COLORIMETRIC DETECTION OF SILVER IONS IN AQUEOUS SOLUTIONS USING THIOL FUNCTIONALIZED MAGNETIC CORE-SHELL Fe₃O₄@SiO₂

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ABSTRACT

Thiol functionalized magnetic silica-core shell (MPTES-Fe₃O₄@SiO₂) is used in the colorimetric sensor for the recognition of silver ions. This detected system acts more sensitive and selectively for silver ions in real-time applications. Thiol functionalized core-shell magnetic nanoparticles interact with silver ions to form a metal-thiol complex with the appearance of yellow color in the solution with surface resonance peak (403cm⁻¹) in UV spectra. This colorimetric sensor is very cheap, and facile in the detection of a silver ion with the lower limit of the detection value of 10 nm. Furthermore, we have applied for the monitoring of the real samples of this sensing system with good recovery results.

Keywords: Thiol, Silica, Fe₃O₄, Colorimetric, Silver, Real Water Samples

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INTRODUCTION

Heavy metals naturally occur in the earth's crust. Anthropogenic activity like mining and other industrial applications may lead to an increase in the concentration of toxic metal ions in the plant, animal and human tissues. The potential toxicity of this heavy metal is specially noted from a health and environmental point of view. The World Health Organization listed out the major toxic heavy metals for major public concern, such as cadmium, mercury, silver, copper, lead, arsenic, selenium, manganese, chromium, cobalt, nickel and zinc.¹⁻⁸ Among the different heavy metals, silver is extensively used in major industries such as jewelry, electroplating, photography, anticorrosive alloys and mirrors. The rapid utilization of silver in industries leads to contamination of soluble silver in aquatic bodies. It has been reported that nearly 80 tons of silver were contaminated with surface water every year. The public consumption of water containing silver more than 0.9 mmol/L is toxic. Higher consumption leads to the deposition of silver in the body tissues resulting in a disease called argyria. The symptoms of this the disease are changing in coloration noticed in the eyes, skin and mucous membranes. The gray coloration of this tissue, sometimes wrongly diagnosed as symptoms of cyanosis.⁹⁻¹⁰

Several conventional methods have been employed for the investigation of trace-level silver ions in aqueous solution, including atomic absorption/emission spectroscopy¹¹, inductively coupled plasma mass spectroscopy (ICP-MS)¹² and ion-selective electrodes. Although these techniques are very sensitive, there are some drawbacks to these techniques. It requires highly sophisticated tools, a more expensive and complicated preparation process which limits the use of this technique in the detection process. More recently, organic species, molecular complexes, nanomaterials, quantum dots and DNA-based materials have been adopted as fluorescent and electrochemical sensors to detect Ag⁺. As far as our knowledge, metal cation sensors based on coordination-driven discrete molecular containers are extremely infrequent.

The most practical and convenient sensors are colorimetric as compared with other fluorescent and electrochemical sensors, colorimetric methods are more superior to others by their properties like an economical, simple instrument, facial procedure and visual appearance in bare eyes after incorporating a specific type of metal ions, even at very low analyte concentrations.^{13,14}

Thiol functionalized magnetic silica-core shell nanoparticles (MPTES-Fe₃O₄@SiO₂) are used in the colorimetric sensor for the recognition of silver ions.^{15,16} This sensing system act as an extremely sensitive and choosy detection of silver ions in real-time applications. Thiol functionalized core-shell magnetic nanoparticles interact with the silver ions to form a metal-thiol complex with an appearance of yellow color in the solutions with the surface resonance peak observed at 403 nm in UV spectra. This colorimetric sensor is an inexpensive and simple way of detection process with a good limit of detection value as 10 nm. Furthermore, we have applied this sensing system for the monitoring of the real water samples with good recovery results.

EXPERIMENTAL

Materials

FeCl₃.2H₂O, ethylene glycol, silver nitrate, 3-mercaptopropyltrimethoxysilane (3-MPTS), and tetraethylorthosilicates (TEOS) were procured from Sigma Aldrich in India. Ammonia solution and hydrochloric acid (HCl, 37%), were purchased from Merck (India).

Preparation of Fe₃O₄ Nanoparticles

The magnetic nanoparticles were synthesized by a solvothermal method. In a 100ml beaker, 50ml of ethylene glycol was taken, to this Sodium acetate (3.60g) and FeCl₃.6H₂O (1.35g) were dispersed and the mixer is continuous stirred with a magnetic stirrer till the solution color turns to yellow. Then the solution is heated for 8 h. at 200°C in a stainless-steel autoclave coated with Teflon. The obtained product was cooled and washed sufficiently with ethanol followed by distilled water. Then allowed to dry in a hot air oven at 65°C for 12 h and stored for further use.

Synthesis of Silica-coated Fe₃O₄ Nanoparticles

By the simple sol-gel method, Silica was coated on Fe₃O₄ nanoparticles. In a 10 ml of ethanol solution, 1 mg of Fe₃O₄ nanoparticles was dispersed and sonicated for 30 minutes. In this solution ammonium hydroxide was included to maintain the solution pH and 3 ml of tetraethylorthosilicates (TEOS) was incorporated and stirred in the solution for 24h. Then it was centrifuged to remove the Fe₃O₄@SiO₂ NPs and washed with ethanol followed by distilled water sufficiently to remove trace level unreacted chemicals.

Preparation of Functionalized Fe₃O₄@SiO₂ NPs

The synthesized Fe₃O₄@SiO₂ nanoparticles were activated by 100 ml HCl (1M) for 12 hrs. After activation, it was brought back to neutral pH by washing with distilled water. The activated Fe₃O₄@SiO₂ further washed with 50ml of ethanol and 20 ml toluene followed by three times. Then it was dispersed with toluene and shifted into a 100 ml round bottom flask. To this 10 ml of 3-MPTS was added. The mixture was kept for reflux under 60° C for 24h. After this period, the obtained product Fe₃O₄@SiO₂-SH nanoparticles were extracted from the solution by an external magnet and dried hot air oven. The schematic preparation of the proposed nanoparticles and the interaction between the silver ions are depicted in Scheme-1.

RESULTS AND DISCUSSION

Characterization

The morphology of Fe₃O₄ and Fe₃O₄@SiO₂ is represented in Fig.-1(a) and (b). In Fig.-1a, the multi-dispersed nanoparticles, Fe₃O₄ nanoparticles with spherical shape are perceptible. After mixing Fe₃O₄ nanoparticles with silica it was prominent that the dark Fe₃O₄ NP well implanted in the light gray SiO₂ matrix and constructed Fe₃O₄@SiO₂. Wide-angle XRD spectrum of Fe₃O₄, Fe₃O₄@SiO₂ is shown in Fig.-2(a). It shows seven peaks resolved at 18.1, 30.1, 35.4, 37.0, 53.3, 56.9 and 62.5 according to JCPDS # 89 0691.¹⁴ This peak shows that these samples are in the inverse spinel structure of Fe₃O₄ and new peaks with broadband centered at 2θ = 22° have appeared assigned to the amorphous form of SiO₂. Further confirmation of surface groups of core-shell magnetic nanoparticles are examined in FT-IR spectra (Fig.-2(b)). Three

types of materials Fe_3O_4 , $\text{Fe}_3\text{O}_4@\text{SiO}_2$ and $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-SH}$ show a wide band around 580 cm^{-1} was assigned to Fe-O band stretching. Whereas the large band observed at 3400 cm^{-1} was ascribed to the band stretching of the O-H bond. The appearance of a strong band around the 100 cm^{-1} was attributed to the Si-O-Si stretching of $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-SH}$. In the FT-IR spectrum of $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-SH}$, there is no absorption peak for the -SH group since it possesses very low thiol content and less IR sensitivity. The stretching frequency at 2900 and 2850 cm^{-1} was attributed to the stretching of the C-H methylenes of the alkyl chain. This confirms that the MPTS is effectively bounded on the surface of $\text{Fe}_3\text{O}_4@\text{SiO}_2$.

Scheme-1: Representation Diagrams for the Synthesis of $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-SH}$ Sorbent and its Detection of Silver in Aqueous Solution (Photograph)

Fig.-1: The SEM Images of (a) Fe_3O_4 and (b) $\text{Fe}_3\text{O}_4@\text{SiO}_2$

Fig.-2(a) XRD Patterns of the Samples of Fe_3O_4 and $\text{Fe}_3\text{O}_4@\text{SiO}_2$, (b) FT-IR Spectra of Fe_3O_4 , $\text{Fe}_3\text{O}_4@\text{SiO}_2$ and $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-SH}$

Colorimetric Sensing of Ag^+ Ions

UV-Vis absorption spectra were taken for different materials such as $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-SH}$, $\text{Fe}_3\text{O}_4@\text{SiO}_2$ and Fe_3O_4 shown in Fig.-3. Except for $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-SH}$, other two materials like magnetic nanoparticles behave similarly not produce any absorption peaks in the range of 250-1100 nm indicate that the coating of silica layer not affect the SPR change of the magnetic nanoparticles. After the addition of silver ions in thiol functionalized silica coated core-shell nanoparticles, the yellow color of the solution was obtained because the formation of metal-thiol complexes and absorption peak appeared at 403 nm.

Fig.-3: UV-Vis Absorption Spectra of Fe_3O_4 , $\text{Fe}_3\text{O}_4@\text{SiO}_2$ and $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-SH}$

Detection of Ag^+ Ions

The sensitivity study of the thiol functionalized silica-coated core-shell magnetic nanoparticles with silver ions in Fig.-4(a). Display the response of UV-Vis spectra of different Ag^+ ion concentrations (10-50 mM). As the concentration of Ag^+ ions increases from 10 to 50 mM in the solutions, corresponding to the absorption intensity also increases in the solutions. The detection limit of this colorimetric sensor is 10mM, which is comparable to other colorimetric sensors. Figure-4b shows the graphical plot between the concentrations of silver ions and absorbance. A good linear relationship was observed with the correlation coefficient of 0.973 and the limit of the detection value of 10nM for Ag^+ ions based on the 3σ method,

which is analogous to other colorimetric sensors. The selectivity study was carried out with the proposed sensing system with Ag^+ and different metal ions. The UV absorption spectra were analyzed for Ag^+ and other counter metal ions. The Pb^{2+} and Hg^{2+} ions show weak absorption peaks and Ag^+ ions show a strong absorption peak at 403 nm in Fig. 4b. Other divalent metals such as Ni^{2+} , Co^{2+} , Cu^{2+} , Zn^{2+} , Mn^{2+} and Mg^{2+} exhibit similar absorption intensity. Figure-4c clearly shows that only Ag^+ ions in the solution are able to produce an absorption peak in intensity at 403 nm with the yellow coloration. The other counter ions have negligible amounts of absorption peaks in UV absorption spectra evident that these ions have no interference with that of Ag^+ in the detection process. Therefore, $\text{Fe}_3\text{O}_4 @ \text{SiO}_2\text{-SH}$ is an excellent colorimetric sensor for the determination of Ag^+ ions in an aqueous solution, which can be utilized for environmental applications.

Fig.-4: (a) Graphical Plot for the Absorption Spectra Vs Concentrations of Silver Ions, (b) Linear Relationship between the Concentrations of Silver Ions and Absorbance, (c) Absorption spectra of Ag^+ with Hg^{2+} and Pb^{2+} , (d) Selectivity Study of Different Metal Ions with Silver Ions

Determination of Ag^+ in Real Water Samples

The projected colorimetric sensing system was investigated with real water applications. The $\text{Fe}_3\text{O}_4 @ \text{SiO}_2\text{-SH}$ nanoparticles used to analyze the tap water samples collected near the college campus since silver ions were absent. Samples were spiked with the silver nitrate stock solution of concentration 10 mM, 20 mM and 30 mM and analyzed for the presence of silver in the samples. All the samples show promising data. The satisfactory results are tabulated in Table-1. The result confirms that the proposed sensor is more capable of the precise detection of Ag^+ in real water samples.

Table-1: The Amount of Ag^+ in Environmental Samples proposed by this Sensor.

Sample	Ag^+ SPIKED (mM)	Detected $\pm$ SD	Recovery (%)
TAP WATER	10	9.897 ± 1.001	97.94
	20	19.785 ± 1.012	97.85
	30	29.676 ± 1.024	98.38

CONCLUSION

We have designed an inexpensive, simple, highly sensitive and choosy recognition of Ag^+ using a colorimetric sensor. The addition of thiol functionalized $\text{Fe}_3\text{O}_4 @ \text{SiO}_2$ NPs with silver ions leads to the formation of metal-thiol complex with a change in color of solution due to the aggregation between NPs and silver ions. The interference of other metal ions with silver ions is negligible with the proposed sensing system. This colorimetric sensing method can achieve a detection limit of Ag^+ of 10 nM in an aqueous

solution. The potential application of the suggested sensor was studied in a real water sample. The results obtained show the projected sensor is more expeditious and economical for on-site detection of Ag^+ ions in environmental monitoring.

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