



# Thiol terminated chitosan capped silver nanoparticles for sensitive and selective detection of mercury (II) ions in water

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## ABSTRACT

In this paper, we report a simple method for the optical detection of environmentally toxic mercury (II) ions ( $\text{Hg}^{2+}$ ) in water using chitosan capped silver nanoparticles (Ch-Ag NPs). The yellow colored aqueous solution of Ch-Ag NPs instantly (10 s) became colorless with addition of  $\text{Hg}^{2+}$  ions.  $\text{Cu}^{2+}$ , and  $\text{Fe}^{3+}$  ions also produced colorless solution after 1 min. To overcome the  $\text{Cu}^{2+}$  and  $\text{Fe}^{3+}$  interference, thiol terminated chitosan was synthesized via amide coupling formation between amine group of chitosan and carboxylic acid group of 3-Mercaptopropanoic acid (3-MPA). The detailed study of selectivity, sensitivity, effect of interfering radicals, and response time confirmed that thiol terminated chitosan capped silver nanoparticles (Mod-Ch-Ag NPs) are highly selective and speedy for  $\text{Hg}^{2+}$  ions detection. The limit of detection was found to be 5 ppb. Furthermore, since the change in color with addition of mercury can be observed by naked eye, the developed nanosensor can also be utilized for real field applications. Hydrogel of Mod-Ch-Ag NPs was successfully synthesized and it was also found highly specific for  $\text{Hg}^{2+}$  ions. It was observed that separation of  $\text{Hg}^{2+}$  ions is also possible by simply changing the pH of the solution containing colorless  $\text{Hg}^{2+}$  with Mod-Ch-Ag NPs.

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## 1. Introduction

The environmental contamination by heavy metal ions is seriously increasing. Amongst all the heavy metals, mercury (II) ( $\text{Hg}^{2+}$ ) is one of the most hazardous and toxic elements [1]. It is also non-biodegradable and hence gets accumulated in the environment resulting in food and water contaminations. Various studies have confirmed that the presence of  $\text{Hg}^{2+}$  has adverse effects on central nervous system, immune system, and endocrine system [2,3]. Thus it is very crucial to detect amount of  $\text{Hg}^{2+}$  present in the contaminated products. World Health Organization (WHO) and Environmental Protection Agency (EPA) have strictly defined the concentration limits (an upper limit of 2 ppb for  $\text{Hg}^{2+}$ ) that are allowed in the drinking water.

Several classical methods for the detection of  $\text{Hg}^{2+}$  are already available. However; their use requires expensive instruments and

tedious lab procedures [2,4–8]. Thus there is a growing demand for the development of  $\text{Hg}^{2+}$  ion sensor, which is on-site, real time, cost effective, straightforward, and convenient. In literature, various systems based on organic compounds [9–12], polymers [13–16], proteins [17,18], DNA [19–22], nanostructures [23–31] have been reported for the detection of  $\text{Hg}^{2+}$  ions. Recently metal nanoparticles have gained considerable attention for chemical sensing application due to their sensitive response to the local environment of the nanoparticle surface. Also, they show a very strong scattering or absorption, which makes the monitoring easier. Amongst all the noble metal nanoparticles (NPs), gold and silver NPs have been widely utilized due to their unique electronic and optical properties, which has made them ideal for the sensing of various analytes. [32–34] Several gold nanoparticles (Au NPs) based colorimetric sensors have been developed for the detection of  $\text{Hg}^{2+}$  ion [23,25,35–38]. A very few reports have focused on silver nanoparticles (Ag NPs) based detection system [8,39,40]. In comparison with Au NPs of the same size, Ag NPs have slight advantage since their extinction coefficients are slightly higher [41]. However, easy oxidation of the surface makes the stabilization of Ag NPs challenging and thus hampers their analytical applications [42].

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Efforts have been made to increase the stability of Ag NPs by functionalizing the interface with suitable ligands. Wang et al. have developed a biosensor using mercury specific oligonucleotides (MSO) and Ag NPs for selective detection of  $\text{Hg}^{2+}$ . The detection was linear in the range of 25–500 nM with a low detection limit of 17 nM [43]. Roy et al. developed a sensor for  $\text{Hg}^{2+}$  using riboflavin stabilized Ag nanoparticle via a turn off–turn on mechanism in an aqueous medium. The sensing time was only 1 min. The minimum concentration of  $\text{Hg}^{2+}$  that could be detected was as low as 5 nM [44]. A Silver nanoparticle-embedded poly(vinyl alcohol) (Ag-PVA) thin film sensor was developed by G. V. Ramesh et al. for the detection of mercury in all its oxidation states [45]. Wang et al. reported a colorimetric sensor for  $\text{Hg}^{2+}$  based on the catalytic reduction of  $\text{Hg}^{2+}$  to elementary Hg using Ag NPs in the presence of  $\text{H}_2\text{O}_2$  [46]. Tao et al. used the poly(acrylic acid)-templated silver nanoclusters (PAA-Ag NCs) for the development of a colorimetric sensor for sensitive detection of  $\text{Hg}^{2+}$  [47]. K. Farhadi et al. reported a colorimetric probe using unmodified and biologically prepared Ag NPs for real time detection of  $\text{Hg}^{2+}$  [48]. Apilux et al. developed a colorimetric detection method for  $\text{Hg}^{2+}$  on a paper based device using silver nanoparticles (Ag NPs) and silver nanoplates (Ag NPIs). The detection of mercury was possible with naked eye via the resulting color change of the Ag NPIs (on the paper-based device) after a 2  $\mu\text{L}$  application of the  $\text{Hg}^{2+}$  test solution. The limit of detection was found to be 0.12 ppm [49]. A more detailed report of colorimetric detection of  $\text{Hg}^{2+}$  can be found elsewhere [2,31].

Biopolymers as matrix materials have been found to control particle growth as well as incorporation of nanoparticles into these biopolymers has been found to be a great approach for stabilization of nanoparticles. Chitosan is an excellent biomaterial with good biocompatibility and low cytotoxicity. It is a linear aminopolysaccharide of glucosamine and N-acetylglucosamine unit. It is obtained by alkaline deacetylation of chitin [50]. Chitosan polymer is an excellent agent for stabilization of metal nanoparticle and bio-compatibilization [51]. In literature Chitosan capped silver nanoparticles have been used to demonstrate improved antibacterial properties [52], as photothermal transducers for in vitro cancer cell therapy [53], visual detection of aromatic *ortho*-trihydroxy phenols [54], colorimetric detection of glucose [55], and detection of toxic mercury ions [56,57].

In literature, there are reports available on the colorimetric detection of heavy metal ions using silver nanoparticles protected with chitosan. However, we found that the yellow color of chitosan capped silver nanoparticle turned colorless with addition of  $\text{Hg}^{2+}$ , as well as  $\text{Cu}^{2+}$  and  $\text{Fe}^{3+}$ . To obtain selectivity towards only  $\text{Hg}^{2+}$  ions, in this work we first synthesized thiol terminated chitosan by simple amide coupling reaction between chitosan and 3-MPA. We used the thiol terminated chitosan as capping agent to synthesize silver nanoparticles (Mod-Ch-Ag NPs). Based on decrease in surface plasmon resonance (SPR) and visual color change from yellow to colorless,  $\text{Hg}^{2+}$  could be detected quickly in less than 5 s. To ensure extremely high selectivity towards  $\text{Hg}^{2+}$  ions, we performed experiments with mixed ions. The mixed ions have no influence on the selectivity. The limit of detection is 5 ppb by UV–vis spectroscopy, which is very close to the mercury toxicity level defined by the U.S. Environmental Protection Agency.

## 2. Experimental details

### 2.1. Instruments

UV–vis spectroscopy measurements were carried out on UV-1800 SHIMADZU spectrophotometer. The FT-IR spectra of chitosan, and thiol terminated chitosan were taken in the range of  $800\text{ cm}^{-1}$  to  $4000\text{ cm}^{-1}$  on a Bruker alpha FT-IR spectrometer with  $1\text{ cm}^{-1}$

resolution. The scanning electron microscope (SEM) image and EDAX measurements were taken on Nova Nano FE-SEM 450 (FEI) microscope with an accelerating voltage of 15 kV. The transmission electron microscopy (TEM) images were obtained on a model JEOL 1200 EX. The Mod-Ch-Ag NPs were deposited onto a 200-mesh copper grid coated with a Formvar film. Dynamic light scattering (DLS) measurements were conducted on a Malvern Zetasizer nano ZS. X-ray photoemission spectroscopy (XPS) data recorded in Oxford Omicron ESCA plus system. Atomic absorption spectroscopic (AAS) analysis was carried out on AAS – Perkin Elmer (Analyst 200) instrument.

### 2.2. Materials

All reagents, Chitosan (low molecular weight MW 50,000–190,000 Da), 3-Mercaptopropanoic acid, N-Ethyl-N'-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDC), N,N-Dimethylpyridin-4-amine (DMAP), Agarose, Acetic acid,  $\text{AgNO}_3$ , NaOH,  $\text{NaBH}_4$ , NaCl, KCl,  $\text{CaCl}_2$ ,  $\text{MnSO}_4$ ,  $\text{CdCl}_2$ ,  $\text{CoCl}_2$ ,  $\text{NiSO}_4$ ,  $\text{AlCl}_3$ ,  $\text{Hg}(\text{OAc})_2$ ,  $\text{MgSO}_4$ ,  $\text{Pb}(\text{NO}_3)_2$ ,  $\text{ZnSO}_4$ ,  $\text{CuCl}_2$ ,  $\text{FeCl}_3$ ,  $\text{Cd}(\text{NO}_3)_2$ ,  $\text{K}_2\text{Cr}_2\text{O}_7$  were purchased from commercial suppliers and used without further purification. All organic solvents were purified and dried by standard methods prior to use. Millipore water was used throughout all experiments. The solutions of metal ions were prepared by dissolving the respective salts in millipore water in 100 ppm concentration.

### 2.3. Synthesis of chitosan capped silver nanoparticles (Ch-Ag NPs)

Chitosan capped Ag NPs were synthesized by the  $\text{NaBH}_4$  mediated reduction of  $\text{AgNO}_3$ . Briefly, 0.1 g chitosan and 0.05 g of  $\text{AgNO}_3$  were dissolved in 150 mL of water. pH of the solution was adjusted at 5 with dropwise addition of glacial acetic acid to obtain a clear colorless mixture. Freshly prepared 10 mL of 1 mM aqueous solution of  $\text{NaBH}_4$  was quickly introduced into the mixture and constantly stirred for 6 h at room temperature. The color of the solution turned from colorless to light yellow indicates the formation of chitosan capped silver nanoparticles (Ch-Ag NPs). For the purification of Ch-Ag NPs, pH of the solution was adjusted to 10 with addition of 1 M NaOH solution to get yellow precipitate of Ch-Ag NPs. The precipitate was separated by centrifugation and washed with millipore water. Finally, Ch-Ag NPs were dissolved in 0.2 M sodium citrate (pH-3.5) buffer. The final concentration of Ag was 0.05 mg/mL in pure Ch-Ag stock solution. The stock solution was kept in refrigerator for further use.

### 2.4. Synthesis of thiol terminated chitosan

The synthesis of thiol terminated chitosan is as follows: 2 mmol (0.21 g) of 3-MPA, 2.5 mmol (0.48 g) of EDC and 2.5 mmol (0.3 g) of DMAP were dissolved in 50 mL of water at  $0^\circ\text{C}$ . The reaction mixture was kept at  $0^\circ\text{C}$  under constant stirring for 1 h. Then 0.1 g of chitosan was introduced into the reaction mixture. The reaction mixture was kept at room temperature under constant stirring for another 24 h. To eliminate the bi-products and isolate the thiolated modified chitosan, Mod-Ch was separated via centrifugation (5000 rpm) and washed three times with ethanol.

### 2.5. Synthesis of thiol terminated chitosan capped silver nanoparticles (Mod-Ch-Ag NPs)

Mod-Ch capped Ag NPs were synthesized by the  $\text{NaBH}_4$  mediated reduction of  $\text{AgNO}_3$  as adopted before. 0.1 g of Mod-Ch polymer was dissolved in 100 mL aqueous acidic solution (pH-5). 50 mL of 0.05 g aqueous  $\text{AgNO}_3$  solution was added into thiol

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