

A Mesoporous Silica Supported Hg^{2+} Chemodosimeter

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A chemical reaction type chemodosimeter immobilized on mesoporous silica materials (**CFMS**) was reported and showed fluorescent ratiometric, colorimetric, and even naked-eye recognizable manner with a detection limit of $\sim 2 \mu\text{M}$ for mercury (II). The characterization of CFMS indicated that the ordered mesoporous structure was well preserved after the immobilization. It was found that only the addition of Hg^{2+} resulted in significant color change and large fluorescence spectral shift whereas other cations didn't induce any color or emission change. In addition, CFMS was also coated as films onto glass substrates. When aqueous Hg^{2+} rapidly passed through the glass substrate, the green emission of supported CFMS became blue under a 365 nm lamp. These considerable signal changes, easy-to-prepare materials, and simple-to-operate technique suggested the potential application of CFMS for fluorescent ratiometric detection of Hg^{2+} ion in the practical environmental field. © 2010 American Institute of Chemical Engineers *AIChE J.*, 56: 2957–2964, 2010

Keywords: cations, chemodosimeter, film, mercury (II), mesoporous silica

Introduction

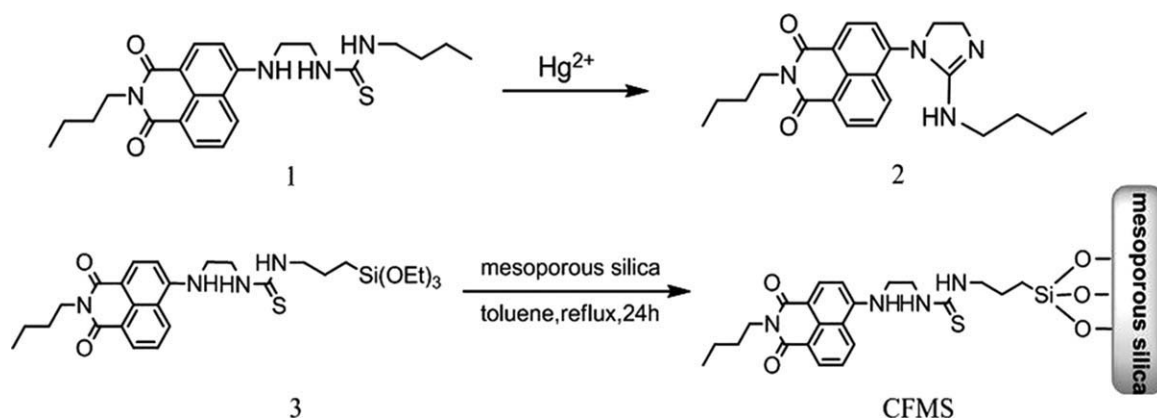
Sensing heavy and transition metal ions is an area of great research activity because of their extremely toxic impact on the environment and human health. Among them, Hg^{2+} is considered as one of the most toxic cations, as mercury and its derivatives are highly toxic and widely distributed in air, water, and soil due to their broad use in industry.^{1,2} Therefore, it is a continuous goal for researchers to develop new and efficient detecting assays for Hg^{2+} ions. In recent years, many efforts have been made to design various optical chemosensors specific for detection, which follow changes in fluorescence or UV-Vis spectroscopy resulting from a Hg^{2+} -induced perturbation of a fluorophore or chromophore.^{3,4} The advantage of the aforementioned methods to detect Hg^{2+} is that their detection process is highly sensitive and can reach a detection limitation to 10^{-6} M, but the disadvantage of these methods are also obvious, that is, they are all reversible chemosensors and the reversibility may result in fault detect reports if a long detection time is involved.³

Compared to the relatively well-developed fluorescent chemosensors that usually respond to Hg^{2+} reversibly, development of fluorescent chemodosimeters has recently emerged as a research area of significant importance.^{5,6} The most attractive approach in this field involves the use of highly selective reactions (usually irreversible) induced by Hg^{2+} ion, including oxymercuration, mercuration, and mercury-promoted desulfurization, etc.^{5–8} However, many fluorometric dosimeters involved only changes in the emission intensities. Still, ratiometric responses are generally preferable and offer several additional advantages, such as providing built-in correction for environmental effects, being less prone to artifacts and facilitate analyte quantification, especially in inhomogeneous samples.^{9,10}

After the synthesis of a fluorescent probe, to make a sensor device, the next step is the immobilization of the probe molecules on a solid support. The support materials afford their exterior surface or inside pores to confine the probe molecules in a physical space.^{11,12} In general, covalent

Additional Supporting Information may be found in the online version of this article.

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Scheme 1. Hg^{2+} -promoted intramolecular guanylation of **1** and grafting of **3** on mesoporous silica.

attachment of the sensitive probe to the support matrix is a preferred method relative to physical adsorption and entrapment in some cases of producing the sensing materials, which can avoid the leaching of the fluorescent probe and improve the stability of these materials.¹³ A number of materials such as silica particles,^{14,15} quantum dots,^{16–18} Langmuir-Blodgett films,^{19,20} and others^{21,22} are used nowadays combined with many indicators to form hybrid materials. Recently, the use of mesoporous silica materials as support matrix for the design and preparation of optical sensors has attracted much attention in the field of environmental analysis.^{23–27} Because of their high porosity, concomitant large surface area, good thermal stability, and facile synthesis, mesoporous silica materials are in principle ideally suited as support materials for sensitive probes and have been extensively used for the detection of cations, anions, and neutral analytes.^{23–28} Organic–inorganic hybrid materials by the incorporation of fluorophores or chromophores into mesoporous silica display highly selective, sensitive fluorescence or absorption changes compared with spherical structures because of their homogeneous porosity and well-defined pores, which make them promising sensing materials.²⁹

To make use of the intrinsic advantages of the mesoporous materials, we designed and synthesized chemodosimeter **1** and its derivative **3**, which possesses an additional triethoxysilane group for the purpose of covalently attaching to the silica network (Scheme 1). Chemodosimeter **1** was designed to adopt mercury-promoted desulfhydrylation between thiourea unit and Hg^{2+} ion to give an irreversible reaction, which is responsible for significant color change and fluorescence spectral shift. This reaction mechanism has been previously used to design and synthesis a naphthalimide-containing chemodosimeter bearing the similar molecular structure as indicator **1** by our group.⁶ The grafting of compound **3** produced chemodosimeter-functionalized mesoporous silica (CFMS) material and its Hg^{2+} sensing ability was thoroughly studied. It should be mentioned that among all the optical sensors from mesoporous silica materials functionalized with chromophores or fluorophores, only a few reports were based on organic chemodosimeter functionalization and still less in the case of involving fluorescence ratiometric responses, which is a highly desirable property.²⁶

Experimental

All information about the starting materials and the detecting apparatus and instruments were listed in Electronic Supporting Information, also including the synthesis of compounds **1**, **2**, and **3**.

Preparation of the mesoporous silica

The pure mesoporous siliceous matrix was synthesized by hydrothermal method.³⁰ In a typical synthesis, 2.4 g of surfactant cetyltrimethylammonium bromide (CTAB) was dissolved in 36 ml of distilled water and 31 ml of ammonia. Then, 10 ml tetraethylorthosilicate (TEOS) was added dropwise into this solution under stirring. After the TEOS was dropped completely, the mixture was stirred for 2 h. The molar composition of the final gel mixture was 1 SiO_2 :0.15 CTAB:11.6 NH_3 :89.6 H_2O . And then, the obtained mixture was transferred into Teflon-lined autoclave and heated at 393 K for 48 h. The white solid was filtered, rinsed with large amount of distilled water, and dried in air. The template agent CTAB was removed by calcination in air at 823 K for 5 h.

Grafting of compound **3** onto the mesoporous silica particles

Compound **3** (50 mg) was dissolved in toluene (10 ml). The mesoporous silica (500 mg) was added as a solid. The suspension of mesoporous silica was stirred under reflux conditions for 24 h in toluene. Then, the collected solid was washed copiously with toluene (100 ml) and ethanol (50 ml) to rinse away any surplus **3** and dried under vacuum.

Preparation of the CFMS-coated plates

To 5 ml of a solution of H_2O (2.5 ml) and EtOH (2.5 ml), 200 mg of CFMS was added and the mixture was shaken for 1 min. Then, the slurry product was spread evenly over a glass surface and was left to dry for ~30 min. The final step is to place the glass plates in an oven for 30 min at a maximum temperature of 100°C.²⁵

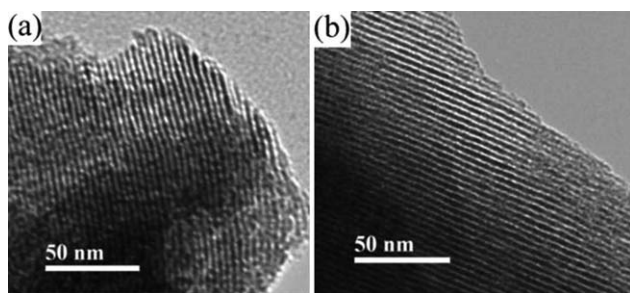


Figure 1. TEM images of (a) mesoporous silica and (b) CFMS.

Results and Discussion

Grafting of compound 3 on mesoporous silica

Both chemodosimeters **1** and **3** consist of naphthalimide as signal subunits and thiourea groups as the reaction units. The structure of compound **2**, which originated from the irreversible reaction of **1** with Hg^{2+} , has been confirmed by ^1H NMR, ^{13}C NMR, and mass spectrometry data. Comparing the ^1H NMR spectrum of **2** with that of **1**, it was easy to find that the two NH signals in the case of **1** disappeared as a result of Hg^{2+} -induced desulfhydrylation. CFMS was obtained by refluxing a suspension of mesoporous silica in a toluene solution of **3**, which was attributed to the reaction between the ethoxysilane groups of the chemodosimeter and the silanol groups of silica (Scheme 1).³¹

Characterization of the mesoporous silica and CFMS

TEM images of both the mesoporous silica and CFMS clearly show the formation of ordered mesostructures (Figure 1), which indicates that CFMS still preserve the ordered mesoporous structure after attachment of the functional unit.

The XRD patterns revealed that both the calcined mesoporous silica and CFMS have one Bragg peak at low reflection angles between 2.0° and 3.0° , which are typical of mesoporous MCM-41 type materials, corresponding to the (100) reflection (Figure 2).³² All the reflections are indexed based on hexagonal symmetry. In addition, the intensity of (100) reflection is decreased slightly after organic chemodosimeter functionalization.

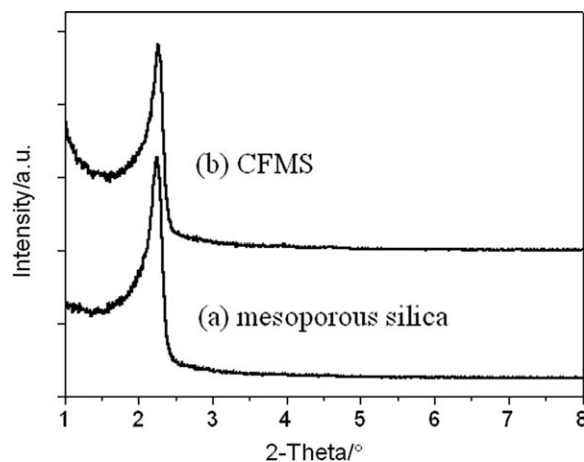


Figure 2. Small-angle XRD patterns of (a) calcined mesoporous silica and (b) CFMS.

To get more information about the pore system of mesoporous materials, the nitrogen adsorption-desorption isotherms and the pore distribution of both mesoporous silica and CFMS were determined and shown in Figure 3. Both the isotherms obtained can be classified as Type IV according to IUPAC, which is characteristic of a mesoporous material.³² The Brunauer-Emmett-Teller (BET) surface area and pore volume of CFMS reduce remarkably compared to calcined mesoporous silica. The mesoporous silica has a BET surface area of $827 \text{ m}^2/\text{g}$ and a pore volume of $0.56 \text{ cm}^3/\text{g}$. In contrast, we observed that CFMS has a BET surface area of $570 \text{ m}^2/\text{g}$ and a pore volume of $0.40 \text{ cm}^3/\text{g}$. Both materials had narrow BJH (Barrett-Joyner-Halenda) pore size distribution and average BJH pore diameters were measured: 2.12 nm for the mesoporous silica material and 2.01 nm for CFMS. The decreased surface area and pore diameter in CFMS are attributable to the attachment of the organic moieties on the pore surface of ordered mesoporous silica.^{24,27,32}

IR spectra of mesoporous silica and CFMS give further evidence about the organic dyes functionalization (Figure 4). Compared with mesoporous silica without dye molecules, CFMS shows new peaks at 2349 , 2320 , 1632 , 1578 , and 1553 cm^{-1} , which originated from the naphthalimide derivative **3**, indicating covalent attachment of **3** on the surface of mesoporous material. In addition, CFMS displayed a

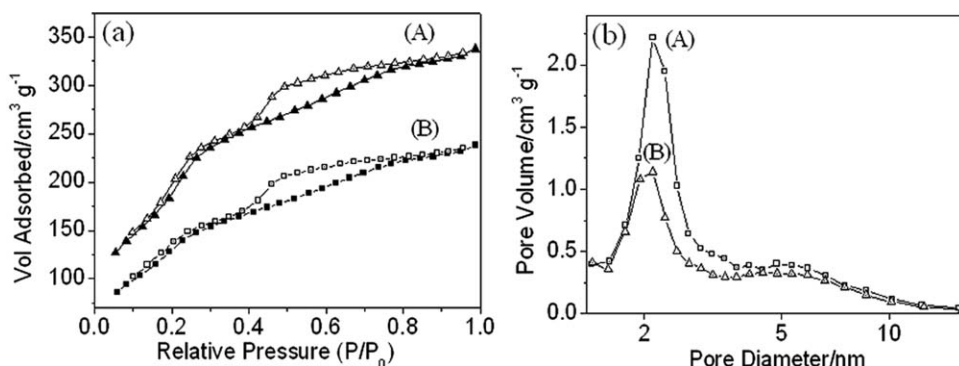


Figure 3. (a) The nitrogen adsorption-desorption isotherms and (b) Barrett-Joyner-Halenda (BJH) pore size distribution of mesoporous silica curve (A) and CFMS curve (B).

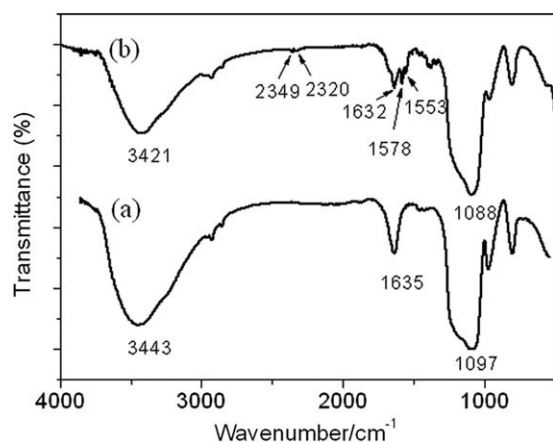


Figure 4. IR spectra of (a) mesoporous silica and (b) CFMS.

yellow–green coloration and strong emission when irradiated with 365 nm using UV lamp, revealing nonoccurrence of the fluorescent self-quenching that sometimes may be caused by aggregate formation in the case of too high loadings of fluorophores.²³ We also performed thermogravimetric analysis (TGA) but failed to obtain the content of organic dyes in CFMS, because the weight decreased continually at the temperature scale from 40 to 800°C and did not reach a plateau.

Hg²⁺ ion sensing ability of chemodosimeter 1

The absorption and fluorescence measurements were carried out using the $\sim 10^{-5}$ M solution of compound **1**. As the naphthalimide derivative **1** used here was hardly soluble in water, ethanol–water (1:1, V/V) solution was chosen as a solvent. Upon addition of Hg²⁺, the 448 nm absorption band decreased significantly, along with the growth of a new band at 346 nm. A clear isosbestic point appeared at 389 nm, indicating that only two chromogenic species coexisted in the solution (Figure 5a).¹⁰ For fluorescence titration upon addition of Hg²⁺, a gradual decrease in the 535 nm band and the steady increase of a hypsochromic-shifted emission band centered at 461 nm were observed with one isoemissive point at 505 nm (Figure 6a). The large blue shifts in absorption (102 nm) and fluorescence (74 nm) spectra were due to the reduction in electron delocalization within the

chromophore/fluorophore as a result of Hg²⁺-induced transformation of the thiourea unit into an imidazoline moiety, which is a much less electron-donating group (Scheme 1).⁶ As a consequence, the yellow–green solution became colorless accompanied by a yellow–green to blue emission color change (Figure S1, Electronic Supporting Information).

To prove practical applicability of **1** as a Hg²⁺-selective indicator, we also tested the UV-Vis and fluorescence behaviors of **1** towards other metal ions. Figure 7 showed UV-Vis and fluorescence spectral modifications of **1** in aqueous solutions upon addition of 2 equiv. of Hg²⁺ and 10 equiv. of other metal ions after 10 min. Obviously, no spectral shift was detected for all these metal ions except Ag⁺ and Hg²⁺. It should be mentioned that Ag⁺ could cause the analogous reaction as Hg²⁺, but the activity was lower and the reaction required much more time (more than 2 h) to achieve completion. Although this is unfortunately a limitation for the selectivity of this chemodosimeter, it is still usable for detecting Hg²⁺ if the existence of Ag⁺ can be ruled out in advance.

CFMS and its Hg²⁺ ion sensing ability

Because the content of organic dyes grafted on the surface of mesoporous silica was hard to be determined, fluorescence measurements were done in a magnetic-stirred suspension of CFMS (15 mg) in 30 ml water (0.5 mg/ml). The absorption and fluorescence spectra of solid CFMS were shown in Figure 8. The solid CFMS exhibited strong emission and the maximum fluorescence peak position (450 nm) and the shape of CFMS were very similar to that of chemodosimeter **1** in solution, as well as in the case of absorption spectra. These results allowed the dye molecules to be considered to exist in monomer form and without any interaction in mesoporous silica due to the high surface area,^{30,33} because the aggregate formation that resulted from too high loadings of fluorophores could cause self-quenching of the fluorescence or the bathochromic shift and broadening of the fluorescence spectrum.^{23,34,35}

As presented in Figure S2 (Electronic Supporting Information), the addition of different concentration of Hg²⁺ (5 μ M, 10 μ M, and 50 μ M) to suspensions of CFMS resulted in gradual color changes from yellow–green to colorless or white that was close to the mesoporous silica without dye grafting. Simultaneously, the emission change from yellow–

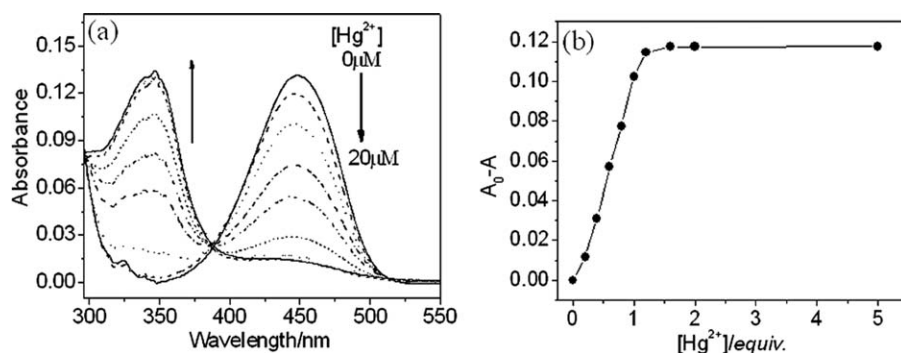


Figure 5. (a) UV-Vis titration spectra of **1** (10 μ M) and (b) titration profile at 448 nm upon addition of various amounts of Hg²⁺ in ethanol–water (1:1, V/V) solution.

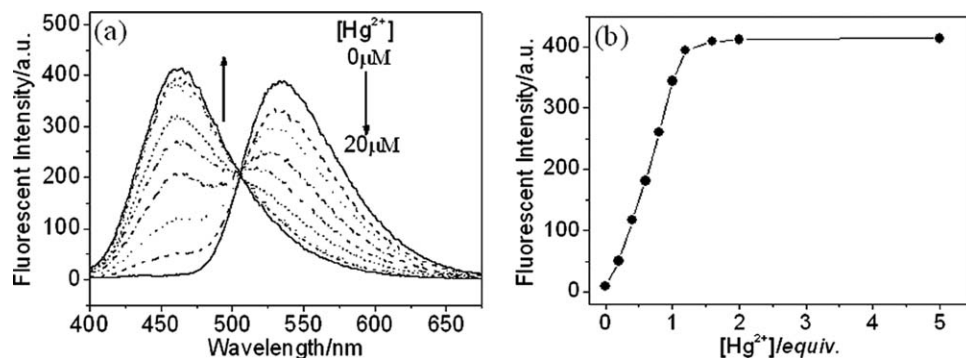


Figure 6. (a) Fluorescence titration spectra of 1 (10 μM) and (b) titration profile at 461 nm upon addition of various amounts of Hg^{2+} in ethanol-water (1:1, V/V) solution, $\lambda_{\text{ex}} = 380 \text{ nm}$.

green to blue was readily detected visually when irradiated by UV lamp (365 nm) (Figure S2, Electronic Supporting Information). These color variations greatly resembled those observed in the case of free chemodosimeter **1** in solution. It is considered that nothing is adsorbed on the unfunctionalized silica material and there is no interaction between Hg^{2+} and support matrix,^{23,36} this can be supported by the UV-Vis spectra of mesoporous silica before and after the addition of Hg^{2+} in Figures S3a, b (control experiments). Accordingly, we rationally attribute the remarkable color change of **CFMS** suspension in water to the reactivity of grafted thiourea derivatives with Hg^{2+} ions (Figure 9a). The mesoporous silica can thus be considered as an inert matrix to provide solid support for the recognition/reaction process, which is in consistent with recent studies.³⁷ The significant color changes indicated that the chemodosimeter preserved its sensory ability after being attached to the surface of mesostructured pores.

To gain an insight into the sensing performance, the emission spectra of **CFMS** suspension and its fluorescence titration with Hg^{2+} were recorded. Figure 9c displayed the normalized fluorescence spectra during the titration process. When Hg^{2+} was added to the suspension of **CFMS**, the band centered at 534 nm progressively decreased accompanied with an appearance and development of a new peak centered at 458 nm. Fluorescence spectral modifications were just like those observed in the case of chemodosimeter

1 in solution. The emission intensity variations at 534 nm and 458 nm implied that **CFMS** could be used as a fluorescent sensing material for the ratiometric detection of Hg^{2+} ion in water.

To further confirm the reaction efficiency of Hg^{2+} by **CFMS**, we isolated the grafted silica after reaction with Hg^{2+} and measured the solid UV-Vis spectra of **CFMS** before/after being stirred in Hg^{2+} -containing solution. As shown in Figure 9b, solid **CFMS** exhibited a maximum absorption at 450 nm, through reacting with Hg^{2+} , however, the 450 nm band decreased and a blue-shifted band at 353 nm appeared that clearly accorded with the visual color change. The large hypsochromic shift (97 nm) and significant color change allowed **CFMS** to sense Hg^{2+} in a colorimetric way.

Considering the high selectivity of chemodosimeter **1** towards Hg^{2+} , the selectivity of **CFMS** could be expected. As shown in Figure S4, after being stirred in the solution containing several metal ions, except Hg^{2+} ion, no significant changes in visual colors and emission were observed in the parallel experiments with Na^+ , Mg^{2+} , Pb^{2+} , Zn^{2+} , Cu^{2+} , Cd^{2+} , Co^{2+} , Ni^{2+} , and Mn^{2+} . **CFMS** clearly showed an extremely good selectivity for mercury against all the other cations tested.

CFMS-coated glass plate

To produce a more applicable sensor, **CFMS** was coated as films of about 0.1 mm thickness onto the glass substrates

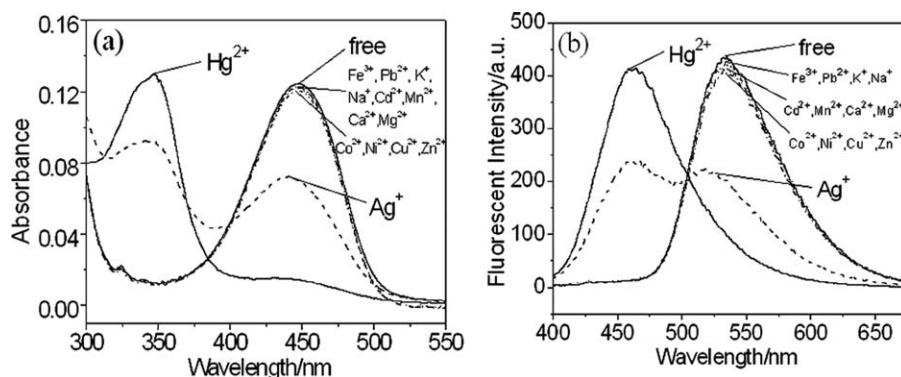


Figure 7. (a) UV-Vis and (b) fluorescence spectra of 1 upon addition of 2 equiv. of Hg^{2+} and 10 equiv. of other metal ions.

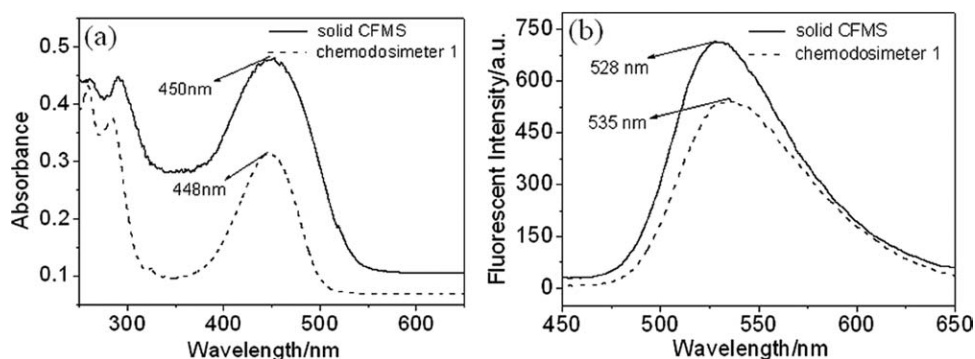


Figure 8. (a) Absorption and (b) fluorescence spectra of CFMS and chemodosimeter 1 in ethanol-water (1:1, v/v) solution.

(15 mm × 15 mm) to perform detection of metal ions. Figure 8 showed the fluorescence responses of these films towards Hg^{2+} and other cations. After being immersed into water solutions containing Hg^{2+} , the original green emission of CFMS-coated substrate became blue emission. In contrast, no significant change in emission was observed after immersion in other cations solution. The obvious fluorescence variations allowed the supported CFMS to detect the low concentrated Hg^{2+} ion up to 1.0×10^{-5} M by naked-eyes upon the UV irradiation (365 nm) (Figure 10). These results suggested the possible and potential practical applicability of CFMS for fluorescent ratiometric detection of Hg^{2+} ion in the environmental field.

Characteristics of CFMS and compound 1 for practical application

As far as the detection limitation, response time, sensitivity, and selectivity are concerned, several properties rendered

both CFMS and compound 1 available for practical application. That is:

(a) Both UV-Vis titration curve of measured absorbance [$A_0 - A$] at 448 nm vs. Hg^{2+} ion concentrations and the linear increase of fluorescence intensity at 461 nm within the equivalent range of Hg^{2+} ion indicated a definite 1:1 reaction stoichiometry (Figures 3b and 4b). These results demonstrated the potential use of dosimeter 1 for calibrating and determining Hg^{2+} ion concentration in water-containing solution.

(b) The reaction responsible for these changes reached completion within the time frame of <1 min for these measurements, which can guarantee the facility of the technique.

(c) In a 1×10^{-5} M solution of 1, Hg^{2+} could be detected as low as 2 μM . For CFMS, the detection limit within appreciable emission color changes was allowable to 5 μM level of Hg^{2+} ion in 0.5 mg/ml water suspension, which was very similar to that of 1.

(d) Among all the involved cations, only Ag^+ showed slight interference, which cannot cover up the excellence of the selectivity of CFMS and compound 1.

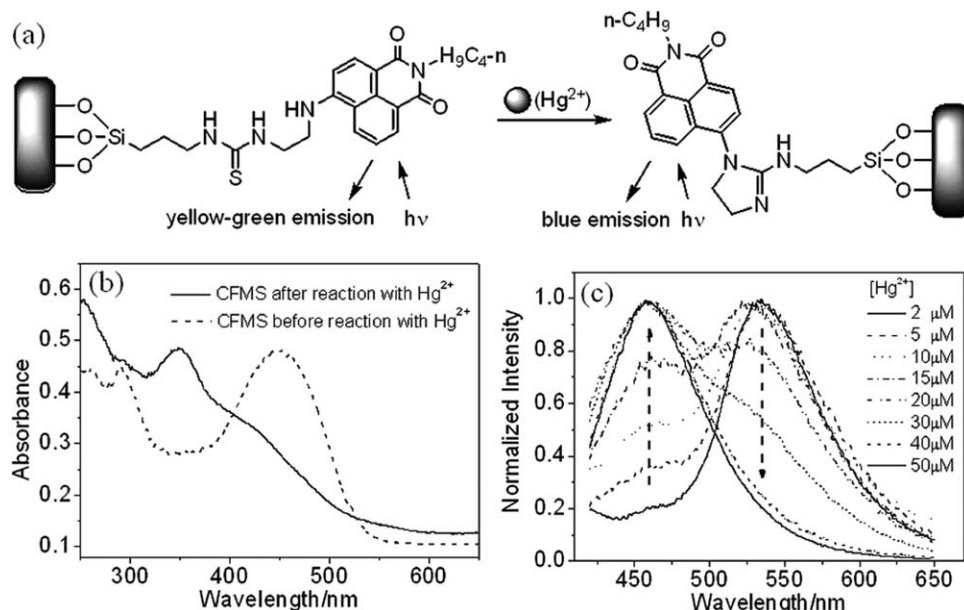


Figure 9. (a) Proposed structures of CFMS before and after reaction with Hg^{2+} , (b) solid UV-Vis spectra of CFMS before and after reaction with Hg^{2+} , (c) fluorescence titration spectra of water suspension of CFMS upon addition of various amounts of Hg^{2+} , $\lambda_{\text{ex}} = 370$ nm.

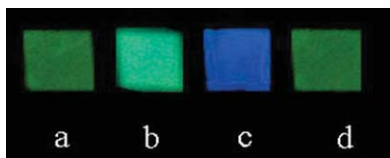


Figure 10. Fluorescence changes of CFMS-coated glass substrates (a) without Hg^{2+} , (b) $1.0 \times 10^{-5} \text{ M Hg}^{2+}$, (c) $1.0 \times 10^{-4} \text{ M Hg}^{2+}$, and (d) other cations (Na^+ , Mg^{2+} , Pb^{2+} , Zn^{2+} , Cu^{2+} , Cd^{2+} , Co^{2+} , Ni^{2+} , and Mn^{2+}).

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

(e) The obvious naked-eye recognizable detection property of thin film of CFMS can further strengthen the advantage of practical application. This means that this easy-to-operate technique can be converted to portable devices after deliberate transformation.

Shortcomings and challenges

The detection technique for Hg^{2+} through optical changes and naked-eye observation, as presented in this investigation, is facile and precise. However, a few critical impediments need to be overcome before the technique is ready for broader applications to rapidly detect the Hg^{2+} in water. First, the presence of Ag^+ would negatively affect the detection precision. Even though the response time of Ag^+ was much longer than Hg^{2+} , to obtain desirable detection results, Ag^+ should be removed in advance by using some well-constructed methods. For example, Ag^+ could be adsorbed by macroporous phosphonic acid resin in the media of HAC-NaAc³⁸ or by the precipitation method.³⁹ Second, the detection process was irreversible, that was, the detection materials can not be recycled, due to its chemical reaction type. The reusable substances with a non covalent interaction mechanism are currently investigated in our team.

Conclusion

In summary, a naphthalimide-based chemodosimeter that can colorimetric and fluorescent ratiometric detection of Hg^{2+} ion with high selectivity in aqueous solution was synthesized and grafted on mesoporous silica. The characterization of this organic-inorganic hybrid material (CFMS) by XRD, TEM, and nitrogen adsorption-desorption isotherms showed that the mesoporous structure of the solid support were not affected after organic dye immobilization. For the inert properties of silica matrix, the sensing process of CFMS was mainly governed by the specific reactivity of the grafted unit towards Hg^{2+} . CFMS suspension in water displayed very similar analytical performances to those of chemodosimeter in solution: spectroscopic ratiometric responses, high selectivity towards Hg^{2+} , and detection limit at the same concentration level. Also, CFMS-coated solid substrate exhibited emission color changes upon exposure to Hg^{2+} , indicating potential applicability as a portable sensor. This work displays the possibility to produce a fluorescent ratiometric sensing material by combination of well defined mesoporous silica with a high selective chemodosimeter. With

the use of mesoporous silica and proper designed probe, the method has the potential to be utilized in general for detection of heavy metals in water.

Acknowledgments

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