# Silver quantum dots for selective detection of mercuric ions

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In this article, we demonstrate a highly sensitive and selective optical sensor for mercuric ions based on silver quantum dot (AgQD) dispersed in functionalized silicate sol–gel matrix in aqueous solution with a detection limit of 5 pM, which is highly sensitive compared to other reported methods. The present optical sensor is simple to prepare, and a cost-effective, and time-saving procedure without any external assemblies attached on the surface of AgQD. The AgQD sensor shows very high sensitivity and selectivity with simple instrumentation technique. We expect that the AgQD-based optical sensor is a promising candidate for the detection of environmentally toxic mercury in aqueous medium.

**Keywords:** Environmental toxicity, mercuric ion, optical sensor, silicate sol–gel, quantum dot.

MERCURIC ion ($Hg^{2+}$) is a highly toxic and widespread common environmental pollutant, causing damage to the brain, nervous system, endocrine system and the kidneys[1–3]. The sensitive and on-site detection of mercuric ions in aqueous medium is of importance in environment and food monitoring, as well as clinical analysis[4,5]. A variety of traditional quantitative detection approaches employ a number of analytical techniques for the detection of mercuric ions such as colorimetric[6], electrochemical[4,7], fluorescent[8–10] and other biosensor-based[11] analytical methods for sensing mercuric ions that have been developed in the past few years. Most of the methods require complicated instrumentation which involves cumbersome laboratory procedures. In some other methods, sophisticated instrumentation and low throughput also limit the scope of their practical applications. Among all sensor approaches, optical sensors that allow on-site and real-time quantitative detection without the use of any substantial or complicated spectroscopic instrumentation have received much attention owing to their potential as promising methods for the determination of the pollutant species in environmental analysis[12–15]. Optical sensors based on the absorption method for sensing mercuric ions have attracted attention due to their easy readout and potential for high throughput formats[1,16]. The development

of sensor materials for the detection of mercuric ions that offer high sensitivity, short response time, and selectivity is important for practical applications. Nanoscale metal particles are of current interest because they mark a material transition range between quantum and bulk properties[17]. Recently, an oligonucleotide-stabilized silver nanocluster as fluorescent probe for sensing 5 nM mercuric ion has been demonstrated[9].

Tuning the nanostructure size and shape is an easy method to enhance the sensitivity of the surface plasmon resonance (SPR) band to design effective sensing platforms. Silver nanoclusters are attractive candidates for making the smallest possible labels[18]. Although this offers considerable advantages over other methods in the area of sensing technologies, there is still a growing demand for nano-optical sensor for the detection and determination of environmentally important toxic species (such as mercuric ions) at a very low level of concentration with a rapid assessment process. In this respect, we report here the use of naked silver quantum dot (AgQD)-based optical sensor for highly sensitive and selective sensing of mercuric ions at picomolar concentrations in aqueous medium. To the best of our knowledge, there are no other reports of a AgQD-based optical sensor for mercuric ions at the picomolar concentration level in aqueous solution at room temperature without any external assemblies attached on the silver nanoclusters.

## Experimental section

### Materials and instrumentation

N-[3-(trimethoxysilyl)propyl]-ethylene diamine (EDAS) was from Aldrich. Mercuric chloride (Qualigens), calcium chloride, sodium chloride, zinc chloride, cadmium chloride, iron chloride, nickel chloride, lead chloride, sodium borohydride (Merck), silver nitrate, copper chloride and cobalt chloride (SRL) were used as received. All other chemicals, unless mentioned otherwise, used in the present work were of analytical grade. Doubly distilled water was used for all the experiments. All glass wares were thoroughly cleaned with aqua regia and rinsed extensively with double distilled water before use. Absorption spectra were recorded for AgQDs using an Agilent 8453 Diode Array Spectrophotometer. The surface morphology

of AgQDs was studied using a high-resolution transmission electron microscope (HRTEM; JEOL make; model JEOL 3010 operating at an accelerating voltage of 300 kV).

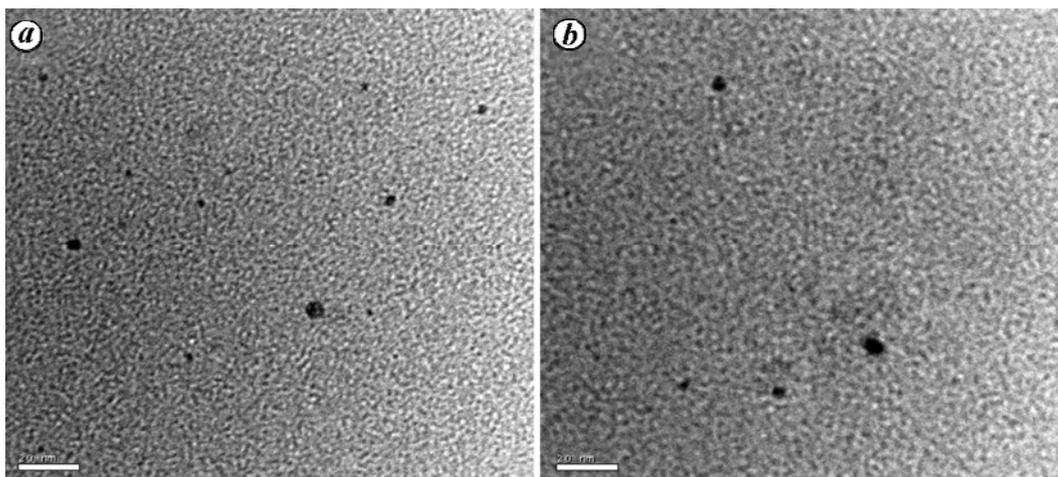*Preparation of silver quantum dot dispersed in silicate sol–gel*

The aqueous dispersion of AgQD was prepared by controlled reduction of $AgNO_3$ (0.01 mM) by adding desired amount of $NaBH_4$ (2 mM). The reaction mixture was stirred vigorously for 30 min and the solution was kept at room temperature for a day[19]. The homogeneous EDAS silicate sol–gel (SG) matrix was prepared by adopting the reported procedure[20] and the dispersion of AgQDs in the functionalized silicate SG matrix was prepared by mixing a known amount of functionalized silicate SG matrix and AgQD solution (SG : AgQD (Si : Ag = 1 : 1 molar ratio)) under vigorous stirring for 2 min. When AgQDs were dispersed in amine functionalized silicate SG solution, AgQDs were stable for three days. The resulting AgQDs dispersed in functionalized silicate SG matrix (SG–AgQDs) were used as optical sensing platform for highly sensitive and selective detection of mercuric ions.

**Results and discussion**

The HRTEM images of AgQDs and AgQDs dispersed in amine functionalized silicate SG were recorded and are shown in Figure 1. Figure 1 *a* shows the HRTEM image obtained for AgQDs. The average particle size was calculated as 2.7 nm from the HRTEM images. Figure 1 *b* shows the HRTEM image of AgQDs dispersed in amine functionalized silicate SG matrix. The HRTEM images recorded for naked silver nanoclusters and also dispersed in silicate SG showed that aggregation/agglomeration had not occurred. This demonstrates that the synthesis method allows the fabrication of well-controlled nanoclusters[19]. Importantly, the absence of larger silver nanoparticles was noted from the SPR band observed at 395 nm (blue, Figure 2 *a*). The absorption spectrum of colloidal silver exhibited a SPR band at 395 nm (blue, Figure 2 *a*). A majority of the reported procedures for silver cluster preparation use either capping agents or surfactants for the stabilization of clusters in solution and it is important to characterize the uncapped silver cluster solution prior to optical sensing. Pederson *et al.*[21] studied the optical properties of naked AgQDs during *in situ* deposition and observed the SPR band around 385 nm. In the present study, the as-prepared AgQDs act as an optical sensing probe for the quantitative determination of mercuric ions in aqueous medium at room temperature. The SPR absorption band of AgQD showed a small red shift with significant decrease in absorbance upon the addition of 50 pM mercuric ions (red, Figure 2 *a*). The SPR absorption band response was monitored during each addition of

50 pM mercuric ions to AgQDs. The SPR absorption intensity of AgQDs decreased at 395 nm with a 2–3 nm red-shift and with increasing mercuric ion concentration. The adsorption of mercuric ions onto the surface of the AgQDs causes the small red shift with a significant decrease in the SPR absorption band. The overall negative surface charge of silver particles obtained due to the adsorption of borohydride and borate onto the silver particles in a competitive manner provides a substantial electrostatic barrier to stabilize the silver clusters[22] and thus the cationic mercuric ions will get adsorbed on the surface of AgQDs due to electrostatic attraction. The mercuric ions can easily be adsorbed on the surface of the silver particles due to the electrostatic attractive force between the mercuric ion and the particle surface. The SPR absorption band position of silver particles is highly susceptible to the adsorption of nucleophile or electrophile onto the particle surface[23]. The electron density of silver clusters was altered by the transfer of electron from silver to metal ions, which brings about a decrease in the SPR absorption intensity with a small red shift[24,25]. The electron density changes at the surface of the silver particle are determined by the adsorption force between the surface of the silver particle and the adsorbate molecule or ion[25]. This suggests that the mercuric ions enter the stern layer and are adsorbed on the surface of AgQDs and cause a change in the surface properties. The difference in the SPR absorption intensity ($I_d$) of AgQDs in the absence and presence of each addition of mercuric ions is plotted against the corresponding mercuric ion concentration. The calibration plot shows a linear correlation in the mercuric ion concentration range 50–350 pM (Figure 2 *b*). The detection limit (DL) of the optical sensor was experimentally estimated as 50 pM and the sensitivity was calculated as 0.0003/pM. The AgQD-based optical sensing system shows higher sensitivity when compared to other systems[4,6–10]. To our knowledge, there are no other reports of a AgQD-based optical sensor and the lowest DL ever reported for mercuric ion sensing. The present sensor detects mercuric ions down to the permitted level of the European Union (5 nM)[26] and the maximum permitted level by the US Environmental Protection Agency (10 nM) in drinking water[9,27].

The selectivity of the AgQD-based sensing probe for mercuric ions was studied by testing the interference of other environmentally relevant metal ions such as $Pb^{2+}$, $Cd^{2+}$, $Cu^{2+}$, $Co^{2+}$, $Fe^{3+}$, $Ni^{2+}$, $Zn^{2+}$, $Na^+$ and $Ca^{2+}$ at a concentration of 50 nM. As shown in Figure 3 *a*, AgQD exhibited selectivity for mercuric ions (5 nM) over a variety of competing metal ions (50 nM). The SPR absorption intensity response of AgQD in the presence of 5 nM mercuric ions and other metal ions with a concentration ten times higher than that of mercuric ions was recorded (Figure 3 *a*). A significant change in the SPR absorption intensity or shift in the SPR band was not observed when 50 nM of other metal ions was added to

**Figure 1.** HRTEM images obtained for (*a*) silver quantum dots (AgQD) and (*b*) AgQD dispersed in amine functionalized silicate sol–gel.
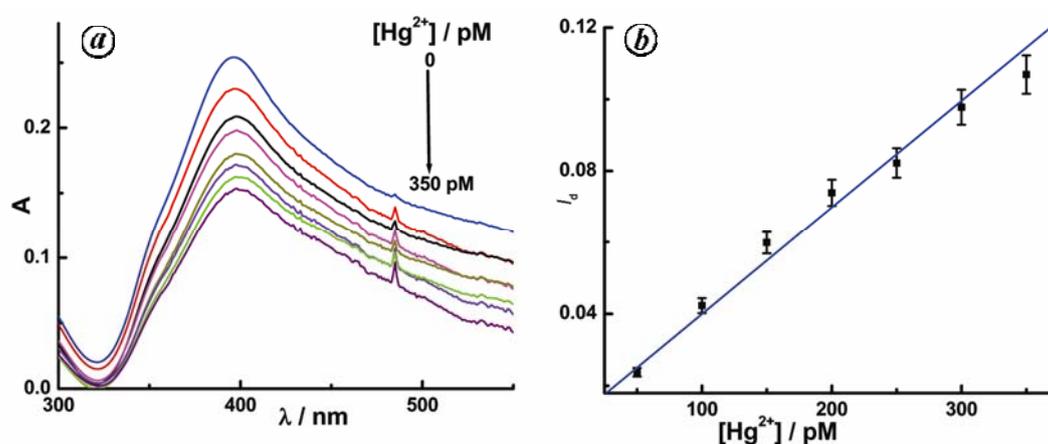


**Figure 2.** *a*, Absorption spectral changes observed for AgQDs upon the addition of mercuric ions of 0 (blue), 50 (red), 100 (black), 150 (magenta), 200 (dark yellow), 250 (violet), 300 (green) and 350 (purple) pM. *b*, Corresponding calibration plot. $I_d$ is the difference in surface plasmon resonance (SPR) absorbance of AgQD in the absence and presence of each addition of mercuric ions.

AgQDs whereas 5 nM mercuric ions showed a significant change in the SPR absorption intensity. The silver nanoparticles strongly donate electron density when the electrochemical potential of the added metal ion is more positive than silver, and the number of charges on the metal cation is not important[25]. The mercuric ion possesses more positive electrochemical potential than silver and can be easily adsorbed selectively on the surface of silver particles even at very low concentration. Figure 3 *b* shows the absorption spectra of each 5 nM addition of mercuric ions to the silver cluster solution in the presence of 50 nM of all other competing metal ions (such as $Pb^{2+}$, $Cd^{2+}$, $Cu^{2+}$, $Co^{2+}$, $Fe^{3+}$, $Ni^{2+}$, $Zn^{2+}$, $Na^+$ and $Ca^{2+}$). The SPR absorption intensity significantly decreased with a small blue shift upon each addition of 5 nM mercuric ions in the presence of 50 nM of other metal ions. The weak interaction of other metal cations with the surface of the silver particles will bring about a change in the refractive index of the silver particles[25,28]. The calibration plot obtained for mercuric ions in the presence of other metal ions shows a linear line in the mercuric ion concentration range 5–35 nM (Figure 3 *c*). The highly selective and sensitive mercuric ion sensing by AgQD without using any other reagent attached on the surface will find potential application in making sensitive sensing devices. To test the potential of our QD-based optical sensor for other metal ions in aqueous solution, the optical sensing of other metal ions such as $Pb^{2+}$, $Cd^{2+}$, $Cu^{2+}$, $Co^{2+}$, $Fe^{3+}$, $Ni^{2+}$, $Zn^{2+}$, $Na^+$ and $Ca^{2+}$ was tested by recording the absorption spectral changes of AgQD during each micromolar addition of each metal ion (Figure 4), and the sensitivities are summarized in Table 1. The interaction of metal cations with different electrochemical potentials influences the absorption spectra of AgQD. The AgQD sensing probe can detect other metal ions at higher concentration compared to mercuric ion since mercury is

slightly more electropositive than silver[25], which explains the strong interaction between the mercuric ions and silver particles. The present study shows that the mercuric ions can be detected selectively in the presence of other metal ions using AgQDs.
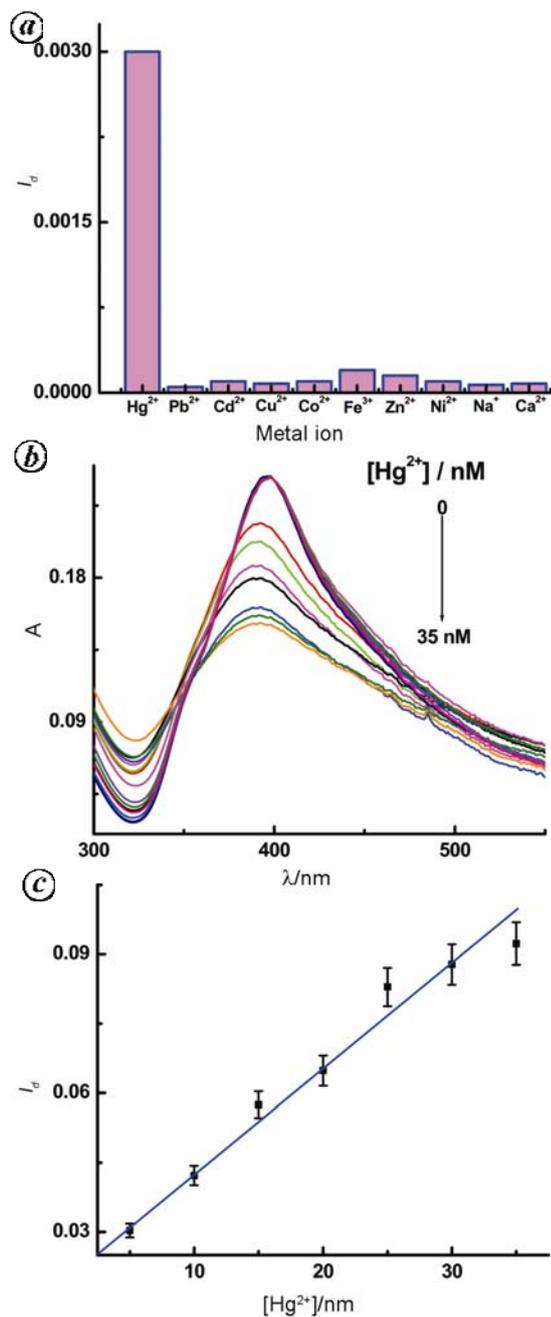


**Figure 3.** *a*, Graph showing the change in SPR absorbance of AgQDs at 395 nm in the presence and absence of various metal ions. Concentration of mercuric ions: 5 nM. Concentration of other metal ions: 50 nM ($Pb^{2+}$, $Cd^{2+}$, $Cu^{2+}$, $Co^{2+}$, $Fe^{3+}$, $Ni^{2+}$, $Zn^{2+}$, $Na^+$ and $Ca^{2+}$). *b*, Absorption spectral changes of AgQDs upon addition of mercuric ions of 0 (blue), 5 (red), 10 (green), 15 (magenta), 20 (black), 25 (violet), 30 (blue) and 35 (orange) nM in the presence of 50 nM concentration of all other metal ions. Addition of 50 nM of other metal ions did not show any observable change in the AgQD spectra. *c*, Corresponding calibration plot.
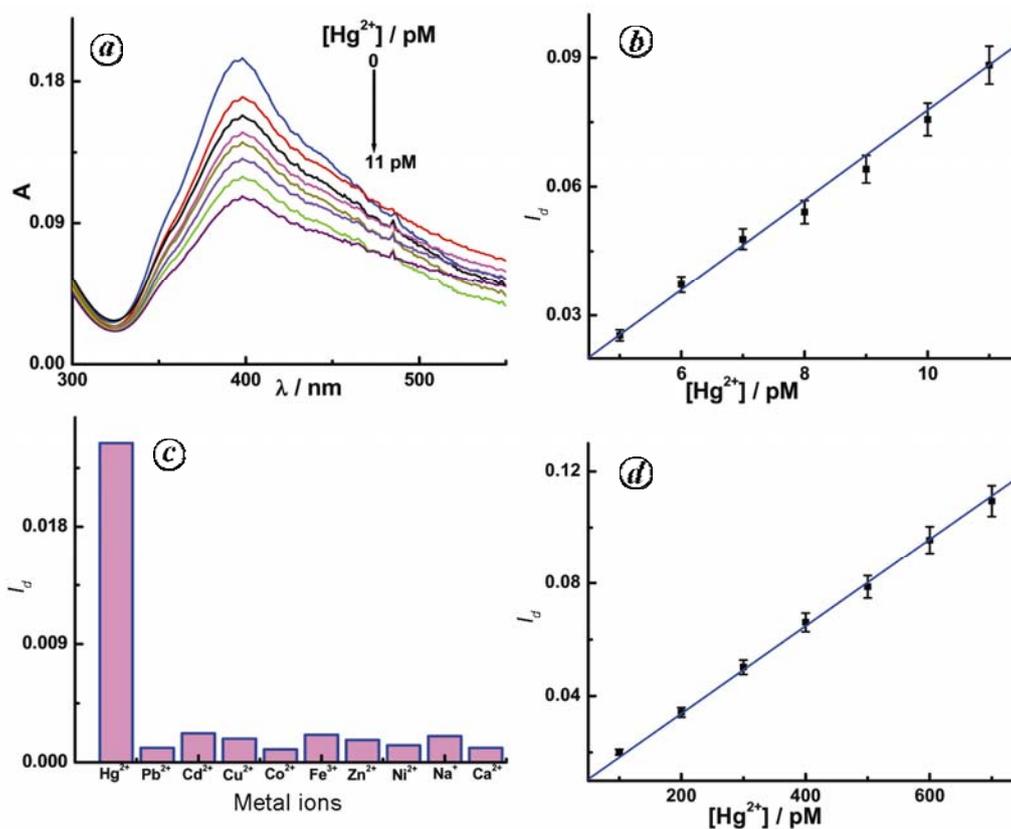
The absorption spectral changes observed for the AgQDs (average particle size was calculated as 2.5 nm) dispersed in amine functionalized silicate SG (SG–AgQDs) upon each addition of 5 pM mercuric ions are shown in Figure 5 *a*. The SPR absorption intensity of SG–AgQDs decreased with increasing mercuric ion concentration (red to purple, Figure 5 *a*). The SPR absorption intensity difference ($I_d$) of SG–AgQDs in the absence and presence of each addition of mercuric ions is plotted against the concentration of mercuric ions (Figure 5 *b*). A linear calibration plot was obtained in the mercuric ions concentration range 5–11 pM. The DL of SG–AgQDs-based optical sensor was experimentally estimated as 5 pM and the sensitivity was calculated as 0.0104/pM. The SG–AgQDs-based optical sensing system shows very high sensitivity compared to other systems[4,6–9]. The interaction between the mercuric ions and the amine functionalized silicate SG matrix embedded on the AgQDs would further improve the DL and selectivity when compared to the naked-AgQD due to the higher affinity of mercuric ions to the amine group[29]. The SG–AgQDs exhibited high selectivity for mercuric ions (100 pM) over a variety of competing metal ions (5 nM; Figure 5 *c*). The SPR absorption intensity of SG–AgQDs was significantly decreased upon the addition of 100 pM mercuric ions, whereas 5 nM of other metal ions ($Pb^{2+}$, $Cd^{2+}$, $Cu^{2+}$, $Co^{2+}$, $Fe^{3+}$, $Ni^{2+}$, $Zn^{2+}$, $Na^+$ and $Ca^{2+}$) did not show any significant change in SPR absorption intensity. With each addition of 100 pM mercuric ions, the SPR absorption intensity significantly decreased in the presence of 5 nM of all other competing metal ions (figure not shown). The calibration plot showed a linear line for selective sensing of mercuric ions in the concentration range 100–700 pM
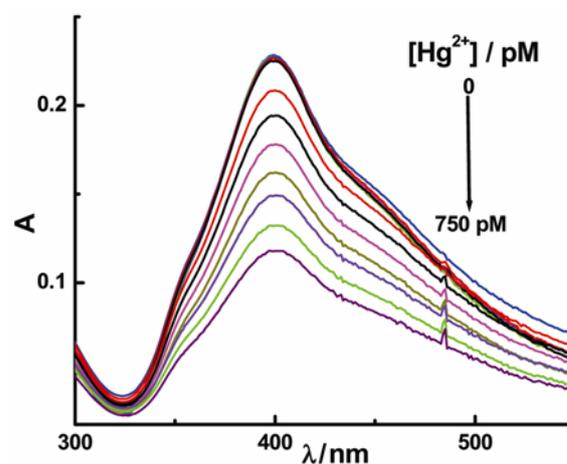


**Figure 4.** Absorption spectral changes of sol–gel (SG) matrix–AgQD upon addition of mercuric ions of 0 (blue), 100 (red), 200 (black), 300 (magenta), 400 (dark yellow), 500 (violet), 600 (green) and 700 (purple) pM in the presence of 5 nM concentration of all other metal ions ($Pb^{2+}$, $Cd^{2+}$, $Cu^{2+}$, $Co^{2+}$, $Fe^{3+}$, $Ni^{2+}$, $Zn^{2+}$, $Na^+$ and $Ca^{2+}$). The addition of 5 nM of other metal ions did not show any observable change in the AgQD spectra.

**Table 1.** Comparison of silver quantum dots based optical probe for sensing various metal ions

| Metal ion | $Hg^{2+}$ | $Pb^{2+}$ | $Cd^{2+}$ | $Cu^{2+}$ | $Co^{2+}$ | $Fe^{3+}$ | $Zn^{2+}$ | $Ni^{2+}$ | $Na^+$ | $Ca^{2+}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| Detection limit | 50 pM | 5 µM | 100 µM | 5 µM | 500 nM | 50 nM | 100 µM | 100 µM | 5 µM | 5 µM |
| Sensitivity | 0.0003/ pM | 0.0002/ µM | 0.0013/ µM | 0.0009/ µM | 0.0001/ nM | 0.0007/ nM | 0.0003/ µM | 0.0001/ µM | 0.0008/ µM | 0.0006/ µM |
| Linear range | 50 pM–3 µM | 5–30 µM | 100–700 µM | 5–30 µM | 0.5–3 µM | 50–350 nM | 100–700 µM | 100–600 µM | 5–35 µM | 5–35 µM |



**Figure 5.** *a*, Absorption spectral changes observed for AgQDs dispersed in functionalized silicate SG matrix upon the addition of mercuric ions of 0 (blue), 5 (red), 6 (black), 7 (magenta), 8 (dark yellow), 9 (violet), 10 (green) and 11 (purple) pM. *b*, Corresponding calibration plot. *c*, Graph showing the change in SPR absorbance of AgQDs at 395 nm in the presence and absence of mercuric ions during the addition of various metal ions. Concentration of mercuric ions: 100 pM. Concentration of other metal ions: 5 nM ($Pb^{2+}$, $Cd^{2+}$, $Cu^{2+}$, $Co^{2+}$, $Fe^{3+}$, $Ni^{2+}$, $Zn^{2+}$, $Na^+$ and $Ca^{2+}$). *d*, Calibration plot obtained from absorption spectral changes of AgQDs dispersed in functionalized silicate SG matrix upon each addition of 100 pM mercuric ion in the presence of 5 nM of other metal ions.

(Figure 5 *d*). The reproducibility of the AgQDs-based optical sensor for mercuric ions was studied in three different experiments. The sensing results were found to be reproducible within ± 10% difference in the $I_d$ values. The underlying concept of the present study for mercuric ion sensing is illustrated schematically (Scheme 1).

**Conclusion**

We have demonstrated a AgQD dispersed in functionalized silicate SG-based optical sensor for mercuric ions in aqueous solution at room temperature with a detection limit of 5 pM. Good sensitivity and selectivity were also observed with no interference of other metal ions. This
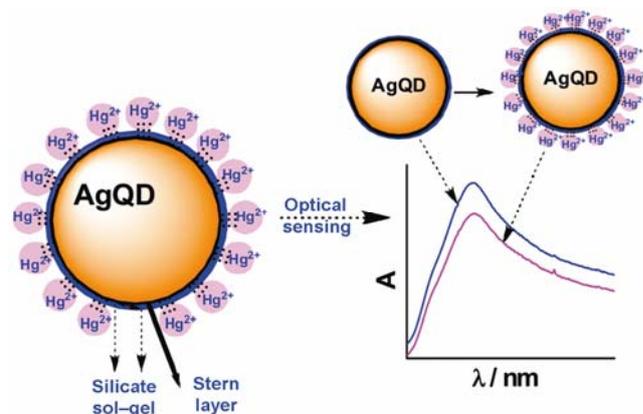


**Scheme 1.** Schematic representation of AgQDs-based optical sensor for mercuric ions.

method is free of light-sensitive dye molecules, lengthy protocols, surface-modified nanoparticles or sophisticated instrumentation and overcomes some of the limitations of the more conventional methods. Unlike most of the chemosensors for sensing mercuric ions in organic media or organic–aqueous mixtures owing to their low water-solubility, the aqueous dispersion of AgQDs allows this assay to be performed in aqueous media without the need for organic co-solvents or without introducing any assembly on the silver particles[6]. Importantly, this method can in principle be used to detect other metal ions at higher concentrations compared to mercuric ion concentration. The demonstrated AgQD-based sensor should pave the way for the introduction of nano- and quantum-structured materials for a broad range of applications in chemosensor technology.

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