Synthesis and characterization of stearic acid capped silver nanoparticles: pH dependent stabilization and colorimetric detection of Hg(II) in water

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Abstract

This work reports, synthesis of Ag nanoparticles in aqueous medium, under ambient reaction conditions using stearic acid as capping agent. Ag nanoparticles have been used for colorimetric detection of Hg^{2+} in water. Effect of pH of the medium on size and stabilization of silver nanoparticles has been studied. Synthesized by chemical reduction of $AgNO_3$ using $NaBH_4$, Ag nanoparticles were characterised by UV-visible spectroscopy, transmission electron microscopy (TEM), FTIR spectroscopy and TGA techniques. Quenching of intensity along with blue shift of SPR band of Ag nanoparticles is observed due to deposition of Hg layer over Ag nanoparticles. Change in colour of Ag nanoparticles from dark yellow to colourless led to naked eye detection of Hg^{2+} in water. The detection limit of Hg^{2+} in water was found up to 1ppm monitored by colorimetric response of Ag nanoparticles by UV-visible spectrophotometer. A simple and cost-effective process allows quick determination of Hg^{2+} in water. Copyright © 2018 VBRI Press.

Keywords: Stearic acid capped Ag nanoparticles, pH dependent stability, Effect of pH on size, Hg detection.

Introduction

Contamination of water by heavy metals is one of the most serious environmental concerns, which possesses grave risk to living organisms. Mercury is one of the most toxic heavy metals that pose threat for both plants and humans. Human exposure to high levels of mercury can cause harm in brain, heart, kidneys, lungs, and nervous system [1]. In Plants mercury reduces photosynthesis and traspiration [2]. Industrial pollution is one of the major emitters of mercury into environment, which is then methylated by microorganisms and enters into water bodies resulting chronic health effects for humans. Increasing industrial pollution aggravates the mercury contamination of environment and thus demands quick and reliable techniques to detect mercury in aquatic ecosystem. Further due to high solubility of Hg^{2+} ion in water, its contamination doesn't either change in colour of water or forms any precipitation, so a sensitive technique to detect even trace amount is highly desirable. Although traditional analytical techniques are available for detection of Hg^{2+} in water but sophisticated instrumentation, tedious sample preparation, lack of portability, makes them unsuitable for onsite and quick detection of Hg^{2+} in water. Efforts have been made for rapid and facile detection of mercury by nanomaterial based tools [3]. Noble metal nanoparticles like Au and Ag have attracted attention as colorimetric sensors [4] for detection of heavy metals, because of their sharp and intense surface plasmon resonance (SPR) band which is sensitive towards local environment and the shape of this SPR band gets affected by various chemisorbed solutes. When metal cations like Hg^{2+} is chemisorbed with silver nanoparticles, the SPR band gets affected strongly. This effect can be attributed to (i) high affinity of Hg^{2+} for Ag and (ii) donation of electron density from Ag to Hg^{2+}. Thus variation in concentration of chemisorbed Hg^{2+} ions on Ag nanoparticles leads to variation in intensity and wavelength of SPR band, facilitating colorimetric detection of mercury in water sample. Au and Ag nanoparticles dispersed in water have shown the blue shift of the SPR peak in response to Hg^{2+} [5]. Utilizing SPR phenomenon, some researchers have reported colorimetric detection of Hg^{2+} using Ag nanoparticles [4,6-8]. Ag nanoparticles, embedded in polymer thin film [9] and coated with biopolymers [10] were used for detection of Hg^{2+}. Along with Ag nanoparticles, mercury specific oligonucleotide, thymine has been reported for colorimetric detection of Hg^{2+} [11]. Ag nanoparticles surface functionalized with β-alanine dithiocarbamate [12], 3,4-Dihydroxy-[L-phenylalanine] (DOPA) [13], rhodamine [14], 4-mercaptopyridine [15] have been used to detect Hg^{2+}. Although efforts were made to provide sensitive and reliable methods to detect Hg^{2+} using Ag nanoparticles but most of the reports involve not only complicated procedure for synthesis of Ag nanoparticles

but also used expensive ligands for surface modification. So unmodified and label free Ag nanoparticles would be simple and inexpensive sensors for detection of Hg^{2+}. Chakraborty and his co-worker [**16**] reported a label free cysteamine capped Ag nanoparticles for colorimetric detection of Hg^{2+}. Wang *et al.* [**17**] reported detection of Hg^{2+} in waste water and blood sample by using label free Ag nanoparticles. Therefore this work was designed for a simple one pot approach for synthesis of silver nanoparticles for colorimetric detection of Hg^{2+} in water without any surface modification.

Usually, Ag nanoparticles have been synthesized by the chemical reduction of a homogeneous solution containing silver salt and a series of capping agents such as reverse micelles [**18**], surfactants [**19**], dendrimers [**20**], alkanethiol [**21**], alkylamine [**22**], amino acid [**23**] and carboxylic acid [**24**]. Among those, long chain carboxylates have been found to be effective for metal nanoparticles. Piao and his co-workers studied effect of chain length of mixed carboxylic acids on stability of Ag nanoparticles [**25**]. Alkyl carboxylate capped Ag nanoparticles have been synthesized from thermal decomposition of silver carboxylates at high temperature and high metal concentration [**26**]. Nakamoto *et al.* [**27**] reported synthesis of Ag nanoparticles from thermal decomposition of silver carboxylates in presence of alkyl amine at 80^0C. Most of the approaches cited in the literature involve tedious multistep thermal treatment or sophisticated techniques for the synthesis of Ag nanoparticles using carboxylates as capping agents. Therefore, synthesis of Ag nanoparticles using ambient reaction conditions is often required. Previously we have reported synthesis of Ag nanoparticles using myristic acid and sodium acetate as capping agents under ambient reaction conditions [**28, 29**]. This encouraged us to study and report a simple and modified method for preparation of monodispersed stearic acid capped Ag nanoparticles at room temperature. Carboxylic acids being prone to conformational changes with pH of the medium, it is also important to study stability of Ag nanoparticles in different pH.

Therefore, the present work reports, a simple and facile method for preparation of Ag nanoparticles using stearic acid as capping agent. To understand the stability of Ag nanoparticles in acidic and basic environment we have treated Ag nanoparticles with CH_3COOH and NH_4OH and reported pH induced capping efficiency of stearic acid and also the influence of pH on size of Ag nanoparticles. Stearic acid capped colloidal Ag nanoparticles of size 3-13 nm have been used to detect Hg^{2+} ions in water without using any further labelling of Ag nanoparticles. This investigation reveals a simple, convenient and quick technique for colorimetric detection of Hg^{2+} ions in water up to 1ppm concentration. Naked eye detection through change in colour of Ag nanoparticle from deep yellow to colorless (**Fig. 5**) after exposure to Hg^{2+} ions has been successfully explored up to the concentration limit 300ppm.

Experimental

Materials

$AgNO_3$(99.99%), $C_{18}H_{36}O_2$(98.5%) and $HgCl_2$ were purchased from Merck. $NaBH_4$(99.99%) was purchased from Sigma Aldrich. Methanol used was of analytical grade. All chemicals were used as received. Millipore water (>18.0MΩ), purified using the Millipore Milli-Q gradient system, was used in all experiments. The glassware was washed with aqua regia and rinsed with millipore water prior to experiments.

Preparation of stearic acid capped silver nanoparticles

10 ml methanolic solution of 2.5mM stearic acid($C_{18}H_{36}O_2$) was put on stirring in a 50-ml round bottom flask equipped with a magnetic stirrer bar. Then 10 ml of freshly prepared ice cold aqueous solution of 4mM sodium borohydride ($NaBH_4$) was added drop wise into the methanolic solution of stearic acid under stirring. 10 ml aqueous solution of 1mM silver nitrate ($AgNO_3$) was added into the above mixture drop wise at a very slow rate and the mixture was continued to stir for 2 hours. $AgNO_3$ was reduced to silver nanoparticles upon addition of $NaBH_4$, manifested by an immediate change in colour of solution from colourless to dark yellow. After elimination of unreacted stearic acid by filtration, the colloid of Ag nanoparticles was centrifuged and washed with water. Colloidal Ag nanoparticles were mixed separately with CH_3COOH to adjust pH 6 and NH_4OH for pH 10. pH of the as prepared colloid was 6.9.

Characterizations

UV-vis absorption spectra were obtained on a Varian Cary 100 dual beam spectrophotometer. Transmission Electron Microscopy (TEM) images were taken on Philips Morgagni 268, 200 KV electron microscopes by using carbon coated copper grids as substrates. For TEM analysis few drops of colloidal nanoparticles were put on a carbon coated copper grid and dried naturally at room temperature. FTIR spectra were recorded at room temperature on Perkin Elmer FTIR Spectrophotometer Spectrum 2000 in the scan range of 400-4000 cm^{-1}. Specimen for analysis was prepared as a KBr pallet of dry samples. Thermogravimetric analysis was performed on a Shimadzu-TA-60-WS Instrument at a heating rate of 30^0 C min^{-1}. pH measurement of silver colloids was performed on Elico Digital pH meter PH-5651.

Colorimetric detection of Hg^{2+} ions in water

The detection of Hg^{2+} was performed by adding 30μL aqueous solution of Hg^{2+} ions of a certain concentration into 2ml of colloidal stearic acid capped Ag nanoparticles. The mixed solution was incubated at room temperature for 5 minutes before spectral analysis. Aqueous solution of $HgCl_2$ was prepared with different concentrations, starting from 1 ppm to 1000 ppm.
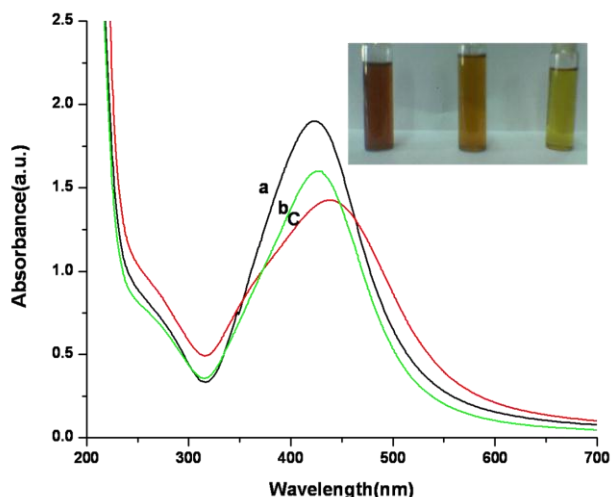
Fig. 1 UV-Visible absorption spectra of stearic acid capped Ag nanoparticle at (a) pH 7, (b) 6 and (c) 10. (inset) Photos of Stearic acid capped Ag nanoparticles, from left: at pH 6, 7 & 10.

Results and discussion

Formation of Silver nanoparticles

The colloidal Ag nanoparticles showed a sharp surface plasmon resonance(SPR) band at the wavelength 423 nm **(Fig. 1),** which arises due to collective oscillations of electrons in the conduction band as a result of interaction with UV-visible light. The well-defined SPR peak is indicative of spherical silver nanoparticles [**23,30**]. Ag nanoparticles at acidic (pH 6), neutral (pH 7) and basic medium (pH 10) exhibit different colours **(inset Fig. 1)** with varied SPR bands in the wavelength range 423-440 nm **(Fig. 1).** From the absorption spectra it is clearly evident that the SPR band of silver nanoparticles is influenced by pH of the medium. This can be attributed to the effect of pH on size and interparticle separation of Ag nanoparticles. At pH 7 maximum absorption occurs at 423nm. At pH 6 and pH10 absorption takes place at 428 and 440 nm respectively. Red shift of plasmon band indicates increase in particle size when pH deviates from neutral range and the result is in agreement with the previous reports [**31,32**] suggesting, red shift of absorption band towards longer wavelength as particles become bigger. This observation from SPR band indicating variation in size of silver nanoparticles with pH is also consistent with TEM analysis. As shown in TEM **(Fig. 2),** at pH 6 average size of the silver nanoparticles is observed as 26 nm, at pH7 it is 3-13 nm and at pH 10 it is 126 nm. Besides size, pH of the medium also influenced interparticle separation. In acidic medium particles are more aggregated in contrast to basic medium, where particles are very well dispersed **(Fig. 2).** This can be attributed to pH induced ionization of capping agent, stearic acid. Since pKa value of stearic acid is 10.15 [**33**], so ionization of carboxylic acid group is prominent in basic medium (pH>10). In basic medium ionization of carboxylic acid to carboxylate ions, leads
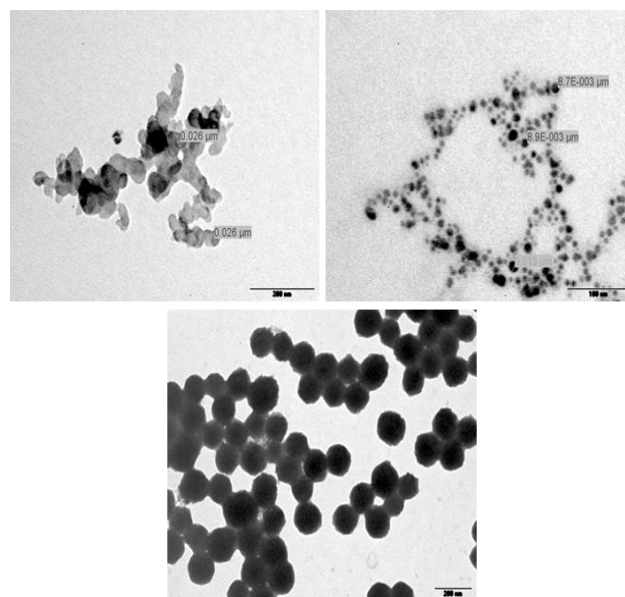

Fig. 2. TEM images of stearic acid capped Ag nanoparticles (from left to right) at pH 6, 7 & 10.

to increase in electrostatic force of repulsion between adjacent carboxylate ions around silver nanoparticles, which ultimately make particles less dense with very good dispersity **(Fig. 3).** However, in acidic medium ionization of stearic acid can be ignored as pKa value is far greater than pH value and thus negligible ionization of stearic acid would decrease the electrostatic force of repulsion, leading to aggregation of silver nanoparticles. Besides this, increase in particle size in acidic medium is due to dissolution of Ag nanoparticles and aggregation with other existing particles in solution, resulting formation of bigger particles. This is consistent with previous observations showing dissolution and aggregation of Ag nanoparticles particles in acidic medium [**34**]. Also in basic medium aggregation of small particles leads to increase in size of nanoparticles, which is in agreement with previous ostwald ripening studies [**35**].
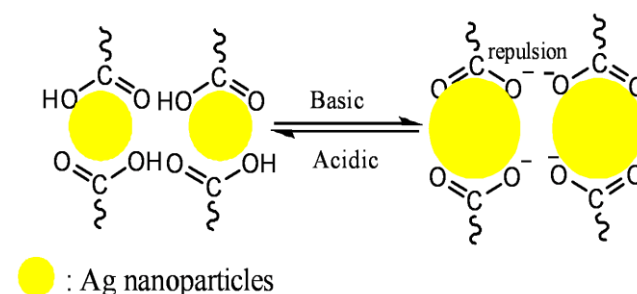

Fig. 3. Schematic representation of pH induced dispersion of Ag nanoparticles.

Presence of stearic acid as capping agent on the surface of Ag nanoparticle is confirmed by FTIR spectra. Appearance of a band at 2850-3000 cm^{-1} is attributable to

the stretching of CH_2 group and terminal CH_3 group. The bands in the region of 1550- 1620 cm^{-1} corresponds to COO- group. Also, the band at 3415 cm^{-1} is due to stretching vibration of OH of carboxylic acid group.

In order to understand the composition and thermal stability of stearic acid capped Ag nanoparticles, thermo gravimetric analysis was performed. TGA profile **(Fig. 4)** shows Ag nanoparticles are stable up to a temperature 250^0C. Weight loss observed after this temperature is due to decomposition/desorption of stearic acid from the surface of Ag nanoparticles. This observation further confirms presence of stearic acid as capping agent on the surface of Ag nanoparticles.
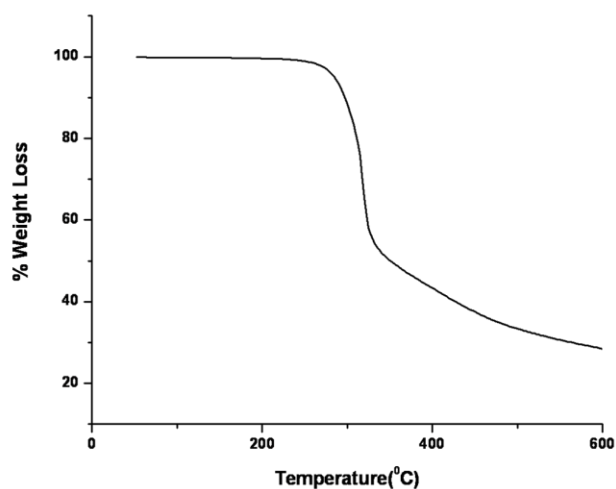
Fig. 4. TGA profile of stearic acid capped Ag nanoparticles.

Colorimetric detection of Hg^{2+} ions by Ag nanoparticles

Stearic acid capped Ag nanoparticles were tested for their application as colorimetric sensor for detection of Hg^{2+} in water sample. Ag nanoparticles having characteristic SPR band at 423 nm, suffers a sharp quenching of its intensity after addition of 1ppm Hg^{2+} solution (Fig. S1, SM). 50% reduction in SPR intensity was observed after addition of 1ppm Hg^{2+} solution into Ag nanoparticles. This strong quenching of SPR intensity of Ag nanoparticles enables stearic acid capped silver nanoparticle to act as a plasmonic sensor for detection of Hg^{2+} ions in water sample. With increase in concentration of Hg^{2+}, the SPR band shifted to lower wavelength (blue shift) besides quenching of intensity (Fig. S2, SM), which is also in agreement with previous report[10]. An appreciable blue shift in SPR band was observed in low concentration (1 to 10ppm) of Hg^{2+} (Fig. S2, SM), however there was significant blue shift as concentration of Hg^{2+} increased beyond 10ppm (up to 200ppm) (Fig. S3, SM). This blue shift of SPR band with quenching in intensity can be attributed to the donation of electrons from Ag metal particles to Hg^{2+} (eq 1) through formation of Hg layer on the surface of Ag nanoparticles [**36**].

$$Ag_m + (m/2)Hg^{2+} \xrightarrow{\quad} mAg^+ + (m/2)Hg \qquad (1)$$

Consistent quenching of SPR intensity along with blue shift was observed up to 200ppm of Hg^{2+}, but beyond this concentration, SPR band was completely disappeared and the solution became colourless from dark yellow **(Fig. 5)**, indicating complete dissolution of Ag nanoparticles. This observation shows, Hg^{2+} in water up to 300ppm can be detected by naked eye, using Ag nanoparticles, below this concentration we need to use spectrophotometric technique. Again, at further higher concentrations of Hg^{2+}, beyond 500 ppm, a shoulder was observed at wavelength 288nm (Fig. S3, SM) and this shoulder is due to formation of mercury drops, which is in agreement with the previous report [36] where it has been reported that mercury sol or mercury drop exhibits an absorption maximum at 285 to 290nm. In the begining, when concentration of Hg^{2+} is low, layer of reduced Hg (Hg^0) gets deposited on Ag nanoparticles but on further increasing concentration of Hg^{2+}, there is an increase in reduced Hg leading to formation of colloidal mercury drops. As a result, SPR band corresponding to Ag nanoparticle dissappears and peak for Hg develops at 288nm (Fig. S3, SM).
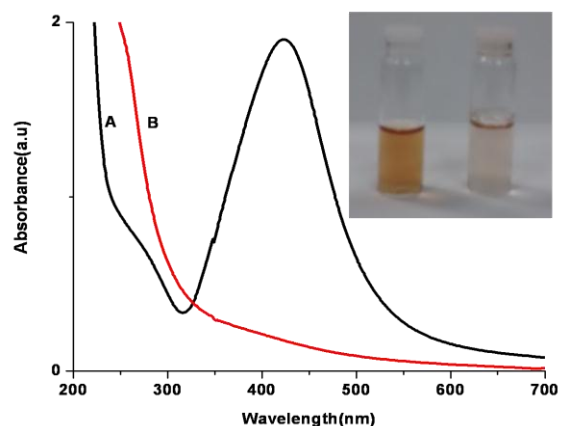

Fig. 5. UV-Visible absorption spectra and the corresponding images of Stearic acid capped Ag Nanoparticles(A) and Stearic acid capped Ag Nanoparticles with 300ppm $HgCl_2$(B).

Conclusion

In this study we have reported, preparation of stearic acid capped Ag nanoparticles in aqueous medium under ambient reaction conditions. Label free stearic acid capped Ag nanoparticles were used as colorimetric sensors for simple and quick detection of Hg^{2+} in water samples. Lowest detection limit of Hg^{2+} in water was observed to be 1ppm by colorimetric spectral analysis and 300ppm by naked eye. We have also investigated modulation of size and dispersity of silver nanoparticles as a result of pH induced ionization of stearic acid. Lower pH favoured the formation of denser nanoparticles because of weak repulsive forces between adjacent molecules of stabilizing agents. On the other hand, larger and well dispersed nanoparticles were formed at higher pH due to the stronger electrostatic repulsive forces

between adjacent molecules of stearic acids. This study of stability of Ag nanoparticles under basic and acidic conditions will provide insights for future applications of silver nanoparticles, where nanoparticles have to undergo acidic and basic environment.

Author's contributions

Conceived the plan: N.A.; Performed the expeirments: N.A.; Data analysis: N.A., N.K.K.; Wrote the paper: N.A. Authors have no competing financial interests.

Supporting information

Supporting informations are available from VBRI Press.

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