



Ultrasensitive fluorescence-quenched chemosensor for Hg(II) in aqueous solution based on mercaptothiadiazole capped silver nanoparticles

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ABSTRACT

This manuscript describes a highly selective and ultra sensitive determination of Hg(II) in aqueous solution using functionalized mercaptothiadiazole capped silver nanoparticles (AgNPs) by spectrofluorimetry. We have synthesized 2,5-dimercapto-1,3,4-thiadiazole (DMT), 2-mercapto-5-methyl-1,3,4-thiadiazole (MMT) and 2-mercapto-5-amino-1,3,4-thiadiazole (AMT) capped AgNPs by wet chemical method. Among these AgNPs, DMT capped AgNPs (DMT-AgNPs) were more stable and highly fluorescent than the other two AgNPs. DMT-AgNPs show the emission maximum at 677 nm while exciting at 400 nm. After the addition of Hg(II), the emission intensity was decreased at 677 nm. The observed decreased emission intensity was ascribed to the aggregation of AgNPs and it was confirmed by TEM. Based on the decrease in emission intensity, the concentration of Hg(II) was determined. The lowest detection limit (LOD = 3 S/m) of 1.0 pg L^{-1} was achieved for the first time using DMT-AgNPs by spectrofluorimetry. The quantum yield (ϕ_F), Stern–Volmer constant (K_{SV}), Gibbs free energy changes (ΔG°), association constant (K_f) were calculated and the quenching mechanism also was discussed. Finally, the proposed method was successfully utilized for the determination of Hg(II) in river water, industrial effluent water and tap water samples. The obtained results were fairly matches with the ICP-AES method.

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1. Introduction

Metal nanoparticles based research has received great attention during the last three decades due to their attractive optical, catalytic and electrical properties [1,2]. These unique properties can be tuned by varying the particle size, shape and surrounding environments [3]. When compared to other metal nanoparticles, research on the synthesis and applications of silver nanoparticles (AgNPs) has received considerable attention around the world in recent years [4,5]. The AgNPs show excellent conductivity, chemical stability and catalytic activity [6,7]. They have been used extensively as an antibacterial agent, food storage, textile coatings and toxic chemicals sensor [8].

Toxic heavy metal ions can cause lethal threat to the environment and human beings. Among them, mercury has received much attention due to its high toxicity and bioaccumulative properties [9,10]. Mercury contamination arises from a variety of natural sources, such as oceanic and volcanic emissions, as well as anthropogenic sources, such as gold mining and combustion of wastes and fossil fuels are the major sources of mercury emission [11].

Bioaccumulation of mercury can affect brain, heart, stomach and intestines [12]. Hg(II) shows strong affinity towards the ligands containing sulfur group and causes the blocking of sulfhydryl groups of proteins, enzymes, membranes and it damage to the central nervous system, DNA, mitosis and the endocrine system [13]. According to Environmental Protection Agency and World Health Organization guidelines, Hg(II) must be in the concentrations of 2 ppm and 5 ppm in drinking water, respectively [14,15]. Because of its serious hazardous effects to human health and environment, there is a strong need to establish a simple inexpensive method to determine Hg(II) with high selectivity and sensitivity in aqueous media. Many methods have been described in the literature for the determination of Hg(II) including colorimetry [16,17], spectrophotometry [18], atomic absorption spectrometry [19], stripping voltammetry [20] and inductively coupled plasma atomic emission spectrometry [21]. Among the different methods, spectrofluorimetric method has several advantages over other methods which include higher sensitivity, selectivity and reproducibility and less time consumption [22,23]. To date only few papers were reported for the determination of Hg(II) in ppt level by spectrofluorimetric method [7,10,24–35].

The present work describes the ultrasensitive fluorescence-quenched chemosensor for Hg(II) in aqueous solution using mercaptothiadiazole capped AgNPs as a fluorophore. We have

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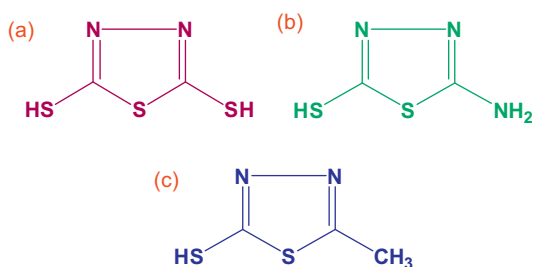


Chart 1. Structure of (a) 2,5-dimercapto-1,3,4-thiadiazole (DMT), (b) 2-amino-5-mercapto-1,3,4-thiadiazole (AMT) and (c) 2-methyl-5-mercapto-1,3,4-thiadiazole (MMT).

synthesized 2,5-dimercapto-1,3,4-thiadiazole (DMT), 2-amino-5-mercapto-1,3,4-thiadiazole (AMT) and 5-methyl-2-mercapto-1,3,4-thiadiazole (MMT) (Chart 1) capped AgNPs by wet chemical method. The synthesized AgNPs were characterized by UV-vis spectrophotometer, spectrofluorimeter, HR-TEM, FT-IR and XRD. The DMT-AgNPs are more stable and highly fluorescent than the other two AgNPs. Therefore, we have chosen DMT-AgNPs for the determination of Hg(II). They show the emission maximum at 677 nm while exciting at 400 nm. The emission intensity was decreased while adding Hg(II) to DMT-AgNPs. Based on decrease in emission intensity the concentration of Hg(II) was determined. The lowest detection limit was found to be 1.0 pg L^{-1} . The present method was successfully applied to determine Hg(II) in environmental samples. The obtained results have a good agreement with ICP-AES method.

2. Experimental

2.1. Chemicals

Silver nitrate, 2,5-dimercapto-1,3,4-thiadiazole, 2-amino-5-mercapto-1,3,4-thiadiazole, 5-methyl-2-mercapto-1,3,4-thiadiazole were purchased from Sigma-Aldrich. Sodium borohydride (NaBH_4) and mercuric nitrate ($\text{Hg}(\text{NO}_3)_2$) were purchased from Merck (India) and were used as received. All other chemicals used in this investigation were of analytical grade and used directly without further purification. Double distilled water was used to prepare the solutions in the present work.

2.2. Instrumentation

Absorption spectra were measured by using JASCO V-550 UV-vis spectrophotometer. Fluorescence spectral measurements were performed on a JASCO FP-6500 spectrofluorimeter equipped with a xenon discharge lamp, 1 cm quartz cell at room temperature. The FT-IR spectra of the solid AgNPs were measured by using JASCO 460 plus FT-IR Spectrophotometer. High resolution transmission electron microscopy (HR-TEM) images of AgNPs were obtained from a JEOL JEM 3010 operating at 200 kV. For TEM measurements, the sample was prepared by dropping $2 \mu\text{L}$ of a AgNPs colloidal solution onto a carbon-coated copper grid. A large volume (250 mL) of DMT-AgNPs was synthesized and centrifuged (10,000 rpm) and the particles were separated. They repeatedly washed with water and dried in vacuum. The dried AgNPs powder was used for XRD and FT-IR measurements. XRD analysis was carried out with a Rigaku X-ray diffraction unit using Ni-filtered $\text{Cu K}\alpha$ ($\lambda = 1.5406$) radiation. Inductively coupled plasma atomic emission spectra (ICP-AES) were measured by using thermo electron IRIS intrepid II XSP DUO model ICP-AES.

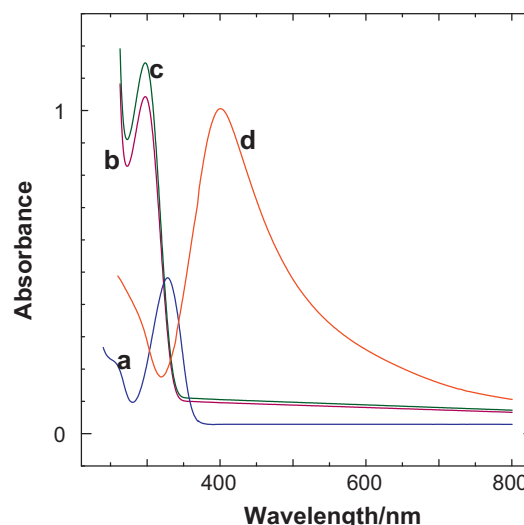


Fig. 1. Absorption spectra obtained for (a) DMT, (b) AgNO_3 and after the addition (c) AgNO_3 to DMT and (d) NaBH_4 to a mixture of AgNO_3 and DMT.

2.3. Synthesis of functionalized mercaptothiadiazole ligand capped AgNPs

All glasswares were thoroughly cleaned with freshly prepared aquaregia (3:1; HCl/HNO_3) and rinsed comprehensively with double distilled water prior to use. The colloidal solution of mercaptothiadiazole capped AgNPs were prepared by the following procedure. 2 mL of AgNO_3 (1 mM) and 1 mL of DMT (1 mM) were added to 92 mL of water in a round bottom flask with constant stirring. To this solution, 5 mL of 0.046 M NaBH_4 was added drop by drop and the stirring was continued for another 30 min. The color of the solution turns into yellow immediately after the final addition, indicating the formation of AgNPs. Same procedure was followed for the preparation of AMT and MMT-AgNPs using 0.5 mM of the respective compound.

3. Results and discussion

3.1. Silver nanoparticles formation and stability

Since metal nanoparticles exhibit strong absorption band due to surface plasmon resonance (SPR) in the visible region, the electronic spectroscopy is one of the simplest techniques to characterize them. Fig. 1 shows the absorption spectra recorded for DMT, AgNO_3 and a mixture of DMT and AgNO_3 in the presence and absence of NaBH_4 . DMT shows an absorption maximum at 318 nm with a shoulder band around at 260 nm (curve a). AgNO_3 in water exhibits an absorption maximum at 300 nm (curve b). Addition of AgNO_3 solution to an aqueous solution of DMT causes the absorption bands characteristics of DMT to vanish while the absorption intensity at 300 nm was increased (curve c). The observed increase in intensity at 300 nm was ascribed to the complex formation between DMT and AgNO_3 . When 5.0 mL of 0.046 M of NaBH_4 was slowly added to a mixture of DMT and AgNO_3 solution, the colorless solution becomes yellow immediately and shows a new absorption band at 400 nm (curve d), corresponding to SPR. The observed SPR band at 400 nm confirms the successful formation of AgNPs. Similar procedure was used to prepare AMT- and MMT-AgNPs. The AMT and MMT-AgNPs show SPR bands at 404 and 396 nm, respectively.

The stability of the metal nanoparticles was usually checked from the changes in their absorption characteristics such as shift in the absorption maximum and decrease in the absorbance. Fig. S1A (Supporting information) shows the absorption spectra

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