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A reusable nanofibrous film chemosensor for highly selective and sensitive optical signaling of Cu^{2+} in aqueous media†

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A novel surface modification strategy for an electrospun nanofibrous film was reported, allowing detection and removal of copper ions in the aqueous solution. This reusable dual fluorescent–colorimetric nanofibrous film can be utilized conveniently to achieve real-time naked-eye sensing in aqueous medium just like using a test paper.

Copper ions are significant environmental pollutants and copper is an essential trace element in biological systems.[1] The unregulated Cu^{2+} ions can lead to oxidative stress, and their concentration in the neuronal cytoplasm may cause the etiology of Alzheimer's or Parkinson's disease.[2] Thus, the development of highly selective sensors for detection of copper ions is of great interest.[3]

Fluorescence detection 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.[4] However, currently, most reported examples of fluorescent sensing application in the homogeneous phase are not suitable for separation, removal and enrichment of target species.[5] The solid substrate sensor may generally be employed in basic laboratory assays, in measurement fields through portable devices, and in household use as commercial indictors.[6–8] The capacity of the solid substrate for adsorbing metal ions can determine the sensitivity of fluorescence detection signals.[9] Enlarging the specific surface areas of the solid substrate can improve the sensitivity of such fluorescence detection. To achieve this goal, we plan to utilize a simple yet effective technology to fabricate a nanofibrous film and apply the film as the solid substrate for fluorescent detection of metal ions.

Electrospinning is an effective and simple method for preparing various composite nanofibers.[10] The electrospinning nanofibers with small diameters have a large surface area per unit mass, which has the potential to provide unusually high sensitivity and fast response time in sensing application.[11] At present, several electrospun fibrous membrane chemosensors for some analytes, including metal ions,[5,7] nitrites,[12] volatile gas[13] *etc.*,[14–18] in the aqueous phase, have been reported. However, these films prepared by covering, dye-doping, or by other physical methods suffer from issues such as aggregation and self-quenching of molecular fluorophores, fluorophore leakage, and inner-layer analyte diffusion.[19–22] A more straightforward method is to modify the surface of polymer nanofibers without affecting bulk properties of the treated nanofibers. The methods used to impart surface modification usually depend strongly on the nature of the fiber-forming polymer and include, but are not limited to, plasma treatment,[23] physisorption,[24] self-assembly,[8] and covalent grafting.[25] Covalent grafting of functional compounds onto polymer fiber surfaces is a simpler and more convenient approach to introduce functionalities permanently with a reasonably high efficiency. One major advantage of this method is that by covalent grafting of organic fluorescent molecules onto the surface of nanofibers, these organic fluorescent molecules could be rationally brought into a detection system by the nanofibers with minimal changes in surface properties such as hydrophilicity and charge. In addition, this kind of method can avoid the aforementioned problems.

In this work, we have successfully developed a novel sensing system, in which the surfaces of polymer nanofibers are modified with rhodamine derivatives to form a colorimetric and 'turn-on' fluorescence sensor for Cu^{2+} (Scheme 1). The experimental details and characterization data are given in the ESI.† We prove that the nanofibrous film (PMAR) as the solid substrate can dramatically improve the sensitivity and response time of fluorescence detection of copper ions in aqueous solution. Furthermore, the prepared nanofibrous film could be utilized as an adsorbent to remove Cu^{2+} in aqueous solution efficiently, and can be reused if it is washed with EDTA solution.

To confirm that the fluorophore moiety was successfully grafted onto the surface of PMAR nanofibers, FTIR was used. Fig. 1 exhibits the FTIR spectra of monomer AHPA (A), pure MMA (B), the poly(MMA-*co*-AHPA) nanofibrous film (C), the PMAR nanofibrous film (D) and RhB–hydrazine (E). The spectrum of the poly(MMA-*co*-AHPA) nanofibrous film (C) differs considerably from that of pure PMMA (B) in the range of 1800–1600 cm^{-1}. Fig. 1(A) and (C) exhibits a strong band at 1750 cm^{-1}, which is ascribed to C=O of ester and carbonyl groups in the AHPA molecule. In particular, a distinct band measured at 800 cm^{-1} for the AHPA monomer disappeared in the sample of the

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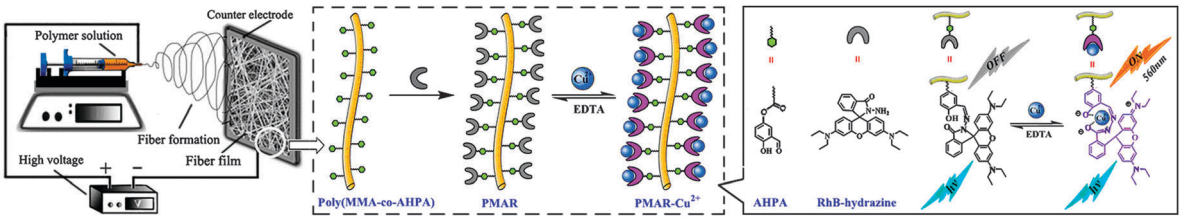

Scheme 1 Chemical and schematic illustration of the preparation of nanofibrous film fluorescent sensors for Cu^{2+} ions.

poly(MMA-*co*-AHPA) nanofibrous film. This band is ascribed to the bending vibration of =C–H out-of-plane from the allyl group in AHPA. Therefore, we confirmed that aldehyde groups of AHPA were successfully introduced into the nanofibrous film. In addition, FTIR measurement shows that the characteristic bands of the RhB–hydrazine fluorescent unit (*E*) at 1510 cm^{-1} (secondary amide N–N bending), 1360–1250 cm^{-1} (aromatic C–N stretching) and 1148 cm^{-1} (aliphatic C–N stretching) are exhibited in spectra of the PMAR nanofibrous film (D). These bands, however, are not present in the spectra of the nanofibrous film (C). The most obvious change in the FT-IR spectra of the nanofibrous film (C) is the near disappearance of the peak at 1670 cm^{-1} (C=O carbonyl groups). From the FT-IR spectra of the PMAR nanofibrous film, the introduction of a fluorophore moiety grafted onto the surface of PMAR nanofibers was confirmed.

Fig. 2 shows the typical SEM images of the poly(MMA-*co*-AHPA) nanofibrous film before and after surface modification. It can be seen that the poly(MMA-*co*-AHPA) nanofibrous film was composed of numerous, randomly oriented nanofibers. Under the optimized conditions, the surface of poly(MMA-*co*-AHPA) nanofibers does not show any serious cracks or degradation. The average diameter of poly(MMA-*co*-NAAP) nanofibers is 495 nm (Fig. 2a). After surface modification, the nanofibers become conglutinate, tortuous, submicron bumps and the average diameter of PMAR nanofibers was 520 nm as analyzed from SEM images (Fig. 2b). The result indicated that the fiber structures were maintained during the modification process, but the fiber diameter increased slightly. Moreover, the Brunauer–Emmett–Teller (BET) surface areas of the nanofibers produced with and without a fluorophore moiety were measured to be 3.3852 and 3.0445 $m^2\ g^{-1}$ respectively. This network structure of the electrospun nanofibrous film provides a surface area-to-volume ratio roughly 1 to 2 orders of magnitude higher than that of known continuous thin films.[26] This unique porous structure could greatly accelerate the targets to diffuse close to the sensing elements and increase the complexation efficiency.

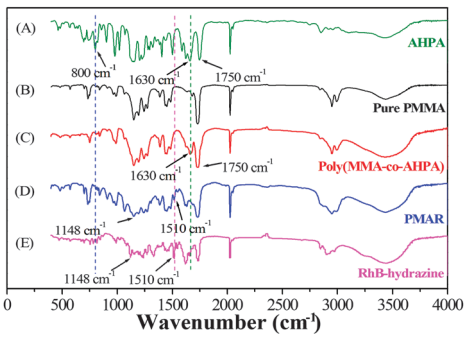

Fig. 1 FT-IR spectra of AHPA (A), pure MMA (B), poly(MMA-*co*-AHPA) nanofibrous film (C), PMAR (D) and fluorophore moieties RhB–hydrazine (D).

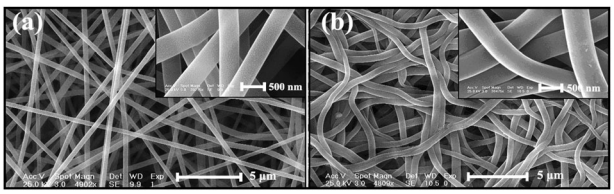

Fig. 2 SEM images of poly(MMA-*co*-AHPA) (a) and poly(MMA-*co*-AHPA)–RhB nanofibrous film (b), the insets show further magnified images of several electrospun nanofibers.

Fluoroionophores are usually disturbed by a proton in the detection of metal ions, so their low sensitivity to the operational pH value was expected and investigated. The fluorescence emission intensities of the PMAR nanofibrous film in ethanol–water (1 : 1, v/v) as a function of pH are shown in Fig. S7 (ESI†). We found that the dispersion exhibits high fluorescence intensity ratios which remained fairly stable from pH 7.0 to pH 12.0, indicating that the sensor can be used under some environmental and most physiological conditions. Considering that most samples for Cu^{2+} ion analysis were neutral, the media for Cu^{2+} ion quantification were then buffered at pH 7.2.

In order to gain an insight into the signaling properties of the film toward Cu^{2+}, fluorescence titrations were conducted. The fluorescence titration behavior of the film was investigated in an ethanol–water (1 : 1, v/v) solution ($[Cu^{2+}] = 1.0 \times 10^{-6}$–$2.0 \times 10^{-4}$ M, 0.1 M HEPES–NaOH buffer at pH 7.20). Fig. 3a shows detailed fluorescence changes of the PMAR nanofibrous film upon using different concentrations of Cu^{2+} ions under the same conditions. The PMAR nanofibrous film was white. After adding the aqueous solution of copper ions, it became pink. Even if the concentration of copper ions was as low as 5×10^{-6} mol L^{-1}, the color of the PMAR film was still visible (Fig. 3b). According to the molecular structure and spectral results of the fluorophore moiety, it was concluded that Cu^{2+} ions could chelate with the imine N, carbonyl O and phenol O atoms of the fluorophore

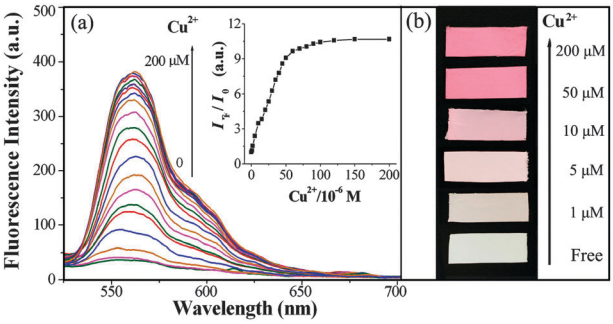

Fig. 3 (a) Fluorescent spectra of the PMAR nanofibrous film in the absence and presence of Cu^{2+} (1.0×10^{-6}–2.0×10^{-4} mol L^{-1}). The inset shows fluorescence intensity change as a function of Cu^{2+} concentration. (b) From bottom to top are photographs of the nanofibrous film after 1 μM, 5 μM, 10 μM, 500 μM, 200 μM Cu^{2+} involvements.

moiety, as depicted in ESI.† In addition, upon the addition of increasing concentrations of Cu^{2+} ions, a significant enhancement of the characteristic fluorescence of a rhodamine B fluorophore moiety in a Cu^{2+} ion concentration-dependent manner is observed at 557 nm, accompanied by an obvious orange fluorescence enhancement. When more than 1×10^{-4} mol L^{-1} Cu^{2+} ions were added, the maximum fluorescence intensity was retained. From the fluorescence titration experiment, a linear relationship ($R^2 = 0.9818$) is observed between the fluorescence intensity of the nanofibrous film and the concentration of Cu^{2+} (Fig. S8, ESI†). The reaction responsible for these changes reaches completion well within the time frame of the measurement (<10 s, $[Cu^{2+}] = 1.0 \times 10^{-6}$–$2.0 \times 10^{-4}$ mol L^{-1}) and the detection limit was found to be 1.5×10^{-6} mol L^{-1} (based on S/N = 3).

The fluorescence responses of the film to various cations and its selectivity for Cu^{2+} are illustrated in Fig. S9 (ESI†). The experiments were carried out by fixing the concentration of Cu^{2+} at 5.0×10^{-5} mol L^{-1}. As can be seen from the black bars in Fig. S9 (ESI†), 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+}, Fe^{2+}, Fe^{3+}, Mn^{2+}, Ni^{2+}, Cd^{2+}, Co^{2+}, Pb^{2+}, Zn^{2+}, Pb^{2+}, Hg^{2+} and Ag^+. The miscellaneous competitive cations did not lead to any significant color in the visible region (Fig. S10, ESI†). In order to further test the interference of other competitive cations in the determination of Cu^{2+} competition experiments were performed in which the PMAR nanofibrous film was added to a solution of Cu^{2+} in the presence of other metal ions (white bars in Fig. S9, ESI†). Experimental results indicate that the increases in fluorescence intensity resulting from the addition of the Cu^{2+} were not influenced by the subsequent addition of miscellaneous cations. Thus, the excellent selectivity toward Cu^{2+} makes the practical application of the PMAR nanofibrous film feasible.

Almost all current Cu^{2+} sensors can only detect the heavy metal ions, but not remove them from solution. In this work, we endowed the nanofibrous film with adsorptive and separable properties to remove the Cu^{2+} ions from aqueous solution. The adsorption equilibrium data of Cu^{2+} ions were analyzed using the following Langmuir adsorption equation, and Freundlich, and Temkin and Pyzhev isotherm models were used (Table S1, ESI†). The adsorption capacity was 14.35 mg of Cu^{2+} ions per gram of adsorbent film. Full details are given in the ESI.†

The reversibility of the chemosensor is a very important aspect of practical application. The film was alternately exposed to the copper ion aqueous solution and EDTA aqueous solution, and the corresponding fluorescence emission was measured. The experiment showed that the emission of the film could be restored, as shown in Fig. S11 (ESI†). In contrast, the emission could not be restored when the film was soaked in pure water even if the soaking was protracted for more than 24 h. This result supported the statement that Cu^{2+} was not simply adsorbed on the film, but complexed with the fluorophore moiety in the film. In addition, the color of the film also exhibits reversibility upon being alternately treated with copper ions and EDTA. The reason for the reversibility is that EDTA has stronger complexation capability with Cu^{2+} than the rhodamine dye and the open-ring state rhodamine turns back to spirolactam–rhodamine upon being treated with EDTA.[3] This regeneration ability indicated that the PMAR nanofibrous film could be reused with proper treatment.

In conclusion, a simple approach for the production of a nanofibrous film is developed based on a surface modification and electrospinning technique. The surface of electrospun nanofibers decorated with molecular fluorophores as a fluorescence probe avoids the aggregation and self-quenching of molecular fluorophores effectively, and exhibits high fluorescence sensitivity, very short response and recovery time, good reversibility and reproducibility. We believe that this technique will provide a promising alternative for developing high-performance sensing materials for metal-ion detection and removal in aqueous solution.

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