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Naked eye sensing of Hg(II)using β-cyclodextrin functionalized Silver nanoparticles

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Abstract : Green synthesis of nanoparticles is an emerging branch of nanotechnology. The characterization and sensing application of microwave synthesized and β-cyclodextrin functionalized silver nanoparticles are reported in this work. The formation of silver nanoparticles was verified by UV-Vis spectroscopy and characterized by TEM and XRD analyses. The silver nanoparticles were used to detect Hg^{2+} ions colorimetrically by visible color change in aqueous medium. At higher pH value the deprotonated secondary hydroxyl group of β-CD functionalized silver nanoparticles shows the highest chelation toward Hg^{2+}ions thereby inducing AgNP aggregation. The prepared silver nanoparticles were successful in sensing of mercury (II) ion even in a very low concentration of the order of 10^{-10} mol L^{-1} with high selectivity and sensitivity over K^+, Mg^{2+}, Mn^{2+}, Na^+, Fe^{3+}, Zn^{2+}, Ni^{2+}, Co^{2+} and Ba^{2+} ions.

Key Words : Silver nanoparticles, Uv-Vis spectrocopy, TEM, XRD.

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1. Introduction

Divalent heavy metal ions can easily bind with the biomolecules present in the living system. It causes adverse side effects in human, even in the trace quantity present. The contamination of drinking water with Hg^{2+} poses a series of threats in the world. Hg^{2+} is one of the most stable inorganic forms of mercury and it is also a caustic and carcinogenic with high cellular toxicity.

Among the heavy metal ions Hg^{2+} can damage the brain [1], nervous system, kidneys, and endocrine system. Hence it is an urgent need to detect Hg^{2+} in wells, rivers, and other bodies of water to evaluate the safety of drinking water and in the environment. Even though many classical instrumental methods [2] such as HPLC [3,4] and capillary electrophoresis [5] are already available, many of them are time-consuming, labor-intensive, require relative expensive instrumentation and are not readily adaptable to field determination hence there is a need for designing a simple, low cost and selective colorimetric sensor for the sensing of mercury. Recently metal nano sensors are used for the sensing of biomolecules [6], metal ions, anions [7] and simple gaseous molecules.

β-CD functionalized Ag NPs were used for the detection of aromatic isomers. Hongliang Tan developed adenosine monophosphate functionalized silver nanoparticles as colorimetric sensor to determine Hg^{2+} ions in aqueous solution [8], mercaptopropionic acid-modified Au nanoparticles in the presence of 2,6-pyridinedicarboxylic acid for the highly selective and sensitive detection of Hg^{2+} ions reported by Huan-Tsung Chang [9], sensing of spectroscopically silent heavy metal ions like Hg^{2+}, Cd^{2+} and Pd^{2+} has been described by Joseph T. Hupp and co-workers [10] . A novel para sulfonatocalix[4]arene modified silver nanoparticles were used to probe histidine in water [11]. Gold and silver nanoparticles and rhodamine 6G based fluorescent sensors for mercury (II) are reported [12-15]. Here in this present work, we report the β-CD functionalized Ag NPs for the sensing of mercury in water.

2. Experimental details

2.1 Chemicals

Silver nitrate (99.99%), metal salts and mercuric chloride were purchased from Himedia Chemicals. Sodium borohydride (A.R.) and β-Cyclodextrin were purchased from Merck. All other chemicals were used as received without further purification. Double deionized water was used throughout the experiments. The metal ion stock solutions were prepared by dissolving a known amount of chloride salts of the metal. All glassware were thoroughly cleaned with aqua regia and rinsed thoroughly with deionized water prior to use.

2.2 Synthesis of silver nanoparticles

Silver nanoparticles were prepared by the aqueous reduction of silver nitrate (1 mM, 50 mL) with trisodium citrate (1%, 1 mL) using the method of Lee and Meisel [8]. The reaction was also carried out under microwave irradiation, employing a domestic microwave oven. During preparation, the solution turned to the characteristic yellowish colour change, indicating the formation of silver nanoparticles.

2.3 Functionalization of silver nanoparticles

The functionalization was modified from previously reported in the literature [9,10], to ensure the successful preparation of the nanoparticles 5 mL of deionised water and 0.6 mg β-cyclodextrin was mixed thoroughly for 10 minutes to form a clear solution of β-CD. The silver nanoparticles were functionalized by mixing 5 mL of 0.12mg ml^{-1} of β-CD solution with 5 mL of synthesized AgNPs. The mixture was diluted with 10 ml of water and stirred thoroughly for 10 minutes to complete the functionalization.

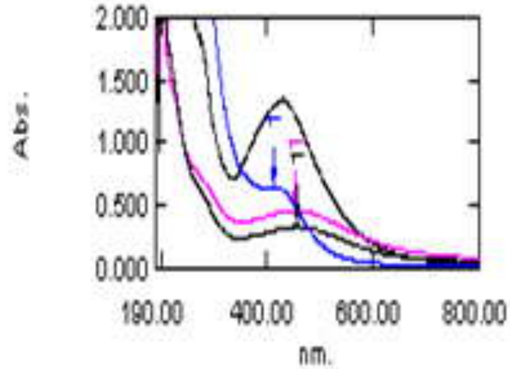
3. Characterization of materials

Absorption spectra of samples were recorded on a UV-2550 UV-Vis Spectrophotometer (Shimadzu) at room temperature. Nanoparticles were analyzed from the conventional TEM micrographs recorded on JEOL JEM-2010 transmission electron microscope. The crystallinity and crystal phases of the prepared nanoparticles was determined by a Rigaku X-ray powder diffractometer (XRD) with Cu Kα radiation (l = 1.54178 Å) with Bragg angle ranging from 30 to 80°.

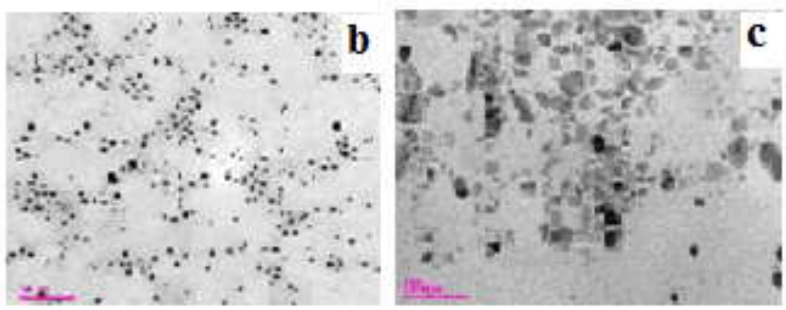
4. Results and Discussions

4.1 Absorption studies

The formation of nanoparticle is confirmed by the yellow color change due to the reduction of Ag^+ ions by trisodium citrate and it is also confirmed by absorption spectra. The synthesized nanoparticles exhibited yellow coloration whose absorption measurements revealed that a sharper surface plasmon resonance (SPR) band was observed at 430 nm (Figure 1a), the characteristic wavelength representing the formation of silver nanoparticles.



a) Absorbption spectrum of AgNPs

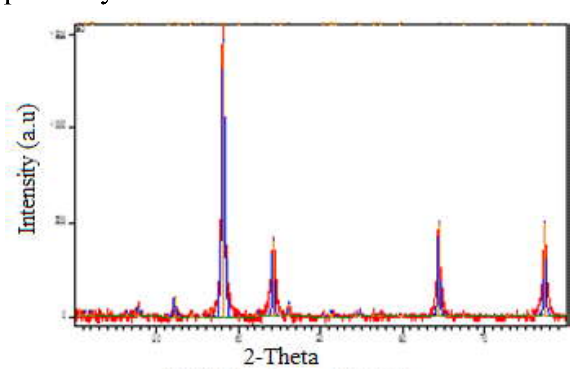


b) TEM images of β-CD functionalized Ag NPs c) AgNPs in presence of Hg^{2+}

Figure 1.

4.2 Diffraction studies

The XRD diffraction peak confirms the crystalline and fcc structure of the silver nanoparticles. The peaks observed at 38.6° 44.5°, 64.6°, and 77.2° were corresponding to 111, 200, 220, and 311 reflections respectively.

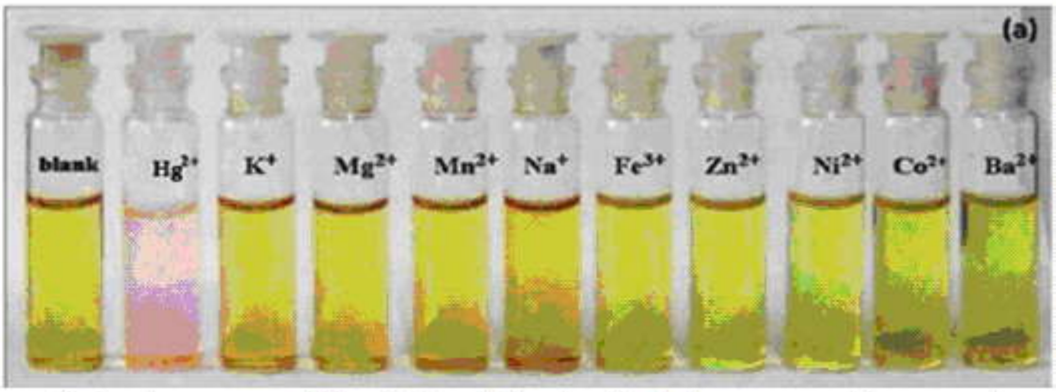


XRD Spectrum of AgNPs

Figure 2.

4.3 Sensing of Hg^{2+} ions

The β-cyclodextrin functionalized colloidal silver nanoparticles solution was used for the sensing of metal ions.



colorimetric response of β-cyclodextrin functionalized silver nanoparticles towards various metal ions

Figure .3

Sensor studies were performed by adding of 1 mL ofβ-cyclodextrin functionalized silver nanoparticles and 1 mL of test solution containing the metallic ions such as copper(II) chloride/ potassium chloride/magnesium(II) chloride/manganese(II) chloride/sodium chloride/ ferric(III)chloride/zinc acetate/nickel(II) chloride/cobalt(II) chloride/barium(II) chloride/ mercuric(II)chloride of 1.0×10^{6} $mol{\cdot}L^{-1}$was added and stirred for 30 min. To investigate the sensitivity effect of the silver nanoparticles toward Hg^{2+}metal ion, mercury ions with the concentrations of $10^{-6}/10^{-7}/10^{-8}/10^{-9}/10^{-10}/10^{-11}/10^{-12}$ $mol{\cdot}L^{-1}$was added to the silver nanoparticles solution. The sensing ability and selectivity of the prepared silver nanoparticles were studied by using UV/visual spectroscopy. At higher pH 10.5 the deprotonated functionalized silver nanoparticles chelates with mercury ions that can be visualized by colorimetric color change, light pink colour in the figure and thereby induced aggregation and increment of particle size confirmed by TEM analyses.

5. Conclusion

A sensitive, selective and simple colorimetric sensor using functionalized silver nanoparticles to detect Hg^{2+} in aqueous solution was reported. Theβ-CD functionalized Ag NPs recognizing mercury ions by quick visual color change at higher pH, induced aggregation of silver nanoparticles and it was confirmed by TEM analyses. Furthermore this method shows excellent sensitivity of the order of 10^{10} mol L^{-1} with high selectivity over K^{+}, Mg^{2+}, Mn^{2+}, Na^{+}, Fe^{3+}, Zn^{2+}, Ni^{2+}, Co^{2+} and Ba^{2+} ions.

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