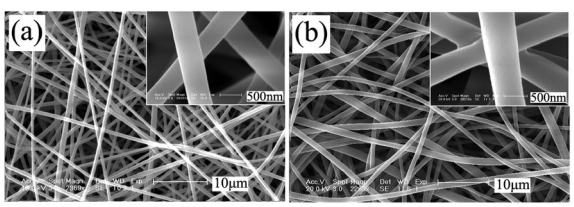

Fig. 2 SEM images of nanofibrous film **2** (a) and **1** (b), insets show further magnified images of several electrospun nanofibers.

Fluorophores are usually disturbed by the protons in the detection of metal ions, so their low sensitivity to the operational pH value was expected and investigated. Fig. S10 (ESI†) shows the fluorescence response of nanofibrous film **1** without and with Hg^{2+} ions as a function of pH. Experimental results show that for Hg^{2+}-free nanofibrous film **1**, under acidic conditions (pH < 6), an obvious off–on fluorescence appeared due to the formation of the open-ring state of the thiocarbamido-SRhB-β-CD based on strong protonation. In a pH range from 6.0 to 13.5, an almost negligible fluorescence signal (excited at 584 nm) was observed, suggesting that the molecules prefer the spirocyclic form. On the contrary, upon addition of Hg^{2+} ions, there was an obvious fluorescence off–on change of nanofibrous film **1** at different pH values. And the pH-control emission measurements reveal that nanofibrous film **1** is able to respond to Hg^{2+} ions in a wide pH range from 6 to 13.5 with only minor changes in fluorescence intensity, suggesting that the nanofibrous film **1** facilitates the quantification of the concentration of Hg^{2+} ions in aqueous solution over a broad pH range. Since most samples for the nanofibrous film **1** analysis of Hg^{2+} ions are neutral, pH 7.2 buffer solution is chosen as the medium for Hg^{2+} ions quantification.

In order to gain insight into the signaling properties of the film toward Hg^{2+}, fluorescence titrations were conducted. Detailed information of fluorescence titration is provided in S3(ESI†). Fluorescence titration of the film was carried out in DMF–H_2O (1 : 10, v/v) solution ([Hg^{2+}] = 0–2.0 × 10^{-4} mol L^{-1}, 0.1 M KH_2PO_4–NaOH buffer at pH 7.20, λ_{ex} = 525 nm, λ_{em} = 584 nm).

Solid UV-vis spectra of the inclusion complex nanofibrous film **1** upon addition of Hg^{2+} are shown in Fig. S8 (ESI†). When Hg^{2+} was added in the solution of the film in DMF–H_2O, the emission intensity at 584 nm was significantly enhanced (Fig. 3), and a clear change in solution color from white to pink-red was observed as shown in Fig. S5 (ESI†). According to the molecular structure and spectral results of fluorophore moiety **3**, it is concluded that the addition of the Hg^{2+} ion induced the N atom of spirolactam to attack the C atom of thiourea, and thus a ring opening of the spirolactam of rhodamine took place, followed by the removal of HgS and the formation of intramolecular guanylation.[3c] Finally, a stable cyclic product was formed through an irreversible desulfurization reaction, as depicted in Fig. S6 (ESI†). It demonstrates that inclusion complex nanofibrous film **1** can sensitively detect

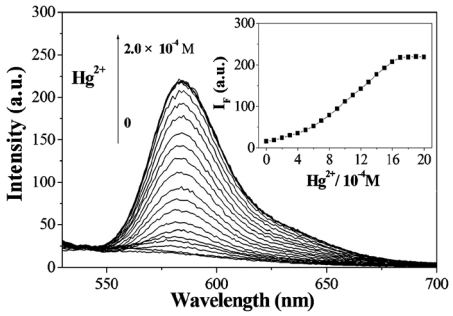

Fig. 3 Fluorescent spectra of the thiocarbamido-SRhB-β-CD fluorophore moiety of nanofibrous film in the absence and presence of Hg^{2+} (1.0×10^{-5}–2.0×10^{-4} mol L^{-1}). The inset shows fluorescence intensity change as a function of Hg^{2+} concentration.

Hg^{2+} with high selectivity over other interfering metal ions, especially the thiophilic metal ions including Cu^{2+}, Ag^{+} and Fe^{3+}. The reaction responsible for these changes reaches completion well within the time frame (<1 min) of the measurement. The fluorescence intensity was well proportional to the amount of Hg^{2+} (1.0×10^{-5}–2.0×10^{-4} mol L^{-1}) with a linear correlation ($R^2 = 0.9950$) (ESI†, Fig. S7). The maximum fluorescence intensity induced by Hg^{2+} was retained when the concentration of Hg^{2+} solution was further increased to be higher than 2.0×10^{-4} mol L^{-1}. The local concentration of thiocarbamido-SRhB-β-CD in nanofibrous film was also determined to be 0.0143 mol m^{-2} based on the spectral results.

The fluorescence responses of the film to various cations and its selectivity for Hg^{2+} are illustrated in Fig. 4 (black bars). The experiments were carried out by fixing the concentration of Hg^{2+} at 2.0×10^{-4} mol L^{-1}. As can be seen from the black bars in Fig. 4, fluorescence almost did not change in the solutions of 1.0×10^{-3} mol L^{-1} representative metal ions, such as Na^{+}, K^{+}, Ca^{2+}, Mg^{2+}, Mn^{2+}, Ni^{2+}, Cd^{2+}, Cu^{2+}, Co^{2+}, Pb^{2+}, Zn^{2+}. Furthermore, the fluorescence was affected to some extent in the solutions of 1.0×10^{-3} mol L^{-1} Ag^{+} or Fe^{3+}. However, when the concentrations of Ag^{+} and Fe^{3+} solutions were decreased to 1.0×10^{-4} mol L^{-1}, our nanofibrous film didn't show any fluorescence enhancement in response to Ag^{+} and Fe^{3+} ions. This observed selective turn-on fluorescence response to Hg^{2+} ions was probably a cooperating result of several combined influences.

In order to further test the interference of other common cations in the determination of Hg^{2+}, competition experiments were performed in which the fluorescent probe was added to a solution of Hg^{2+} in the presence of other metal ions (white bars in Fig. 4). Experimental results indicate that these ions have no obvious interference in the Hg^{2+} detection. Thus, the excellent selectivity toward Hg^{2+} makes the practical application of our nanofibrous film **1** feasible. Further stability experiments showed that there is no leakage of the dye from the thiocarbamido-SRhB-β-CD/poly (MMA-*co*-ADMA) inclusion complex nanofibrous film after soaking in DMF–H_2O for 24 h. After the soaking test, the nanofibrous film can be repeatedly used for fluorescent titration without losing its sensitivity (ESI†, Fig. S9).

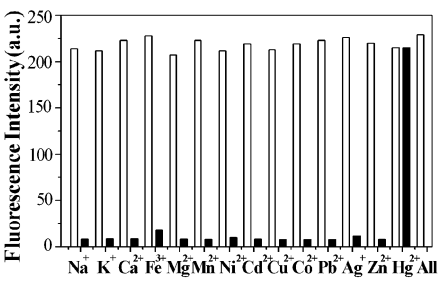

Fig. 4 Black bars: fluorescent emission response of the film in the presence of different metal ions in DMF–H_2O solution. White bars: fluorescent response of the film upon addition of 2.0×10^{-4} mol L^{-1} Hg^{2+} in the presence of 1.0×10^{-3} mol L^{-1} each of background metal ions.

In conclusion, a simple approach for the production of nanocomposite fibers was developed based on self-assembly and the electrospinning technique. The selectivity and sensitivity of the nanofibrous film for Hg^{2+} were satisfactory and the detection limit was found to be 6.0×10^{-5} mol L^{-1} (based on $S/N = 3$). We believe that this technique would provide a very promising alternative for developing high-performance sensing materials for metal-ion detection in aqueous solution.

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