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Label-Free Cysteamine-Capped Silver Nanoparticle-Based Colorimetric Assay for Hg(II) Detection in Water with Subnanomolar Exactitude

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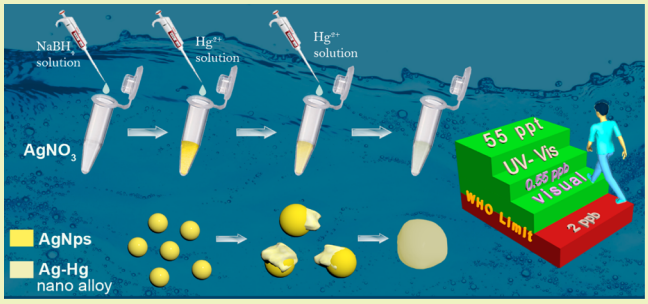
Supporting Information

ABSTRACT: Precisely probing heavy metal pollutants in water warrants novel methods and materials. To this end, functionalization of nanoparticles using biologically important substances through a green route is a novel aspect in the design of an optical sensor. In this article we report a green preparative strategy for the synthesis of cysteamine stabilized silver nanoparticles (Ag-Nps) in aqueous medium. The water-soluble Ag-Nps are found to be highly sensitive and selective for rapid colorimetric detection of Hg(II) ion with a limit of detection (LOD) of 0.273 nM (55 ppt). This system also enables us to detect Hg(II) through the naked eye with an LOD of 2.73 nM (0.55 ppb) which is below the World Health Organization (WHO) permissible limit (10 nM or 2 ppb). Cysteamine undergoes cooperative coordination with the mercury ion leading to spontaneous formation of a mercury−cysteamine complex and consequently forms Ag−Hg nanoalloy, which in turn changes the surface plasmon property of Ag-Nps to allow detection of Hg(II) ion with subnanomolar precision. Furthermore, Ag-Nps were tested for detection of Hg(II) in different real water samples with satisfying recoveries over 96−102%.



KEYWORDS: *Silver nanoparticles, Mercury sensing, Cysteamine, Subnanomolar, Nanoalloy*

INTRODUCTION

Heavy metal ion contamination poses a severe threat to human civilization and the environment. Mercury has been well-known as an environmental pollutant for several decades.[1] This bioaccumulative species, considered to be a highly toxic heavy metal element, is distributed in every aspect of environment and biota.[2−5] Mercury is highly toxic in all its oxidation states, notwithstanding differences in solubility and possible redox interconversion.[6−9] Among them Hg(II) is one of the most common and stable forms of mercury pollutant. Because of its solubility in water, it provides a pathway for contaminating a large amount of water. Once introduced into the aquatic ecosystem, bacteria convert inorganic mercury into neurotoxic methylmercury, which enters the food chain and accumulates in higher organisms, especially in large edible fish, resulting in prenatal brain damage, various cognitive and motion disorders, and the most deadly minamata disease.[10−13] Therefore, monitoring the levels of potentially toxic metal Hg^{2+} in aquatic ecosystems becomes important.

Escalating consciousness of the lethal effect of Hg(II) has sparked interest in many researchers in building up tools for detecting Hg(II) in the environment.[2−4] To date, a variety of methods[14−37] are reported in the literature for the detection of Hg(II). Although these methods provide satisfactory limits of detection (LOD), they are sophisticated, time-consuming, high-cost operations that require complicated, nonportable equipment and are, consequently, not suitable for field monitoring. Thus, development of a simple, rapid, highly sensitive, cost-effective method for selective detection of Hg(II) is still a major pursuit.

In the last few decades, noble metal nanoparticles like gold and silver have attracted great attention because of their distinctive property of surface plasmon resonance (SPR).[38] Unlike dyes, silver nanoparticles are quite photostable and do not undergo rapid photobleaching, allowing these nanoparticles to be utilized as optical probes for ultrasensitive Hg^{2+} detection through the formation of amalgams.[39] However, existing methods for Hg(II) sensing require a rather complicated procedure for the synthesis of silver nanoparticles. A more facile and economic method for sensing Hg^{2+} is, therefore, desirable.

Cysteamine is an aminothiol compound used as an inexpensive drug for the treatment of cystinosis[40,41] and found significant therapeutic effects in recent years. In this article, we report a green, straightforward synthesis of cysteamine stabilized silver nanoparticles in aqueous medium and its application toward a colorimetric assay for Hg^{2+} ion with a detection limit

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down to 55 ppt (275 pM). This system also enables us to detect Hg(II) through naked eye with a LOD of 2.73 nM (0.55 ppb) which is below the WHO permissible limit (10 nM or 2 ppb). To the best of our knowledge, cysteamine-capped Ag-Nps has not been studied yet for colorimetric detection of Hg(II) ion in aqueous medium.

In this simple analytical method, an aqueous solution of Hg^{2+} was added to an aqueous dispersion of silver nanoparticles leading to a change in the surface property of Ag-Nps and consequently the color of the solution changes from yellow to colorless.

MATERIALS AND METHODS

Instruments. All the UV−vis measurements were carried in Cary100-Bio spectrophotometer. For the calibration plot, optical density (OD) was measured at 402 nm (λ_{max} value of yellow color Ag-Nps). Transmission electron microscopy (TEM) analysis and Energy-dispersive X-ray spectroscopy (EDX) mapping were carried in JEOL JEM-2100F and Oxford Extreme-Inca respectively.

Materials. Silver nitrate ($AgNO_3$) and sodium borohydride ($NaBH_4$) were obtained from Avra Synthesis Private Limited. Cysteamine hydrochloride ($SH-CH_2-CH_2-NH_2 \cdot HCl$) was obtained from SigmaAldrich and used without further purification. Milli-Q water was used for all the experiments. Silver nanoparticles (Ag-Nps) were synthesized by a procedure discussed below.

Synthesis of Cysteamine Stabilized Silver Nanoparticles (Ag-Nps). A 30 mL portion of 0.2 mM sodium borohydride ($NaBH_4$) was taken in an Erlenmeyer flask fitted with a magnetic stir bar and placed in an ice bath with constant stirring for 20 min. In an another flask, 20 mL of 0.1 mM $AgNO_3$ solution was placed in an ice bath and 3 mL of 0.3% of cysteamine hydrochloride was mixed with it. Then cold $NaBH_4$ solution was added to it dropwise at very slow rate until the solution became vivid yellow. The flask containing yellow Ag-Nps was removed from the ice bath and was allowed to come at room temperature with constant stirring. The solution was centrifuged, washed several times with MQ-water and redispersed in MQ-water.

Characterization of Cysteamine Stabilized Silver Nanoparticles (Ag-Nps). The synthesized silver nanoparticles were characterized by UV−vis spectroscopy, TEM, and EDX analysis. The TEM images of colloidal Ag-Nps is displayed in Figure 1b; it reveals that the particles are multifaceted and spherical in nature with an average size of about 20 nm with a dynamic range of 14−26 nm (Figure 1c).

RESULTS AND DISCUSSION

UV−vis Spectroscopy. The colloidal Ag-Nps in water showed a surface plasmon resonance (SPR) band with maximum absorption at the wavelength of 402 nm and thus exhibited a vivid yellow color (Figure 1a).

Sensing Detection of Hg^{2+}. The sensitivity of functionalized Ag-Nps toward Hg^{2+} ions in aqueous medium was investigated. The Ag-Nps solution was diluted to an extent (4 nM) which resulted in a recognizable change in color by naked-eye, upon minimum addition of Hg(II). This assay provides us a detection limit of 0.55 ppb as shown in Figure 2. This LOD is well below the permissible limit (2 ppb) in drinking water declared by the World Health Organization (WHO), rendering it suitable for analysis of real life samples.

Use of UV−vis spectroscopy further improved the sensitivity. As expected, functionalized Ag-Nps provided a good linear calibration range over 55−2700 ppt (Figure 2b).

Selective Detection of Hg^{2+}. The second essential feature of a chemical sensor is its selectivity for the target in mixtures that are present in natural environments and field measurements. We therefore proceeded to determine the selectivity of Hg^{2+} in the presence of thousand folds of other metal ions including Na^+, K^+, Ca^{2+}, Mg^{2+}, Al^{3+}, Cr^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Pb^{2+}, Ba^{2+},

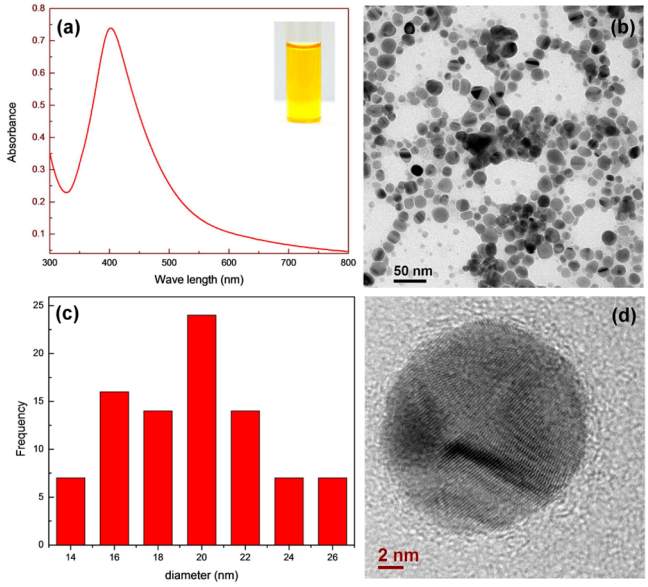

Figure 1. (a) UV−vis plot of Ag-Nps. (inset) Digital image of Ag-Nps aqueous solution. (b) TEM image. (c) Size distribution plot. (d) High resolution TEM image of Ag-Nps.

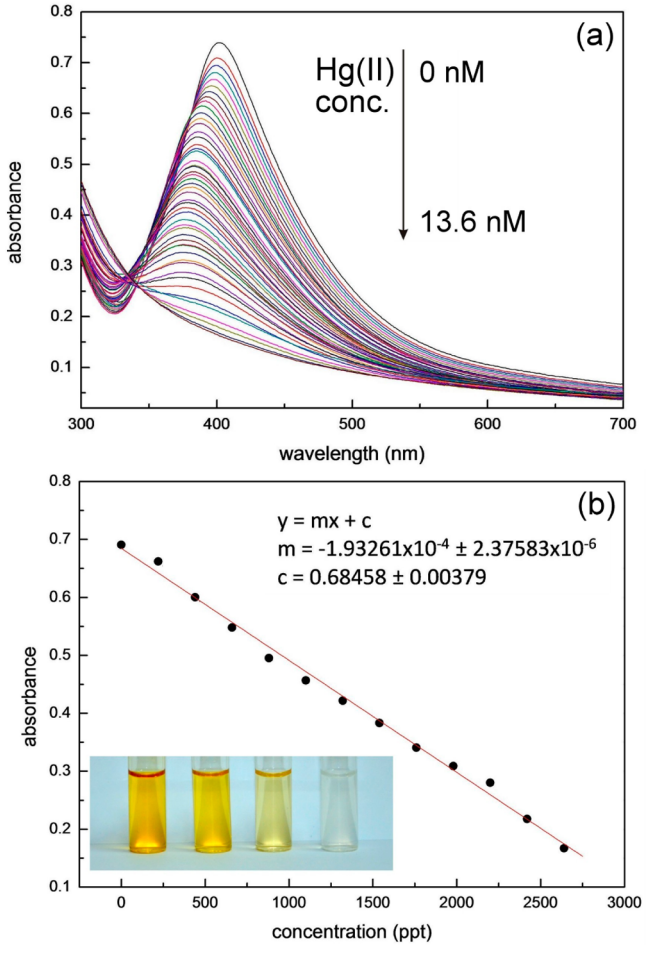

Figure 2. (a) UV−vis absorption spectra of Ag-Nps after the addition of different concentration of Hg^{2+}(0−13.6 nM). (b) Linear calibration plot of concentration of Hg^{2+} vs optical density (OD) at 402 nm. (inset) Photos for different concentration of Hg^{2+}; from left: 0, 550, 1500, and 2700 ppt.

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Cd^{2+}, Bi^{3+}, Sr^{2+} (50 mM), and mixed metal ions (Pb^{2+}, Mn^{2+}, Cu^{2+}; with and without Hg^{2+}). To check the versatility of the sensing system, we perform the selective detection test with the metals those are chemically more similar to Hg^{2+}, such as Au^{3+}, As^{5+}, and As^{3+}. Comfortingly, a satisfactory experimental outcome which is similar to that of other metal ions was observed. The above-mentioned metal ions do not influence the absorbance of silver nanocolloidal system, indicating that the sensor displayed excellent selectivity toward Hg^{2+} ion. The relative absorbance plot and the digital photograph (inset in Figure 3), shown below, corroborate this fact.

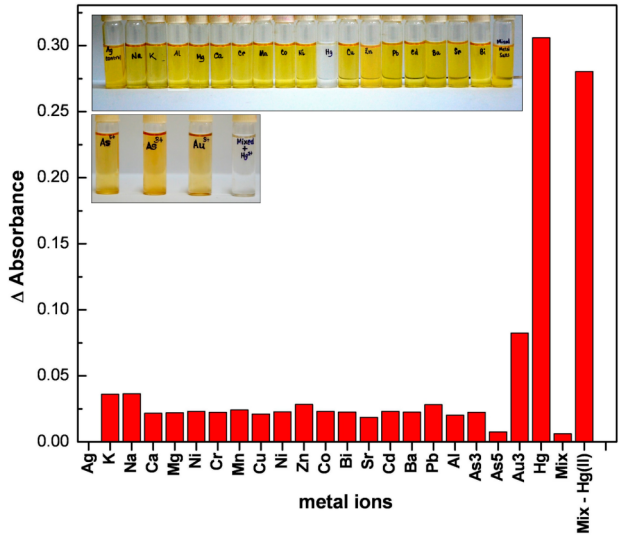

Figure 3. Change in absorbance of the Ag-Nps solution in the presence of 11 μM Hg^{2+} and 1000 fold other metal ions (50 mM). (inset) Digital photograph of the colorimetric response of the same.

Comparison of Other Methods for the Detection of Hg^{2+} with Our Proposed Method. Our sensing system provides ultrasensitivity in terms of naked eye detection and so also UV−vis spectroscopy. Many methods have been developed in last decades where mostly complex and sophisticated techniques[18−37] have been utilized to detect Hg(II) ion from nanomolar to subnanomolar level. Our simple, green, and economically viable technique gives the detection limit of 275 picomolar (55 ppt) which is mostly superior[14−22,26−28] or at par[23−25] to those methods (Table S3, Supporting Information).

Transmission Electron Microscopy (TEM). Direct evidence for Hg^{2+} stimulated diffusion followed by aggregation of the Ag-Nps could be further supported by TEM analysis. The TEM images after addition of 6.8 nM (1.36 ppb; Figure 4b) and 13.5 nM (2.7 ppb; Figure 4c) Hg^{2+} to the solution of Ag-Nps clearly show the intriguing changes (Figure 4). In addition, the EDX of selected zone during TEM analysis confirms the gradual formation of Ag−Hg nanoalloy (Figure 4d−f).

In order to study the surface elemental composition and atomic distribution throughout the Ag−Hg nanoalloy, a detailed chemical analysis was carried out using EDX mapping. The Ag and Hg signals after addition of 6.8 and 13.5 nM of Hg^{2+} are represented by Figure 5a−d and e−h, respectively.

EDX mapping also indicated that the elements Ag and Hg were uniformly distributed from the inner core to the periphery, thus facilitating formation of nonuniform Ag−Hg nanoalloy.

Effect of pH. In order to test the sensitivity and also the linearity of our sensing system in different pH, we performed the detection of mercury through our sensing system at different pH. A pH range of 6.0−8.0 appears to provide protection for the life of freshwater fish and bottom dwelling invertebrates. In this context, the effect of pH on the linearity and sensitivity of our probe was studied at different pH values, ranging from 3.2 to 8.0 as shown in Figure 6. The UV-absorption values were not affected by the solution pH value over the pH range of 3.2−8.0. The Hg(II) sensitivity shows excellent linear calibration over the range 55−2700 ppt in different pH values ranging from 3.2 to 8.0.

Proposed Mechanism for the Sensing Assay. On treatment with Hg(II), thiophillic Hg^{2+} would lead to partial exchange of cysteamine ligand[42] from silver to mercury leaving patches of exposed surface of silver. Then a redox reaction involving Ag^0 and Hg^{2+} would lead to the formation of Ag−Hg nanoalloy (eq 1).[43,44] This in turn changes the surface plasmon property of Ag-Nps and consequently color of the solution changes. This is the basis of this assay for Hg^{2+} ion in water (Scheme 1).

$$Ag_n + Hg^{2+} \rightleftharpoons Ag_{n-2}Hg + 2Ag^+ \quad (1)$$

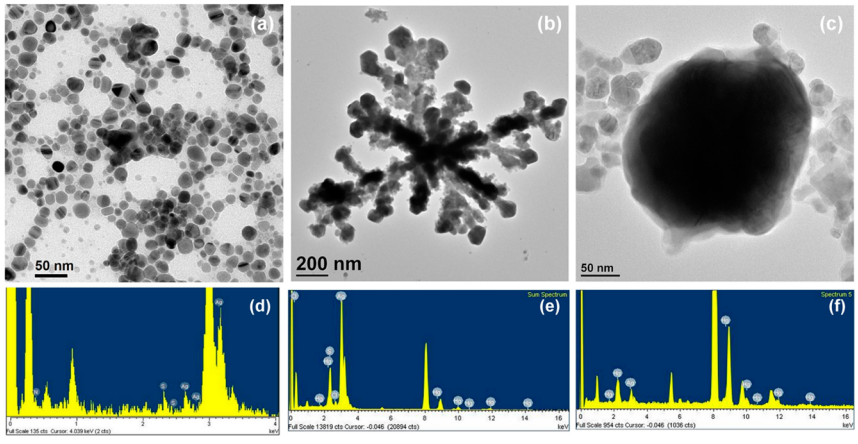

Figure 4. TEM images and EDX analysis of Ag-Nps in the presence of (a and d) 0, (b and e) 6.8, and (c and f) 13.5 nM Hg^{2+} ions.

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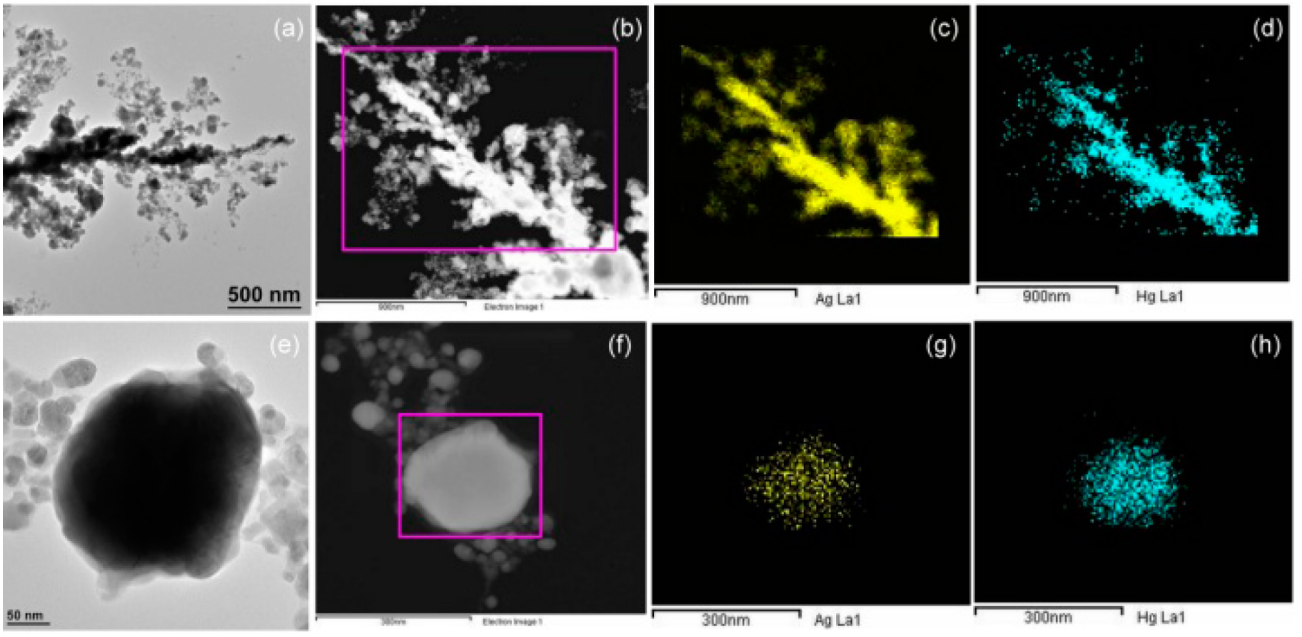

Figure 5. (a and e) TEM images of Ag-Nps. (b and f) Dark filled STEM images. Ag (yellow, c and g) and Hg (cyan, d and h) elemental maps of selected area in the presence of (a–d) 6.8 and (e–h) 13.5 nM Hg^{2+} ions, respectively.

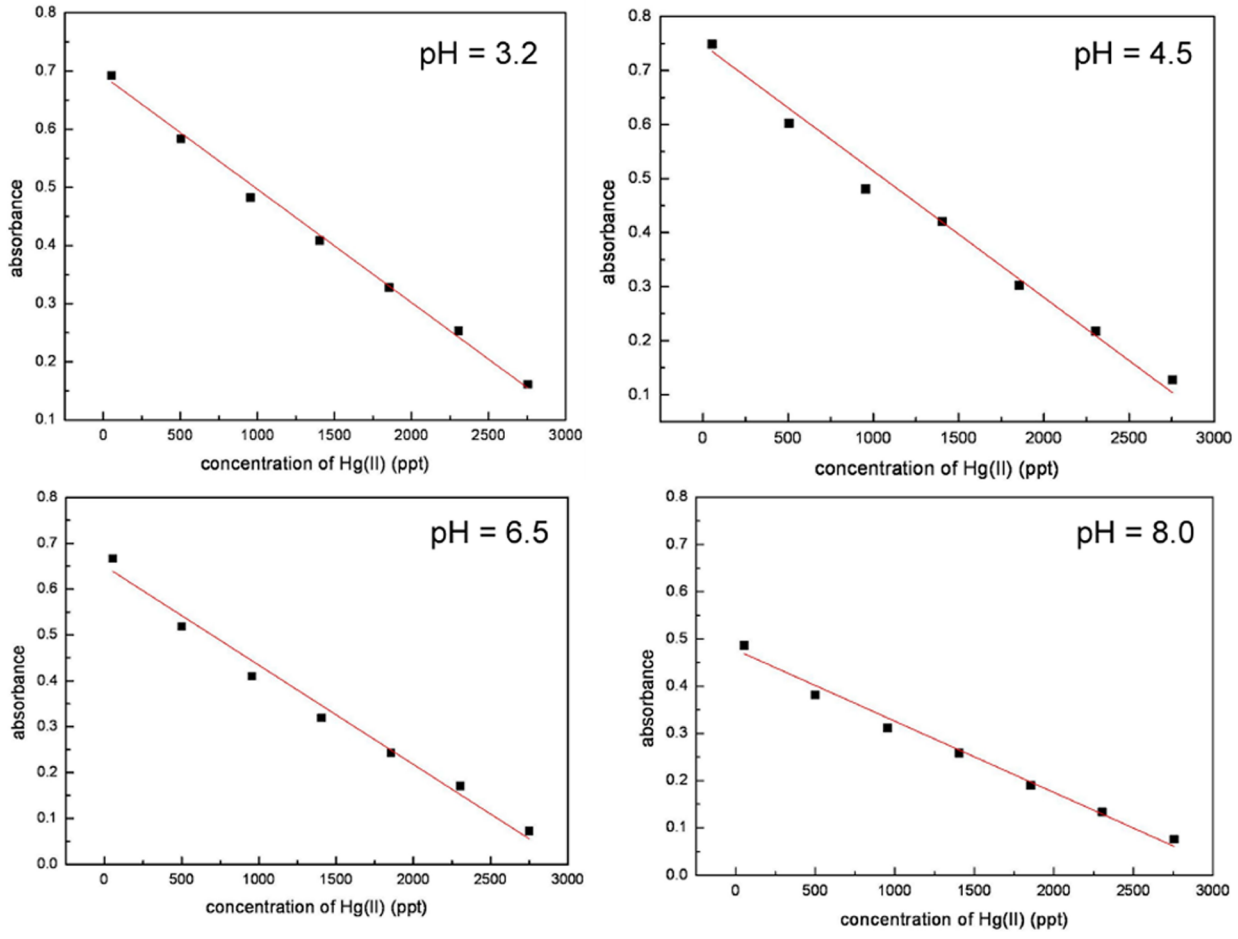

Figure 6. Linear calibration plot of concentration of Hg(II) vs Optical density (OD) at pH 3.2, 4.5, 6.5, and 8.0.

Practical Application: Analysis of Real Water Samples. To further ensure the potency of our sensing system, the sensor was tentatively applied to detect Hg^{2+} in real samples like lake water, tap water, and packaged drinking water, where the concentration of other metal ions or unknown contamination are significantly higher than that of Hg^{2+}. Therefore, practical assay is

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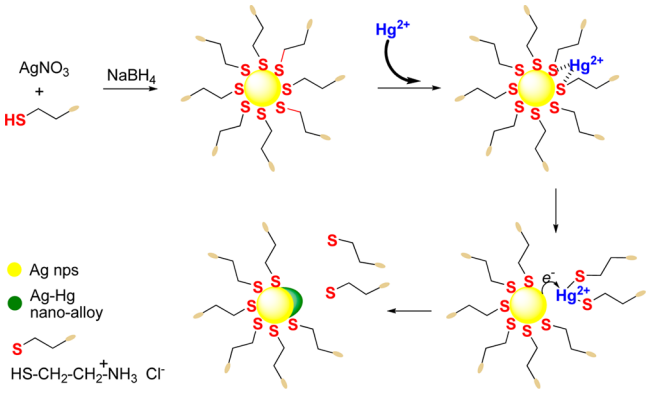
Scheme 1. Representation of Sensing Mechanism of Hg^{2+} Ions



an obligatory and decisive issue as well, for most of the common sensors. Tap water (obtained from our institute), packaged drinking water (from a commercial source, *Bisleri*), and a lake water sample (collected from Mahendra Sarovar on the campus of IACS) were filtered through Whatman-1 (90 mm) filter paper to remove the suspended particles.

Mercury contamination in these real water matrices was found to be undetectable. Therefore, a known concentration of mercury (5 nM) was spiked in the real water matrices, and the recovery of the system was detected to be within the range of 96−102% (Table S3, Supporting Information). This experimental outcome suggested that the cysteamine-capped silver nanoparticles based optical sensor has high prospective for the detection of Hg(II) in environmental samples.

CONCLUSION

In this article, we have demonstrated the design of a simple, cost-effective chemo-sensor based on label-free silver nanoparticles. The use of cysteamine-capped silver nanoparticles offers a convenient "mix-and-detect" approach for ultrasensitive and rapid detection of Hg(II) ion in aqueous medium. This Hg^{2+} sensor can provide a LOD of 55 ppt (275 pM) Hg^{2+} ion with excellent discrimination against other heavy metals. To the best of our knowledge, this is the most sensitive optical sensor for visual detection (LOD of 0.55 ppb) of Hg^{2+} in water. Low-cost, linear response over a wide range of concentrations, and high sensitivity are the prominent features of this sensor that promises to be a powerful optical method for the detection of Hg^{2+} in water.

ASSOCIATED CONTENT

Supporting Information

Experimental details of Hg^{2+} detection assay. This material is available free of charge via the Internet at http://pubs.acs.org/.

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Notes

The authors declare no competing financial interest.

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