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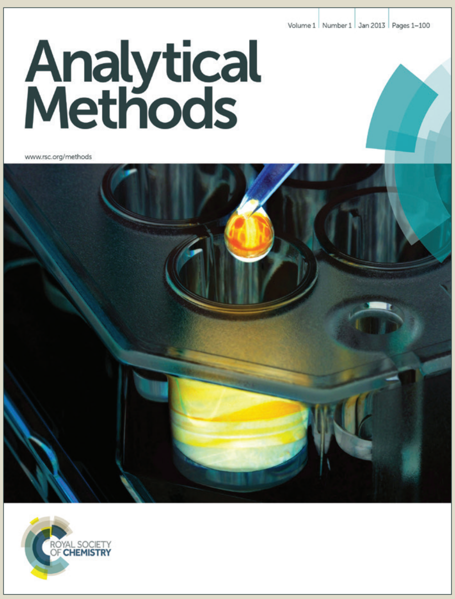
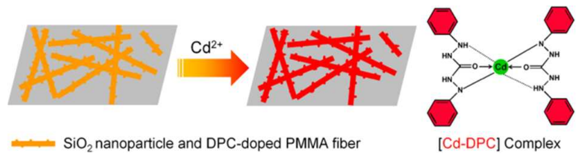


Graphic abstract



A method for Cd^{2+} detection was developed by using SiO_2 nanoparticles and diphenylcarbazide doped polymethylmethacrylate electrospun fibrous film.

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ARTICLE

SiO_2 nanoparticles and diphenylcarbazide doped polymethylmethacrylate electrospun fibrous film for Cd^{2+} colorimetric detection†

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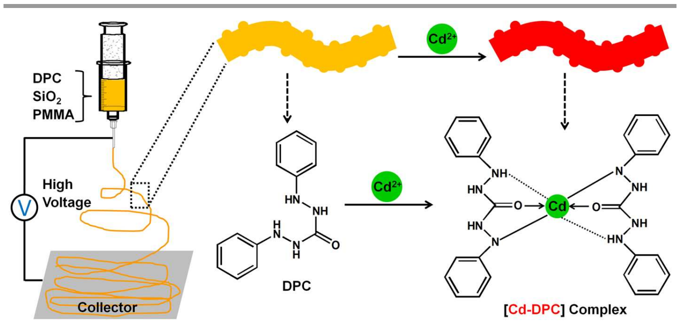
Based on the formation of a red [Cd-diphenylcarbazide] complex, a simple and visible method for Cd^{2+} colorimetric detection was developed by doping SiO_2 nanoparticles and diphenylcarbazide in polymethylmethacrylate electrospun fibers. Benefiting from the large surface area due to the addition of SiO_2 nanoparticles, the color of the fibrous film changed clearly even in the presence of extremely low concentration of Cd^{2+}. The detection limit was found to be 1×10^{-8} M. Investigation of the selectivity of the fibrous film on the detection of various metal ions showed that only Cd^{2+} could induce a yellow-to-red color change. The results demonstrated that SiO_2 and diphenylcarbazide doped polymethylmethacrylate fibrous films could act as highly selective strips for the detection of Cd^{2+} with little interference from other metal ions.

Introduction

Cadmium ion (Cd^{2+}), one of the most toxic heavy metal ions and a severe environmental pollutant, has serious deleterious effects on human health. Chronic exposure to Cd^{2+} has been implicated as a cause of cancers of the lung, prostate, pancreas and kidney.[1–3] Accordingly, the rapid and sensitive detection of Cd^{2+} is demanded. Some known methods, such as flame atomic absorption spectrometry,[4] electrothermal atomic absorption spectrometry,[5] plasma mass spectrometry,[6] and atomic fluorescence spectrometry,[7] are being used to detect Cd^{2+} from aqueous solutions. However, the requirements of specific instrumentation and well-trained personnel make these methods complex, time-consuming and expensive.[8,9] Therefore, a simple, rapid and reliable detection method for Cd^{2+} is highly desirable. Particularly, equipment-free sensors such as colorimetric detection by the naked eye would be among the best and most practically useful methods, which can make the rapid detection of Cd^{2+} possible at low cost.[10]

As a newly reported technique, electrospinning has been found to be a unique and cost-effective approach to fabricate various composite nanofibers.[11] The electrospinning nanofibers with small diameters have a large surface area, which has the potential to provide unusually high sensitivity and fast response time in sensing applications.[12,13] Electrospun fibrous film-based sensors have been reported for metal ions,[14–16] organic small molecules,[17–19] and proteins.[20] However, the fabrication of fibrous sensors with the advantage of being highly sensitive to color change for naked-eye detection of Cd^{2+} remains a challenge.

Herein, we present a simple and visible method for colorimetric detection of Cd^{2+}, constructed by doping SiO_2 nanoparticles and diphenylcarbazide (DPC) in polymethylmethacrylate electrospun fibers (Scheme 1). Based on the fact that the binding of Cd^{2+} with DPC leads to the formation of red [Cd-DPC] complexes,[21] the fibers successfully achieve a color change in the presence of Cd^{2+}. Moreover, the presence of SiO_2 nanoparticles in the fibers provides large surface area,[22–24] resulting in an improved color change.



Scheme 1. Chemical and schematic illustration for the preparation of SiO_2 nanoparticles and DPC doped PMMA electrospun fibrous film for Cd^{2+} colorimetric detection.

Experimental

Materials and reagents

Polymethylmethacrylate (PMMA, Mw = 30, 000 kDa), diphenylcarbazide (DPC), SiO_2 nanoparticles, and $Cd(NO_3)_2$•$4H_2O$ were purchased from Aladdin (Shanghai, China). All solvents and other chemicals were purchased from local commercial suppliers and were of analytical reagent grade unless otherwise specified. Deionized water (Milli-Q, Millipore, Bedford, MA) was used to prepare aqueous solutions.

Fabrication of SiO_2 and DPC doped PMMA fibrous film

Electrospun fibrous films used in the current study were fabricated following the method reported previously.[25] Briefly, the electrospinning solution was prepared by dissolving 30 wt% PMMA, DPC (1 wt%, 3 wt%, or 5 wt%), and SiO_2 (1 wt%, 3 wt%, or 5 wt%) in N,N-dimethylformamide. The stock solution was then electrospun under a fixed electric field of 10 kV/15 cm, and a solution flow rate of 0.02 mL/min, onto an aluminum sheet wrapped around a rotating cylinder (diameter of the cylinder ≈ 12 cm) that was used as the collector. Each of the electrospun fiber films was collected continuously for 3 h.

Determination of Cd^{2+}

The desired concentration (10^{-1}, 10^{-2}, 10^{-3}, 10^{-4}, 10^{-5}, 10^{-6}, 10^{-7}, 10^{-8} and 10^{-9} M) of Cd^{2+} solution was prepared by dissolving Cd $(NO_3)_2$•$4H_2O$ in deionized water. The SiO_2 and DPC doped PMMA fibrous film was placed in Cd^{2+} solution for 2 min, then took out and dried at room temperature. Simultaneously, the images were recorded and the color change was analyzed.

pH effect and selectivity

The pH effect was studied to optimize the conditions for quick and visual detection of Cd^{2+}. In a typical experiment, a solution that contained a specific concentration (10^{-4} M) of Cd^{2+} was adjusted to various pH values by 0.1 M HCl or 0.1 M NaOH. To evaluate the specificity of the SiO_2 and DPC doped PMMA fibrous film to Cd^{2+} detection, we prepared other metal salt solutions such as Ag^+, Al^{3+}, Na^+, Mg^{2+}, Ca^{2+}, Mn^{2+}, K^+, Ba^{2+}, Fe^{3+}, Fe^{2+}, Cr^{3+}, Hg^{2+}, Pb^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+} with the concentration of 10^{-4} M. The test procedures were similar to those described above. Thiourea (CN_2H_4S) was used as Cu^{2+} masking agent for the selective detection.

Characterization

The morphology of the prepared fibers was investigated by scanning electron microscopy (SEM, JSM-6360LV, Hitachi, Japan) and field emission scanning electron microscope (FE-SEM, S-4800, Hitachi, Japan). The images of the post-reaction fibrous films were recorded using a standard digital camera and their color intensity was analyzed using software Image-Pro® Plus 6.0 (Media Cybernetics Inc.). The UV-Vis absorption spectra of the fibrous films were recorded on a Hitachi U-4100 UV-vis-near-IR spectrometer.

Results and discussion

Fiber morphology

Morphologies of the pure, DPC-doped, as well as SiO_2 and DPC doped PMMA fibrous films were observed by SEM (Fig. 1), which shows that the surfaces of pure PMMA fibers were smooth and the diameters of these fibers were uniform, with an average value being 760 ± 98 nm (Fig. 1a, d and g). Doping of DPC in PMMA fibers caused thick fiber formation with an average diameter of 1.49 ± 0.2 μm, although no visible influence on the fiber surface morphology was observed (Fig. 1b, e and h). Nevertheless, doping of SiO_2 nanoparticles in DPC@PMMA fibers greatly affects the fiber surface morphology (Fig. 1c, f and i). To compare with PMMA and DPC@PMMA fibers, SiO_2 nanoparticles and DPC doped fibers (average diameter, 1.5 ± 0.2 μm) showed a rough surface. This result indicated that SiO_2 nanoparticles have a critical influence on generating the convexity structure throughout the fiber backbone. The dispersibility of SiO_2 nanoparticles in DPC@PMMA fibers seems to be much difficult, which may contribute to the final irregular surface of fibers.

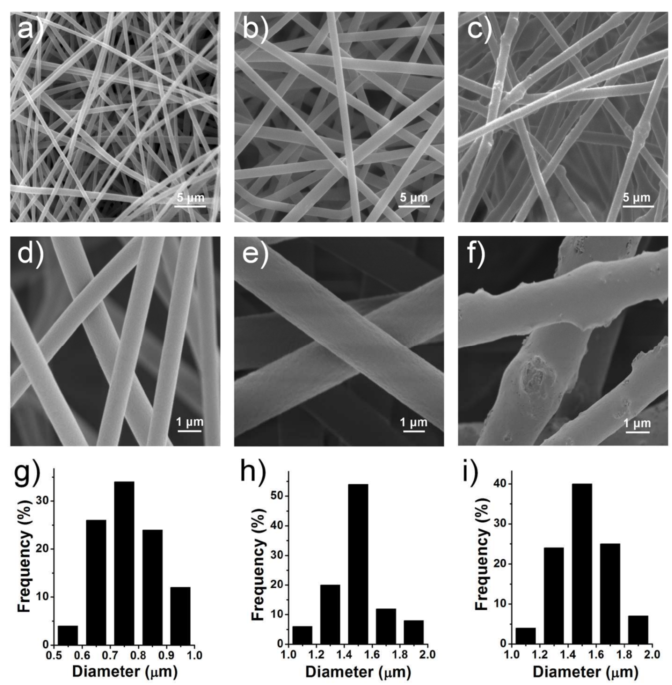


Fig. 1 SEM images (a, b, c, d, e and f) and the diameter distribution (g, h and i) of the electrospun fibers. (a), (d) and (g), PMMA fibers; (b), (e) and (h), DPC-doped PMMA fibers; (c), (f) and (i), SiO_2 nanoparticles and DPC doped PMMA fibers.

Responses of the fibrous films to Cd^{2+}

The color intensity change of the fibers with different contents of DPC and SiO_2 nanoparticles was studied in the presence of the same concentration of Cd^{2+} (ESI Fig. S1 and S2†). The color intensity of the fibers can be enhanced by increasing DPC concentration or the addition of SiO_2 nanoparticles from 1 wt% to 5 wt%. But as the SiO_2 or DPC concentration increased to 8 wt%, some discontinuities were observed in polymer jet formation during electrospinning, which can damage the fibrous structure formation. Accordingly, 5 wt% DPC and 5 wt% SiO_2 were doped in PMMA to prepare the final fibers for Cd^{2+} detection.

Fig. 2 shows the color intensity of the DPC-doped PMMA fibrous film as well as the SiO_2 nanoparticles and DPC doped fibrous film at different Cd^{2+} concentrations. The color intensity of the SiO_2 and DPC doped fibrous film is found to increase with increasing the concentration of Cd^{2+}, which attains the maximum at 10^{-1} M. The same phenomenon was also observed for the DPC-doped fibrous film. However, the corresponding color intensity is much lower than that of the SiO_2 and DPC doped fibrous film at the same Cd^{2+} concentration. The addition of SiO_2 nanoparticles results in both an increase in surface roughness and an increase in the surface area of the fibers.[22–24] The color intensity improvement can be attributed to the high specific surface area of the SiO_2 and DPC doped fibers by which Cd^{2+} could react with DPC efficiently. The detection limit of the SiO_2 and DPC doped fibrous film for Cd^{2+} was found to be 10^{-8} M.

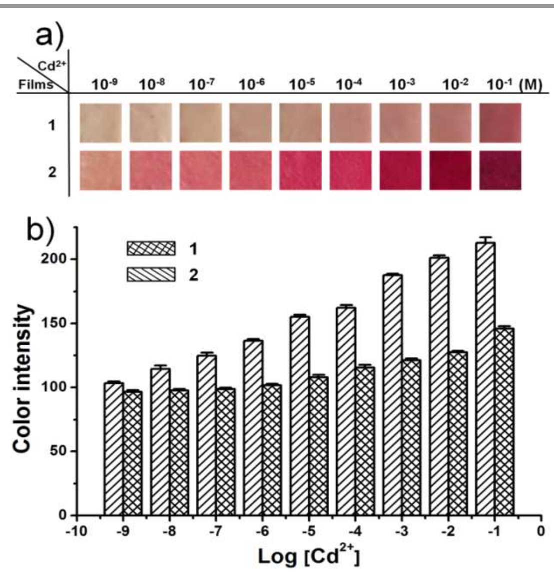


Fig. 2 (a) Optical images of the fibrous films after various concentrations of Cd^{2+} involvements. (b) The color intensity change as a function of Cd^{2+} concentration. 1: DPC-doped PMMA fibrous films; 2: SiO_2 nanoparticles and DPC doped PMMA fibrous films.

Although the formation of a red-pink complex of Cd^{2+} ion and DPC was observed by naked-eye, UV-vis spectroscopy measurements were also performed. The UV-vis absorption spectra (Fig. 3) of the fibrous film showed a strong Cd-to-DPC charge transfer band at 523 nm and the absorbance intensity kept increasing with increasing Cd^{2+} concentration, similar to the color intensity change, and there also exists a linear relationship between absorbance intensity and Cd^{2+} in the low concentration range from 10^{-8} to 10^{-4} M (ESI Fig. S3†). However, at lower than 10^{-8} M Cd^{2+} concentration, the changes of the fibrous film color and absorbance spectrum were not obvious and did not allow a significant difference to be measured. Therefore, it was concluded that the SiO_2 and DPC doped fibrous film could be used for Cd^{2+} detection at the concentration ranging from 10^{-1} to 10^{-8} M.

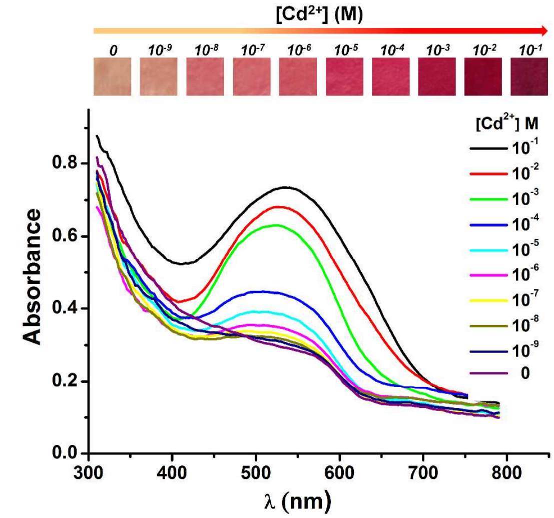


Fig. 3 Color responses (top optical images) and solid UV-vis absorbance spectra (bottom) of the SiO_2 and DPC doped fibrous films after various concentrations of Cd^{2+} involvements.

pH effect on Cd^{2+} detection

To evaluate the effect of pH value on the determination of Cd^{2+}, the color intensity change of the SiO_2 and DPC doped fibrous film was carefully monitored over a wide range of pH solutions (ESI Fig. S4†). The optimum change in color intensity was found at approximately pH 5.0. The pH graph (ESI Fig. S4†) implied that Cd^{2+} can strongly bind to the fibrous film with high stability after the formation of [Cd-DPC] complexes at pH 5.0.

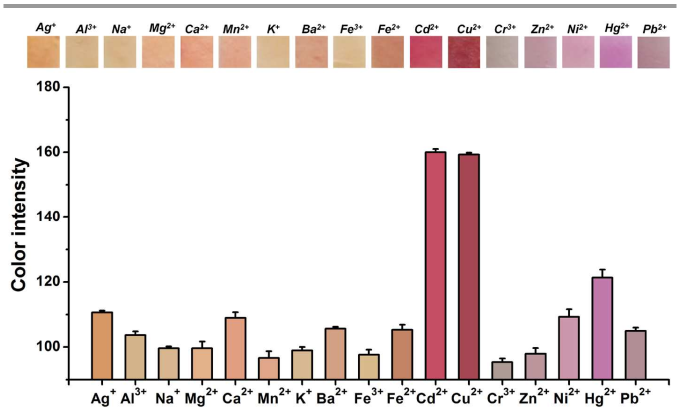


Fig. 4 Colorimetric responses of SiO_2 and DPC doped fibrous films after incubated with 10^{-4} M various metal ions.

Selectivity of the fibrous films for Cd^{2+}

The selectivity of the SiO_2 and DPC doped fibrous film was evaluated with other metal salts such as Ag^+, Al^{3+}, Na^+, Mg^{2+}, Ca^{2+}, Mn^{2+}, K^+, Ba^{2+}, Fe^{3+}, Fe^{2+}, Cr^{3+}, Hg^{2+}, Pb^{2+}, Ni^{2+}, Cu^{2+}, $Zn^{2+}$and Cd^{2+} at concentration of 10^{-4} M. The results were shown in Fig. 4, which indicates that no interference was found during Cd^{2+} determination in the presence of other metal ions except for Cu^{2+}. The color of the fibrous films turned to yellow or light pink after the addition of other metal ions and films turned brown in the presence of Cu^{2+}. However, only when Cd^{2+} was added, the color of the SiO_2 and DPC doped fibrous film changed from yellowish to red. The results confirmed the selectivity of the proposed assay to Cd^{2+} in the water without Cu^{2+}.

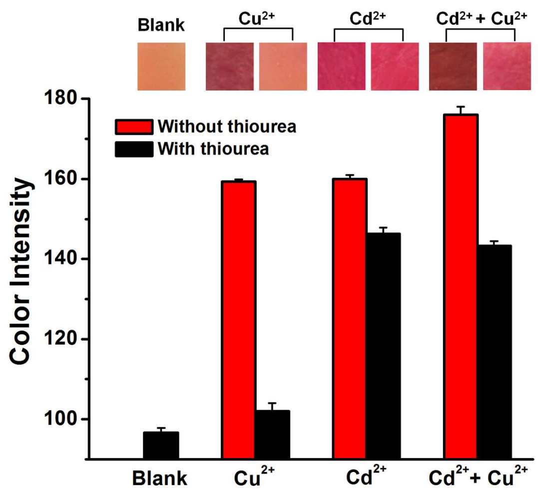


Fig. 5 The color intensity of SiO_2 and DPC doped fibrous films after incubated with 10^{-4} M Cd^{2+}, Cu^{2+}, and Cd^{2+} and Cu^{2+} solutions without or with 10^{-3} M thiourea. Blank: only 10^{-3} M thiourea.

To improve the fibrous film selectivity to Cd^{2+}, thiourea was used as Cu^{2+} masking agent because thiourea can form a stable complex with Cu^{2+}.[26,27] As indicated in Fig. 5, before thiourea addition, the fibrous films turned brown in the presence of Cu^{2+}. After adding thiourea, the color of the fibrous film had no significant change during Cu^{2+} detection and still appeared yellowish compared with the blank control. However, target Cd^{2+} could induce the color of the fibrous films to change to red. The results demonstrated that thiourea could specifically act as Cu^{2+} masking agent in this system during Cd^{2+} detection.

Conclusions

In this study, a simple and visible method for the colorimetric detection of Cd^{2+} was developed using SiO_2 nanoparticles and DPC doped PMMA electrospun fibers. SEM analysis showed that the prepared fibers were uniform (average diameter, 1.5 ± 0.2 μm). Because the binding of Cd^{2+} with DPC can form a red [Cd-DPC] complex, the DPC-doped fibers can successfully achieve a color change in the presence of Cd^{2+}. In addition, the addition of SiO_2 nanoparticles in the fibers can enhance the color intensity due to the formation of a rough surface. Further analysis showed that the color intensity change is directly proportional to Cd^{2+} concentration in the range of 10^{-1} to 10^{-8} M, which was similar to the conventional UV-vis absorption assay. The detection limit of the fibrous film for Cd^{2+} was 10^{-8} M at pH 5.0. Investigation of the selectivity showed that only Cd^{2+} can induce the SiO_2 and DPC doped fibrous film to produce a yellow-to-red color change. All the results demonstrated that the proposed colorimetric method can used for simple and rapid detection of Cd^{2+} by the naked eye.

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Notes and references

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