

# Highly sensitive detection and removal of mercury ion using a multimodal nanosensor

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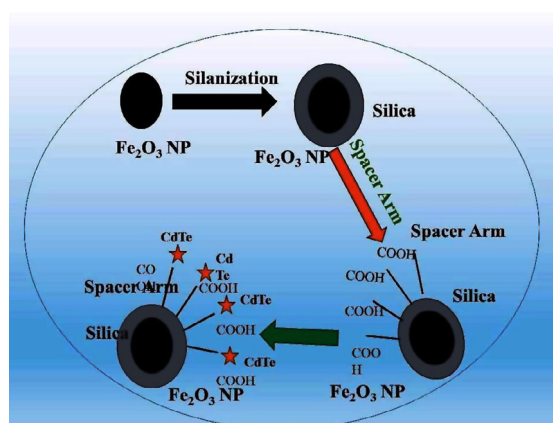
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## HIGHLIGHTS

- A highly sensitive and novel multimodal nanosensor encompassing magnetic and fluorescent functionality is designed.
- The design of the multimodal nanosensor employed for the simultaneous detection and removal of mercury ion.
- Significant fluorescence quenching is observed with surprisingly low limit of detection.
- A novel facile route towards field based mercury sensor development.

## GRAPHICAL ABSTRACT



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## ABSTRACT

A highly sensitive and environment friendly multimodal nanosensor encompassing magnetic and fluorescent functionality is designed for the simultaneous detection and removal of mercury ion in water. A significant fluorescence quenching is observed with the increasing concentration of  $Hg^{2+}$  with surprisingly low limit of detection. The detected analyte is successfully removed with the help of a bar magnet leaving no residual secondary pollution. The details mechanism of sensing is also investigated. The simple and elegant nanochemistry reported here provides a facile route towards field based mercury sensor development in future.

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## 1. Introduction

Recently, the sensitive and selective detection of mercuric ions ( $Hg^{2+}$ ) has attracted considerable attention because of its deleterious effects on the environment and human health [1]. Mercury is a

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highly toxic heavy metal and its exposure can cause serious damage to the brain, kidneys, and nervous system [2–6]. The United States Environmental Protection Agency (EPA) has set a maximum  $Hg^{2+}$  contaminant level in drinking water at  $0.002 \text{ mg L}^{-1}$  ( $10.0 \text{ nM L}^{-1}$ ) [7]. Commonly, mercury contamination comes from a variety of sources, both natural (e.g., volcanic activity) and industrial (e.g., mining, fossil fuels) [8,9]. Ionic mercury is easily converted into the neurotoxic monomethyl mercuric cation which then builds up in aquatic system and enters the food chain [10].

It is thus very important to monitor its level in water and develop a simple yet environmentally friendly sensor with high selectivity and sensitivity.

In the past few years, several optical sensor systems have been developed for the detection of  $\text{Hg}^{2+}$  in the aqueous environment [11]. This includes small organic molecules (fluorophores or chromophores), biomolecules (proteins, antibodies, oligonucleotides, DNAs, etc.), polymer [12], inorganic materials and the nanoparticles [13–18]. Yan and co-workers reported 4-4'-bis-(carboxyl phenyl)-dibenzo-18-crown-6 dye and its application for colorimetric detection of  $\text{Hg}^{2+}$  [19]. Song et al. have reported a “Turn-off” fluorescent sensor incorporating benzothiadiazole moiety for the  $\text{Hg}^{2+}$  detection [20]. Li and co-workers have synthesized a naphthalimide derivative based fluorescent “Turn-on” chemosensor for aqueous phase detection of  $\text{Hg}^{2+}$  [21]. Milan Balaz and co-workers developed a Pyridylporphyrin–DNA conjugates for  $\text{Hg}^{2+}$  recognition [22]. Recently, we have designed a fluorescent resonance energy transfer (FRET) based chemosensor which was highly selective to a variety of analytes [23]. Several reports based on fluorescent semiconducting nanomaterial, CdTe quantum dots (CdTe-QDs), have been reported for the  $\text{Hg}^{2+}$  detection due to their unique optical, electronic properties [23–26]. Paramanik et al. has developed a single probe of Au–NC–CdTe QD nanocomposite by using tripeptide-capped CdTe quantum dots (QDs) and BSA-conjugated Au25 nanocluster (NC) [27]. The conjugation was formed through an H-bonding interaction between tripeptidylglutathione (GSH) and BSA protein-capped NC. The limit of detection of  $\text{Hg}^{2+}$  is detected to be 7 nM by using photoluminescence quenching. Although many of these systems, are capable of detecting  $\text{Hg}^{2+}$  with high sensitivity, they are constrained with respect to simplicity, sensitivity and selectivity, or limited in practical applications (e.g. incompatible with aqueous environment) [28–30].

Furthermore, these chemosensors are inconvenient for the removal of the target species which would cause secondary pollution. Towards this end, the incorporation of a fluorescent and magnetic functionality in a single nanocomposite particle would be a promising alternative [31]. Previously, magnetic nanoparticles have widely been used in many fields such as drug delivery, protein resistant, bio-separation and magnetic resonance imaging for their attractive properties of superparamagnetism and the size tenability [32–34]. It can be attracted to the target zone in the presence of an external magnet or an implanted permanent magnet. However, the strong photoluminescence quenching of fluorescent moiety in the presence of magnetic nanoparticles possesses a serious challenge to develop this kind of nanocomposite. To address this issue, various molecular interactions, such as electrostatic and hydrophobic interactions, covalent linkage and hydrogen bonding such as quantum dots (QDs) deposited onto the surface of polymer-coated  $\text{Fe}_2\text{O}_3$  beads through thiol chemistry, gold nanoparticles immobilized on the surface of various materials including  $\text{Fe}_2\text{O}_3$  nanoparticles, silica microspheres via electrostatic interactions have been developed [35,36]. In this paper, we have used a nano-chemistry to synthesize a multilevel, hierarchically built nanoparticle, which we define as a multimodal nanosensor, for efficient detection and removal of  $\text{Hg}^{2+}$  ion in aqueous media. This nanosensor produced by multistep synthesis process, consists of a thin silica shell encapsulating magnetic ( $\text{Fe}_2\text{O}_3$ ) nanoparticles, a fixed spacer arm and fluorescent quantum dot for simultaneous detection and removal of detected mercury. The surface of this prototype nanosensor is functionalized with a (triethoxysilyl propyl-carbamoyl) butyric acid to make it negatively charged. The cysteamine capped positively charged cadmium telluride (CdTe) QD is electrostatically adsorbed on the surface. Previously, various chemical syntheses were adopted to develop fluorescently coated magnetic beads for biomedical applications like MRI contrast agent and multiphoton imaging. However, to the best of our knowledge, the synthetic route developed here to synthesize multimodal

nanoparticles and also their use as aqueous mercury sensor has not been reported in the literatures before. These nanosensor are capable of detecting  $\text{Hg}^{2+}$  in nano-molar level with limit of detection (LOD) of 1 nM. The detected analyte was also removed with the use of an external bar magnet leaving no residual pollution.

## 2. Experimental section

### 2.1. Synthesis of multimodal nanosensor

A multistep process was involved for the fabrication of multimodal nanosensor. Fig. 1 represents the schematic diagram of synthetic protocol. The superparamagnetic  $\text{Fe}_2\text{O}_3$  nanoparticles were prepared by the chemical coprecipitation method. Initially, the pristine  $\text{Fe}_2\text{O}_3$  NPs tend to aggregate into large clusters, and thus lose the special magnetic properties associated with single domain. Citric acid was employed as a surfactant to create an electrostatic double layer, thereby, reducing their tendency to aggregate. Coating  $\text{Fe}_2\text{O}_3$  nanoparticles with silica was carried out at room temperature by a modified Stöber method through a sol-gel approach involving the hydrolysis and condensation of tetraethyl orthosilicate (TEOS). The surface of the colloidal  $\text{Fe}_2\text{O}_3$  NPs has a strong affinity to silica, thus silica can be directly deposited on the  $\text{Fe}_2\text{O}_3$  NPs without other pretreatment. 3-(Triethoxysilylpropyl-carbamoyl) butyric acid (spacer arm) was prepared by incubating 3-(triethoxysilyl) propylamine (4.5 mmol) with 4.5 mmol of succinic anhydride in 1 mL of anhydrous DMF. The resulting product was dispersed in DMF containing 10 mg of particles. After the solution was stirred for 24 h at room temperature, the particles were repeatedly washed with DMF and dried. The COOH-coated nanoparticles (2 mg) were dispersed in 1 mL of  $\text{H}_2\text{O}$  using sonication. Finally, the multimodal nanosensor were electrostatically attached with the cysteamine capped CdTe QDs.

### 2.2. Synthesis of cysteamine capped CdTe QD

Colloidal solution of CdTe QD was synthesized using the reaction between  $\text{CdCl}_2$  and NaHTe solutions with some modification. At first, NaHTe was prepared by adding 0.53 mmol of  $\text{NaBH}_4$  (Merck) and 0.18 mmolTe powder (Aldrich) in a round-bottom flask, containing 2 mL of Milli-Q water in inert atmosphere. On the other hand 0.50 mmol  $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$  (Aldrich) and 1 mmol of cysteamine (Aldrich) were dissolved in 70 mL of Milli-Q water. The pH of the cysteamine solution was maintained to 5.5 by adding required amount of HCl. The mixture was bubbled by  $\text{N}_2$  for 45 min to make  $\text{O}_2$  free. Then 0.06 mmol NaHTe was immediately injected into the mixture under vigorous stirring for 30 min followed by refluxing at 110 °C in aerial atmosphere. A solution of different size was taken out from the reaction mixture with the growth time of 15, 30, and 50 min. These nanocrystals are stable for more than three months when stored at 10 °C.

### 2.3. Characterizations

Room temperature optical absorption spectra were taken using a UV-Vis spectrophotometer (Shimadzu). Room temperature photoluminescence spectra were taken by a Fluoromax-P (Horiba JOBIN YVON) photoluminescence spectrophotometer. For the time correlated singlephoton counting (TCSPC) measurements, the samples were excited at 440 nm using a nanosecond diode laser (IBH Nanoled) in an IBH Fluorocube apparatus. The typical full width at half-maximum (FWHM) of the system response using a liquid scatter was about 40 ps. The repetition rate was 1 MHz. The fluorescence decays were analyzed using IBH DAS6 software. The transmission electron microscopy (TEM) image was taken by using a JEOL-JEM-2100F transmission electron microscope.

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