Rapid Photoluminescence Quenching Based Detection of Cu\textsuperscript{2+} in Aqueous Medium by CdS Quantum Dots Surface Passivated by Thiourea

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Presented here is a simple yet rapid and efficient analytical method for visual as well as spectroscopic method for sensing of trace concentrations of Cu\textsuperscript{2+} ions in aqueous medium by systematic photoluminescence quenching of a highly water soluble probe made of CdS quantum dots surface modified by thiourea. The salient features of this work describe rapid detection (2 min equilibration time) of Cu\textsuperscript{2+} ions at wider linear concentration range (0.025 - 10 mg/L) corresponding to a sensitivity of 2.81(mg/L)\textsuperscript{-1} and limit of quantification of 47.3 μg/L, respectively, suitable for Cu\textsuperscript{2+} sensing in drinking water and ground water. Further, the detection of Cu\textsuperscript{2+} ion was free from most interfering cations and anions, except for minor interference from Cr\textsuperscript{3+}, Hg\textsuperscript{2+} and Pb\textsuperscript{2+}. The robustness of our probe for Cu\textsuperscript{2+} sensing is demonstrated from efficient Cu\textsuperscript{2+} spike recovery analysis in groundwater and river water samples.

Keywords CdS quantum dots, photoluminescence quenching, Cu\textsuperscript{2+}, Stern–Volmer equation, limit of detection, water analysis

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Introduction

Copper (Cu\textsuperscript{2+}) is one of the most essential transition metal ions in humans that serves as a catalytic cofactor for metalloenzymes and plays an important role in various biological activities.\textsuperscript{1} Drinking water and edible crops constitute the primary sources of copper for the human body. Usually, copper concentrations in drinking water are less than 1 mg/L, except for the groundwater rich in minerals where the copper concentrations are reported to be above 10 mg/L.\textsuperscript{2} The regulatory limits for copper in drinking water established by the United States Environmental Protection Agency (U.S. EPA) is 1.3 mg/L.\textsuperscript{3} Notably, deficiency as well as excess of copper levels is harmful to the human system. For example, deficiency of copper may cause pancytopenia or anemia, while excess of copper can trigger oxidative processes due to generation of reactive oxygen species (ROS) in the human body. Some of the oxidative neurodegenerative diseases are Wilson disease, Menkes disease, Alzheimer’s disease and Parkinson’s disease, which are correlated with accumulation of Cu\textsuperscript{2+} ions in the neuronal cytoplasm.\textsuperscript{4}

There has been a growing demand for global monitoring Cu\textsuperscript{2+} in drinking water as revealed from the technical reports of WHO and USEPA.\textsuperscript{4,5} Various instrumental-based analytical techniques are now available for analyzing Cu\textsuperscript{2+} at trace concentrations, but these techniques involve expensive and sophisticated instruments, time consuming sample preparation, and skilled technicians. Therefore, a genuine demand exists for developing a low-cost, field-deployable, easy-to-use, fast-sensing, sensitive and reproducible analytical method for on-site routine monitoring of Cu\textsuperscript{2+} concentration in natural water. In this pursuit, fluorescent sensors are found to be an excellent probe for detecting Cu\textsuperscript{2+} ions in aqueous medium.\textsuperscript{6} The detection is based on analyte-induced changes in the physicochemical properties of the fluoroprobe, e.g., fluorescence intensity, lifetime and anisotropy, which are broadly related to charge transfer or energy transfer processes between the fluoroprobe and the analyte.\textsuperscript{7}

In general, fluorescent probes are either organic dyes or inorganic compounds. The major advantages of organic compounds as sensors are their commercial availability with well established labeling protocols and possibilities of synthesizing smaller structures that minimizes possible steric hindrance.\textsuperscript{8} However, the major disadvantages are generally associated with rapid photobleaching, poor solubility in aqueous media and narrow excitation spectrum, which limits their applications.\textsuperscript{9,10} Alternately, inorganic fluoroprobes composed of II–VI type semiconductor type quantum dots (e.g., CdS, CdSe, CdTe, ZnS), graphene oxide (GO), carbon dots (CDs) and metallic clusters have emerged as alternative fluorophores due to their unique properties.\textsuperscript{11–13} For example, quantum dots possess broad excitation profiles, narrow and symmetric emission spectra, high photostability, tunable optical properties, high quantum efficiency, size-dependent fluorescence emission peaks and potential multiplexed detection capability.\textsuperscript{14} The other advantage of using quantum dots is attributed to surface modification that leads to improved hydrophilicity and enhanced specific interaction with an analyte of interest to bring out sensitive changes in its optical emission properties. However, from a practical point of view, the use of quantum dots as fluoroprobe for copper ion sensing in drinking water would depend on satisfying the US EPA recommended limit of quantification of 50 μg/L or better.\textsuperscript{1} In this regard, CdS quantum dots have been explored as a photoluminescent probe for

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detecting Cu\(^{2+}\) ions with excellent limit of quantification.\(^{15-17}\) These studies lacked faster kinetics of photoluminescence quenching by Cu\(^{2+}\) ions and revealed a narrow linear concentration range for detecting Cu\(^{2+}\) ions.

In this study, we have focused on instant or rapid detection of copper ions at a wider concentration range together with high sensitivity and selectivity suitable for water analysis. It was accomplished by improving the hydrophilicity of the CdS quantum dots by surface passivating the mercaptaoctic acid capped CdS quantum dots with amine bearing ligand like thiourea. The same photoluminescent probe was developed by us earlier for highly sensitive detection of uranyl ions in aqueous medium.\(^{18}\) In our reported work the uranyl ion detection was performed at pH 4, and the probe was non-responsive to uranium species conditioned at pH 7. Whereas in the present study, Cu\(^{2+}\) ions are detected at neutral pH (i.e., pH 7).

Furthermore the equilibration time for achieving steady state photoluminescence quenching by Cu\(^{2+}\) ions was much faster than that for uranyl ions. The laboratory results were translated to real time studies by recovery analysis of spiked Cu\(^{2+}\) ion concentration in groundwater and river water samples. A possible mechanism for photoluminescence quenching of the CdS probe by Cu\(^{2+}\) ions has been discussed in the light of zeta potential measurements.

Materials and Methods

Synthesis of probe

The CdS quantum dots were synthesized by nucleation and growth method by capping with mercaptaoctic acid and subsequently surface passivated by thiourea. The CdS is capped with mercaptaoctic acid via formation of S-S bond. Detailed method of synthesis is given in our earlier work.\(^{18}\) Briefly, a batch of 200 \(\mu\)L of mercaptaoctic acid (SHCH\(_2\)COOH) was added dropwise into 25 mL of freshly prepared 10 mM cadmium chloride solution. A turbid white colloidal solution was formed, whose pH was 2. After 30 min of magnetic stirring, 25 mL of homogenized 5 mM thiourea (NH\(_2\)CSNH\(_2\)) solution was added dropwise and was further homogenized by vigorous stirring for 30 min. The turbid solution became clear by adding NaOH solution, whose final pH was 6. It was further treated with 25 mL of 5 mM sodium sulfide solution and stirred magnetically for 1 h. Finally, the CdS quantum dots were precipitated by adding ethanol. The as-synthesized quantum dots were washed several times by ethanol-water mixture and separated by centrifugation for further studies. All chemicals used in the study were of analytical grade and were used as procured without any further purification.

Characterization techniques

The UV-visible absorption spectra were recorded on a Shimadzu UV-1800 spectrometer. The photoluminescence emission spectra were recorded using a HORIBA FluorEssence spectrometer, equipped with a xenon lamp as the light source. The excitation and emission slit widths (2 nm) were fixed throughout the experiments. The emission spectra were recorded at an excitation wavelength (\(\lambda_{ex}\)) of 370 nm. The dynamic light scattering (DLS) and zeta potential (\(\zeta\)) measurements were performed on a Malvern Nano-ZS90 (Zetasizer Nanoseries) equipped with 4 mW He-Ne laser (632 nm) as a light source.

\(pH\) and contact time optimization of the probe

It was noted that the optimum concentration of the probe
Results and Discussion

Characterization of CdS quantum dots surface passivated by thiourea

The band gap of the CdS quantum dots surface passivated by thiourea was determined from the edge of the intersection of the base line and the slope of the UV-visible spectrum (Fig. 1a). The measured band gap (3.18 eV) was larger than that of bulk CdS, which could be attributed to synthesis of nanoparticles. The particle size ($d$) was empirically determined from the wavelength corresponding to the maximum absorbance ($\lambda_{\text{max}}$) using the formula:19

$$d(\text{nm}) = (-6.6521 \times 10^{-8})\lambda^3 + (1.9557 \times 10^{-4})\lambda^2 - (9.2352 \times 10^{-2})\lambda + 13.29$$

The size of the CdS particles was calculated as 2.1 nm, which rendered better dispersion in water. Furthermore, the size of the particles was less than the Bohr-exciton diameter for electron-hole pair of CdS and hence exhibit quantum confinement effect. Because of this, the as-synthesized nanoparticles can be referred to as CdS quantum dots (QDs).20

The photoluminescence emission property of these quantum dots was evident from Fig. 1b, which revealed a broad and strong emission profile with maximum intensity centered at $\lambda = 494$ nm. The photoluminescence property of the CdS quantum dots was improved by passivating with NH$_2$ group of thiourea via hydrogen bonding with the carboxylic acid group of the mercaptoacetic acid as shown in Scheme 1. The full width at half maxima (FWHM) of the emission peak was 125 nm. The large shift in the emission peak with respect to the band gap together with peak broadening is attributable to trap state emission, owing to sulfur rich or metal vacancies defect sites near to the valence band.21

Scheme 1 A schematic representation showing synthesis CdS quantum dots by nucleation and growth method by capping with mercaptoacetic acid via formation of S-S bond. The surface defects of the CdS quantum dots were passivated by thiourea via a proposed hydrogen bonding with NH$_2$ group. Detection of Cu$^{2+}$ ion is due to photoluminescence quenching, likely to be due to aggregation of QDs proposed on the basis of electrostatic interaction between Cu$^{2+}$ and the mercaptoacetic acid.

Probe optimization: pH and contact time

The pH plays a significant role on the fluorescence intensity of the surface passivated CdS QDs as probe. The photoluminescence intensity profile of the probe conditioned at different pH ranging between 2 and 9 is given in Fig. 2a. The measured band gap (3.18 eV) was larger than that of bulk CdS, which could be attributed to synthesis of nanoparticles. The particle size ($d$) was empirically determined from the wavelength corresponding to the maximum absorbance ($\lambda_{\text{max}}$) using the formula:19

$$d(\text{nm}) = (-6.6521 \times 10^{-8})\lambda^3 + (1.9557 \times 10^{-4})\lambda^2 - (9.2352 \times 10^{-2})\lambda + 13.29$$

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Fig. 2 (a) Showing variation in the emission property of the CdS-MAA-TU probe recorded at different pH. (b) Showing pH dependent emission profile of probe treated with 1 mg/L of Cu$^{2+}$ ions. (c) Kinetics of photoluminescence quenching of the probe treated with 1 mg/L of Cu$^{2+}$ ions at pH 7, respective photoluminescence spectra are given in the inset.
As the pH was increased, the photoluminescence intensity of the quantum dots increased and was saturated at pH 7, owing to deprotonation of thiol group. Further, the feasibility of the probe for sensing Cu\textsuperscript{2+} ions was confirmed by recording the changes in the photoluminescence emission of the probe treated with 1 mg/L Cu\textsuperscript{2+} ions for an arbitrary contact time of 60 min for the batches maintained at pH in the range of 2 and 9 (Fig. 2b). The photoluminescence quenching by 1 mg/L Cu\textsuperscript{2+} ions was maximum at pH 7. Therefore, further photoluminescence quenching measurements were recorded using tris–HCl buffer medium at pH 7.

The kinetics of the photoluminescence emission of the probe treated with 1 mg/L Cu\textsuperscript{2+} ions is given in Fig. 2c and the respective photoluminescence emission spectrum of probe treated with Cu\textsuperscript{2+} ions for each contact time is given in the inset of Fig. 2c. Notably, the maximum photoluminescence quenching was achieved in 2 min and thereafter the quenching was saturated. The optimized contact time in this study was significantly improved (5 – 20 fold lesser) as compared to earlier studies on Cu\textsuperscript{2+} sensing by CdS QDs as probe.\textsuperscript{23,24} All further studies were therefore performed with contact time of 2 min.

Sensitivity, limit of detection and limit of quantification

Figure 3a reflects a linear increase in the photoluminescence quenching of 0.15 mM surface passivated CdS QDs treated with increasing Cu\textsuperscript{2+} ions concentrations ranging between 0.025 and 10 mg/L at the optimized pH and contact time. The corresponding photoluminescence emission spectra of the QDs treated with respective Cu\textsuperscript{2+} ions are given alongside of Fig. 2a. Notably, there was no shift in the emission peak, which meant that the QDs were not affected due to interaction with Cu\textsuperscript{2+} ions. The correlation between the measured photoluminescence quenching and the concentration of the Cu\textsuperscript{2+} ions satisfied the linear Stern–Volmer equation, given as:\textsuperscript{25}

\[
\frac{I}{I_o} = 1 + K_{sv}[Cu^{2+}]
\]

where \(I_o\) and \(I\) are the photoluminescence intensities of the probe and the probe treated with Cu\textsuperscript{2+} ions, respectively; \(K_{sv}\) is the Stern–Volmer photoluminescence quenching constant and [Cu\textsuperscript{2+}] represents the concentration of Cu\textsuperscript{2+} ions. The linearity of the Stern–Volmer plot established with correlation coefficient \(R^2 = 0.99\). The slope of the Stern–Volmer plot i.e., \(K_{sv}\) corresponds to the sensitivity of the probe towards Cu\textsuperscript{2+} detection, which was determined to be 2.81(mg/L)\textsuperscript{-1}. The limit of detection (LoD) is given as \(3\sigma/sensitivity\), where \(\sigma = 0.0133\) corresponds to the precision of the photoluminescence intensity of the probe, which was determined from five independent measurements. The LoD was calculated as 14.2 \(\mu\)g/L and the limit of quantification (LoQ) is 10 times standard deviation/sensitivity, i.e., 47.3 \(\mu\)g/L. Notably, the limit of quantification is less than that recommended by the US EPA (i.e., 50 \(\mu\)g/L),\textsuperscript{2} and hence according to the US EPA the surface passivated CdS QDs qualified as a probe for sensing Cu\textsuperscript{2+} ions in drinking water or groundwater.

Visual detection

The scope for visual detection of Cu\textsuperscript{2+} ions was tested by illuminating the batch of 0.15 mM probe solution by UV light of excitation wavelength = 365 nm. The colorless probe solution under normal light revealed a bright bluish colored photoluminescence emission when exposed to 365 nm UV light. The intensity of the photoluminescence decreased systematically with the increasing concentration of Cu\textsuperscript{2+} ions. The decrease in
the photoluminescence emission due to quenching was visually detectable at 1.0 mg/L of Cu^{2+} concentration and was significantly quenched at 2 mg/L (Fig. 3b). It may therefore be remarked that the surface passivated CdS QDs can be efficiently used as a probe for determining the trace contamination of Cu^{2+} ion in drinking water or groundwater and can also be used for sensing higher concentrations of Cu^{2+} ions in wastewater.

Cu^{2+} ion detection mechanism

Photoluminescence quenching was used as the analytical response for Cu^{2+} ion sensing. In order to get a better insight of the quenching mechanism for our probe, the zeta potential measurements of a pristine probe and probe treated with Cu^{2+} ions were studied. The zeta potential of the pristine probe was measured to be \(-33.6\) mV (Fig. S1a, Supporting Information), which indicated a negative surface charge on the CdS quantum dots owing to the carboxylate groups of the capping agent. However, in the presence of 1 mg/L Cu^{2+} ions the zeta potential of the probe decreased to \(-8.18\) mV (Fig. S1b, Supporting Information). The decrease in the negative sign of zeta potential implied a possible aggregation of quantum dots that can be attributed to electrostatic interaction between the probe and Cu^{2+} ions, as shown in Scheme 1. The affinity of Cu^{2+} for sulfide could be a driving force for selective quenching of the CdS probe. Similar mechanism for photoluminescence quenching by metal ions has been discussed earlier.26

Interference studies

In order to realize the practical applications of surface passivated CdS QDs for Cu^{2+} ion detection in water sample analysis, it is important to verify the influence of other relevant cations and anions on the photoluminescence quenching of the probe i.e., surface passivated CdS QDs. In this context, we examined the selectivity of the probe towards Cu^{2+} sensing by recording the photoluminescence quenching of the probe treated with interfering cations and anions that are relevant to water sample at the optimized pH and contact time. The respective batches of probe (0.15 mM) solution were treated with Na^{+} (200 mg/L), K^{+} (50 mg/L), Mg^{2+} (30 mg/L), Ca^{2+} (75 mg/L), Fe^{2+} (10 mg/L), Mn^{2+} (10 mg/L), Zn^{2+} (10 mg/L), Co^{2+} (10 mg/L), Ni^{2+} (10 mg/L), Cr^{3+} (5 mg/L), Cd^{2+} (10 mg/L) and Hg^{2+} (0.2 mg/L) in the absence and presence of 1 mg/L of Cu^{2+} ions. The concentrations of the interfering cations were chosen as per the recommended limits by the Bureau of Indian Standard (BIS)27 and WHO.28 The corresponding photoluminescence emission spectra of the probe treated with respective interfering...
cations revealed negligible photoluminescence quenching for Na⁺, K⁺, Mg²⁺, Ca²⁺, Ni²⁺, Cd²⁺ (quenching <2%); Fe³⁺, Co⁴⁺, Mn²⁺, Zn²⁺ (quenching ~4%); Cr³⁺ (quenching ~6%); Hg²⁺ and Pb²⁺ (quenching ~8%), as compared to 70% photoluminescence quenching for 1 mg/L Cu²⁺ ions (Fig. 4a). Similarly, Fig. 4b represents respective $I/I_0$ values of interfering cations with and without 1 mg/L concentration of Cu²⁺ ions. Further, the photoluminescence quenching spectra of the probe treated with an arbitrary 5 mM concentration of interfering anions, e.g., F⁻, Cl⁻, NO₂⁻, CO₃²⁻, HPO₄²⁻, SO₄²⁻, BH₄⁻, OH⁻, HCO₃⁻, OAc⁻, NO₂⁻ and AsO₄³⁻ revealed negligible photoluminescence quenching (Fig. 4c). The reflected $I/I_0$ values due to these anions in the absence and presence of 1 mg/L of Cu²⁺ ions is shown in Fig. 4d. Any measurable interference in the presence of the foreign metal ions or anions could not be observed.

The mild interference by Hg²⁺ and Pb²⁺ was due to their affinity towards sulfur group in the CdS or the sulfur bearing capping agent, e.g., mercaptoacetic acid. As a consequence, several studies reported simultaneous detection of Cu²⁺, Pb²⁺ and Hg²⁺ ions in aqueous medium. Though various semiconductor type probes (e.g., CdSe, CdTe, CdSe/ZnS) were developed for highly sensitive detection of Cu²⁺ ions but selectivity in the presence of Hg²⁺ and Pb²⁺ is not well documented. It may be remarked that our surface passivated CdS QDs satisfied the required sensitivity and selectivity for Cu²⁺ ion detection in the presence of almost all relevant cations and anions as interfering agents that simulate drinking water or groundwater composition. However, in our recent study we have demonstrated that the probe is highly sensitive to uranyl ion detection at sub parts per billion (ppb) concentrations (i.e., less than 1 μg/L). Needless to mention here that the detection of Cu²⁺ ions will be affected in the presence of sub-trace concentrations of uranyl ions.

**Spike and recovery analysis**

The feasibility study of using the surface passivated CdS QDs as a probe for determining the concentration of Cu²⁺ in environmental samples was performed by spiking groundwater (Roorkee, India) and river water (Ganga Canal, Roorkee India) samples with known concentrations of Cu²⁺ ions (ranging between 0.5 and 2 mg/L). The groundwater and the river water samples were first filtered to avoid any particulate suspension prior to spiking with Cu²⁺ ions at optimum contact time and pH conditions. These batches of spiked samples revealed linear Stern-Volmer plots (Fig. 4e), and the corresponding LoDs were found to be 15.11 and 15.77 μg/L respectively. These LoDs were very similar to that determined by spiking the same concentration of Cu²⁺ in deionized water. Our results implied that our probe and the methodology are suitable for analyzing ultra trace levels of Cu²⁺ in real water samples.

The recovery study was performed for three Cu²⁺ ion concentrations, 0.5, 1 and 2 mg/L, spiked in groundwater and river water samples and the results are presented in Table 1. The recovery of Cu²⁺ concentrations for all the spiked batches in deionized water were in the range of 98 to 106%. In the case of groundwater and river water matrices, the recovery concentration of Cu²⁺ ions were close to 100% (ranging between 95 and 110%) only for the batches spiked with Cu²⁺ ion concentrations of 1 and 2 mg/L. However, for the batches treated with very low concentrations of Cu²⁺ ions (0.5 mg/L) the recoveries were 112% for ground water and 113% for river water. At such low Cu²⁺ concentrations, 12 to 13% positive error is attributable to possible interferences from Pb²⁺ and Hg²⁺ ions in the groundwater and river water samples. Further studies may be suggested for improving the recovery of very low concentrations of Cu²⁺ ion in groundwater and river water by suitable masking of Pb²⁺ and Hg²⁺ ions. It may be concluded that the as developed method is suitable for sensing trace levels of Cu²⁺ in drinking water as well as in groundwater by our probe, i.e., surface passivated CdS QDs.

### Table 1: Recovery analysis of Cu²⁺ concentrations for Cu²⁺ spike in deionized water, groundwater and river water

| Spiked Cu²⁺ concentration/mg L⁻¹ | Deionized water | Groundwater | River water |
|---------------------------------|-----------------|-------------|-------------|
|                                 | Measured/mg L⁻¹ | Recovery, % | Measured/mg L⁻¹ | Recovery, % | Measured/mg L⁻¹ | Recovery, % |
| 0                               | 0.0042 ± 0.005  | —           | 0.075 ± 0.006 | —           | 0.093 ± 0.011  | —           |
| 0.5                             | 0.491 ± 0.011   | 98 ± 2.20   | 0.558 ± 0.034 | 112 ± 6.82  | 0.565 ± 0.041  | 113 ± 8.20  |
| 1                               | 1.064 ± 0.020   | 106 ± 1.99  | 1.098 ± 0.022 | 110 ± 2.20  | 1.096 ± 0.056  | 110 ± 5.61  |
| 2                               | 1.997 ± 0.001   | 99 ± 0.05   | 1.905 ± 0.042 | 95 ± 2.09   | 1.860 ± 0.068  | 93 ± 3.40   |

The concentrations are given as mean ± standard deviation calculated from three independent measurements ($n = 3$).

**Conclusion**

A rapid, sensitive and robust analytical method has been developed for sensing Cu²⁺ ions at trace concentrations by thiourea modified surface passivated CdS quantum dots. The present method revealed excellent sensitivity and selectivity for Cu²⁺ in the presence of most common interfering cations and anions expected in drinking water or groundwater. The robustness of our method has been demonstrated by excellent spike recovery analysis for higher concentrations of spiked Cu²⁺, while there was approximately 10 to 15% positive bias especially for measurement of lower concentrations of Cu²⁺ (0.5 mg/L). It may be concluded that there exists a tremendous potential for developing a rapid and sensitive analytical kit using surface passivated CdS quantum dots for estimating Cu²⁺ ion concentration in drinking water and groundwater.

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**Supporting Information**

The zeta potential of probe measured at pH 7 and the probe at pH 7 after equilibration with 1 mg/L of Cu²⁺ is given as Supporting Information. This material is available free of charge on the Web at [http://www.jsac.or.jp/analsci/](http://www.jsac.or.jp/analsci/).
References

1. E. I. Soloman, D. E. Heppner, E. M. Johnston, J. W. Ginsbach, J. Ciera, M. Qayyum, M. T. Kieber-Emmons, C. H. Kjaergaard, R. G. Hadt, and L. Tian, *Chem. Rev.*, **2014**, *114*, 3659.

2. U.S. EPA, “Final Report: Integrated Science Assessment for Particulate Matter”, *2009*, U.S. Environmental Protection Agency, Washington, DC, EPA/600/R-08/139F. P. A. Balch, “Prescription for Nutritional Healing”, 4th ed., **2006**, Penguin Group, New York.

3. J. Liu and Y. Lu, *J. Am. Chem. Soc.*, **2007**, *129*, 9838.

4. D. J. Waggoner, T. B. Bartnikas, and J. D. Gitlin, *Neurobiol. Dis.*, **1999**, *6*, 221.

5. U.S. EPA, “Guidelines for Developmental Toxicity Risk Assessment”, EPA/600/FR-91/001, Dec. **1991**.

6. Z. Li, Y. Zhang, H. Xia, Y. Mu, and X. Liu, *Chem. Commun.*, **2016**, *52*, 6613.

7. O. Ostroverkhova, *Chem. Rev.*, **2016**, DOI:10.1021/acs.chemrev.6b00127.

8. H. N. Kim, W. X. Ren, J. S. Kim, and J. Yoon, *Chem. Soc. Rev.*, **2012**, *41*, 3210.

9. P. Zrazhevskiy, M. Sena, and X. Gao, *Chem. Soc. Rev.*, **2010**, *39*, 4326.

10. U. Resch-Genger, M. Grabolle, S. Cavaliere-Jaricot, R. Nitschke, and T. Nann, *Nat. Methods*, **2008**, *5*, 763.

11. Q. Zhang, J. Li, Y. Zhang, Z. Hu, and C. Yu, *Anal. Sci.*, **2016**, *32*, 1035.

12. Y. Dong, R. Wang, G. Li, C. Chen, Y. Chi, and G. Chen, *Anal. Chem.*, **2012**, *84*, 6220.

13. S. Basumallik, *Graphene*, **2014**, *3*, 45.

14. M. Vazquez-Gonzalez and C. Carrillo-Carrion, *J. Biomed. Opt.*, **2014**, *19*, 101503.

15. Z. Cao, Z. Gu, J.-L. Zeng, J.-H. Liu, Q. Deng, J. B. Fan, and J.-N. Xiang, *Anal. Sci.*, **2011**, *27*, 643.

16. J. Tao, Q. Zeng, and L. Wang, *Sens. Actuators, B*, **2016**, 234, 641.

17. Y.-H. Zhang, H.-S. Zhang, X.-F. Guo and H. Wang, *Microchem. J.*, **2008**, *89*, 142.

18. R. K. Dutta and A. Kumar, *Anal. Chem.*, **2016**, *88*, 9071.

19. W. W. Yu, L. Qu, W. Guo, and X. Peng, *Chem. Mater.*, **2003**, *15*, 2854.

20. A. P. Alivisatos, *Science*, **1996**, *271*, 933.

21. A. Veamatahau, B. Jiang, T. Seifert, S. Makuta, K. Latham, M. Kanemara, T. Teranishi, and Y. Tachibana, *Phys. Chem. Chem. Phys.*, **2015**, *17*, 2850.

22. J. Aldana, N. Lavelle, Y. Wang, and X. Peng, *J. Am. Chem. Soc.*, **2005**, *127*, 2496.

23. S. Lai, X. Chang, and C. Fu, *Microchim. Acta*, **2009**, *165*, 39.

24. M. Zhang, F. Wan, S. Ge, and J. Yu, *Adv. Mater. Res.*, **2011**, 306-307, 1134.

25. J. Keizer, *J. Am. Chem. Soc.*, **1983**, *105*, 1494.

26. D. Saikia, P. Dutta, N. S. Sarma, and N. C. Adhikary, *Sens. Actuators, B*, **2016**, *230*, 149.

27. Indian Standard for Drinking Water-Specifica, IS 10500:1991.

28. WHO, “Guidelines for Drinking Water Quality”, 3rd ed., **2003**

29. B. Tang, J. Niu, C. Yu, L. Zhuo, and J. Ge, *Chem. Commun.*, **2005**, *33*, 4184.

30. Y.-W. Lin, C.-C. Huang, and H.-T. Chang, *Analyst*, **2011**, *136*, 863.

31. Y.-H. Chan, J. Chen, Q. Liu, S. E. Wark, D. H. Son, and J. D. Batteas, *Anal. Chem.*, **2010**, *82*, 3671.

32. L.-H. Jin and C.-S. Han, *Anal. Chem.*, **2014**, *86*, 7209.