



Picomolar reversible Hg(II) solid-state sensor based on carbon dots in double heterostructure colloidal photonic crystals



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ABSTRACT

Mercury contamination in water is a persistent issue due to both natural geological and anthropogenic activities. Portable, facile and affordable sensors for detection and sensing different species of mercuries are highly desirable. We report a highly effective fluorescent, solid state sensor with high sensitivity, good selectivity and excellent reversibility for Hg(II) ion. Hg(II)-responsive carbon dots immobilised polystyrene spheres were fabricated as a middle layer in double heterostructure colloidal photonic crystal film. Significant fluorescence enhancement was achieved due to doubly resonant of the modes of photonic crystals and multi beam interface inside the double heterostructure film. The amplified fluorescence enhances the sensitivity of detection, achieving a detection limit of 91 pM for Hg(II) ion, even 17 times lower than that of carbon dots solution probe. The polystyrene-based film sensor is negligibly responsive to other metal ions and can easily be recovered by rinsing with cysteine.

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1. Introduction

Amongst all heavy metal contaminants in water, mercury is listed on top in terms of the spreading scale and toxic potency [1]. Due to its low boiling point, the emission of mercury is almost inevitable, from both anthropogenic and natural activities, such as volcanos, forest fires, coal combustion and mining activities. Because Hg(0) can be easily oxidized to water soluble Hg(II), mercury contamination of water and soil is bound to happen. To mediate its environmental impact, it is highly important to be able to continuously and accurately monitor the mercury level in water.

Many analytical methods for Hg(II) detection have been developed including quartz crystal microbalance [2], surface-enhanced Raman scattering (SERS) technique [3], surface plasmon resonances [4], fluorescence chemosensors [5] and electrochemical methods [6], etc. Among them, fluorescence (FL) chemosensors have received increasing attention in recent years, because of their compatibility with portable devices and reduced cost. [7] Recently, carbon nanodots [8], a class of carbon-based nanoparticles that comprise discrete carbogenic nanoparticles with sizes below 10 nm

and highly photoluminescent, have been shown to exhibit excellent sensitivity and selectivity to Hg(II) as a fluorescence probe. Li and co-workers [9] have reported an organosilane functionalized carbon dots (CDs) with nanomolar sensitivity (detection limit: 1.35 nM), high stability in electrolytes and organic solvents.

However, most research and development of the fluorescence-based sensors remain at solution based set-up, i.e. the sensing molecules or nanoparticles need to be dispersed in solutions for functioning as a sensor. This may be caused by reduced or even loss of sensitivity when sensing agents are immobilized on a solid surface. Solid-state sensors are highly desirable because they are easier to handle and transport, more compatible with small-footprint devices, and more stable. Very importantly, solid-state sensors can allow washing steps, hence constituting a sensor, which, by strict definition, should respond to its analytes reversibly.

In selecting a solid-state matrix for immobilizing the fluorescent sensing agents, colloidal photonic crystals (CPhCs) have recently received keen attention because of their extraordinary enhancement effect on signal intensity and the ease in fabrication [10–13]. Photonic crystals can strongly modulate electromagnetic waves and, with sufficient dielectric contrast and an appropriate geometry, may exhibit a photonic band gap (PBG), which affect photons in a manner similar to the effect of semiconductor energy band gaps on electrons and diffract the light with the wavelength located into their PBGs. The CPhCs films could play the role as a Bragg

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mirror to enhance the intensity of excitation light and/or fluorescence with the wavelength located into their PBGs and thus improve the sensitivity of the sensor [14,15]. Moreover, by combing photonic modes with other optical effects, such as plasmonics [16] and multiple beam interference [17], the fluorescence signal can be further amplified by several-fold. The strategy of combing with multiple beam interference results in an all-polymer film, therefore significantly more affordable as a technology solution. One of the technical challenges in employing CPhCs as the substrate is how to stably incorporate the fluorescent sensing molecules or nanoparticles. Eftekhari et al. [18] have demonstrated an ‘under the skin’ coating method can stably anchor Rhodamine B in CPhC polymer film with uncompromised fluorescence enhancement effect.

In this work, we have adopted a novel CPhC superstructure comprising three layers of monolithic CPhCs [19]. A double heterostructure CPhC is formed by successive deposition of CPhCs in a sequence of E-F-E from bottom to top (where E refers to the monolithic CPhC with a periodicity overlapping the excitation wavelength and F refers to the monolithic CPhC with a periodicity overlapping the emission wavelength). The thickness of the F layer is tuned to support constructive multiple beam interference of the excitation wavelength. Hg(II)-responsive CDs were immobilized by ‘under the skin coating’ method [18] on the surface of F polystyrene spheres (CDs@F), which were deposited as a middle layer in double heterostructure (E-(CDs@F)-E). In such a double heterostructure, the two E layers both reflect any excitation light that may propagate in the (CDs@F) layer. Hence, when the thickness of (CDs@F) supports constructive interference, the excitation light is effectively recycled many times (photon recycling) through the F layer, increasing the excitation efficiency [19]. Therefore, it would be interesting to explore the extent of sensitivity enhancement that the double heterostructure could afford to the fluorescent sensing agent.

This study is comprised of four parts: 1) Development of an effective immobilization method for incorporating CDs on polystyrene surface without compromising their sensitivity to analytes. 2) Investigation of E-(CDs@F)-E fluorescence enhancement. 3) Evaluation of E-(CDs@F)-E film’s sensitivity and selectivity to Hg(II) in various water samples. 4) Testing the sensor reversibility of E-(CDs@F)-E film. Owing to the novel immobilising approach and double heterostructure, the FL intensity significantly enhanced and the detection limit was improved to 91 pM for Hg(II), which is significantly lower than previously reported [20–25]. Moreover, high level of sensing reversibility has also been achieved by this film sensor. Such significant sensitivity, selectivity and reversibility of E-(CDs@F)-E film sensor shows the potential for further solid-based sensor development in complex water samples and harsh environments.

2. Experimental section

2.1. Materials

Dimethyl formamide (DMF), Tetrahydrofuran (THF), acrylic acid (AA), acetone and ethanol (all purchased from Sigma Aldrich), were of analytical grade and used as received without further purification. N-(b-aminoethyl)-c-aminopropylmethyl- dimethoxysilane (AEAPMS) was purchased from Beijing Shenda Fine Chemical Co., Ltd. Glass slides were used as the substrates for fabrication of CPhCs.

2.2. Preparation of CDs

The low temperature (150 °C) solvothermal synthesis of organosilane-functionalized CDs with dual long chain functional groups of $-NH_2$ and $-Si(OCH_3)_3$ uses citric acid as the carbon

source and AEAPMS as the solvent, which has been detailed in our previous study [9]. The as-prepared CDs possess abundant amine groups on surface and show excellent sensitivity and selectivity to Hg(II) [9].

2.3. Synthesis and fabrication of CPhCs

The size selection of polystyrene spheres (PS) was based on the excitation and emission peak of CDs using Bragg’s diffraction calculation [26].

$$\lambda_{\max} = 2d_{(111)} \sqrt{n_{\text{eff}}^2 - \sin^2 \theta} = 2 \sqrt{\frac{2}{3}} \cdot D \cdot \sqrt{n_{\text{eff}}^2 - \sin^2 \theta} \quad (1)$$

Where λ_{\max} indicates the wavelength value of the reflection peak, $d_{(111)}$ the distance between adjacent (111) lattice planes, D the sphere diameter and n_{eff} is the effective refractive index of the structure. Therefore, Acrylic acid functionalised PS spheres with the two different diameter sizes of 185 ± 5 nm (E) and 230 ± 5 nm (F) with carboxyl group on the surface were synthesized by an emulsifier free emulsion polymerisation method and purified by several cycles of centrifugation as per earlier reports [27].

To experimentally investigate the difference between introducing the CDs on the F spheres, two approaches were used in this study. 1) *Superficial coating*: F polystyrene suspension and MilliQ water (5:5 vol%) were first purified by several cycles of centrifugation. F spheres were functionalized with acrylic acid to endow abundant amount of $-COOH$ functional groups on the surface of polystyrene spheres, which could have strong electrostatic attraction with the $-NH_2$ groups on CDs. Then, 2 mL of washed 230 nm F suspension was mixed with 2 mL of CDs (10^{-3} mol L $^{-1}$) for 24 h. Finally, CDs coated on surface of F spheres were washed and purified by several cycles of centrifugation to remove excess CDs. This sample donated as CDs-F spheres. 2) *Under-the-skin coating*: CDs immobilised on F spheres (CDs@F) were obtained by a diffusion and entrapment method [28]. In detail, 2 mL of CDs (10^{-3} mol L $^{-1}$) dissolved in DMF was added drop-wise to 2 mL aqueous suspension of F spheres (5 vol%). After a period of mixing ranging from 2 min up to 15 min, the CDs coated F spheres were washed and purified by several cycles of centrifugation.

To investigate the fluorescence enhancement, three films were fabricated on the glass substrate by horizontal deposition method [18]: 1) Monolithic CDs@F film was fabricated by self-assembly of CDs@F spheres. 2) Heterostructure of E-(CDs@F) film was fabricated by horizontal deposition of CDs@F spheres on top of the monolithic E layer. 3) Double heterostructure E-(CDs@F)-E was fabricated by sequential horizontal deposition method [19]. The glass substrates were first treated with a Piranha solution to ensure super hydrophilic surfaces.

To illustrate the difference in selecting the reference point for FL enhancement factor calculation, we have prepared a control sample. F spheres were self-assembled by horizontal method on the glass then heated at 120 °C for 2 h to melt and form an amorphous film. 2 mL of CDs (10^{-3} mol L $^{-1}$) was then infiltrated into the amorphous film. This reference sample is referred to as a control film. In this study, we fabricated monolithic, heterostructure and double heterostructure films with same thickness of 6 μm .

2.4. Stability test on CDs coating

The four step solvent treatments were designed for stability test as follow: 1) CDs@F and CDs-F were separately mixed in DI water by ultrasonication for 5 mins. Centrifugation was then applied to separate the spheres and the solution, and the supernatant solution was collected for FL analysis. 2) CDs@F and CDs-F were separately mixed in 98% ethanol by ultrasonication for 5 mins. Centrifuga-

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