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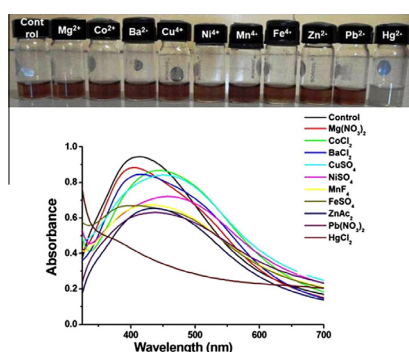
## Structural, morphological and optical studies of L-cysteine modified silver nanoparticles and its application as a probe for the selective colorimetric detection of Hg<sup>2+</sup>

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### HIGHLIGHTS

- L-Cysteine capped silver nanoparticles-synthesised by chemical reduction method.
- Characterised using UV/Vis spectroscopy, TEM, zeta potential, XRD and SERS.
- Cysteine is bound to the Ag surface through the thiolate moiety.
- Selective colorimetric detection of Hg<sup>2+</sup> through free COO<sup>-</sup> end of adsorbate.

### GRAPHICAL ABSTRACT



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### ABSTRACT

We report an extensive study on the evolution of a highly facile, selective colorimetric probe for Hg<sup>2+</sup> detection using cysteine modified silver nanoparticles. The nanoparticles are stable in a basic medium and the Surface Enhanced Raman Spectrum (SERS) reveal that the cysteine is bound to the Ag surface through the thiolate moiety with the charged carboxylate group pointing outwards in a morphology that lends itself to sensor applications. In the presence of Hg<sup>2+</sup>, the absorption peak is quenched resulting in a drastic colour change. The sensor displays high selectivity to Hg<sup>2+</sup> over other metallic ions.

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### Introduction

Noble metal nanoparticles (NPs), especially of silver (Ag) and gold, have attracted much attention due to their remarkable optical, electrical and chemical properties. Ligand protected metal NPs improve the surface to volume ratio and have been

increasingly explored as analytical tools in many fields [1–4]. The incorporation of organic ligands onto NP surfaces provides not only stability to these nanoentities, but also important surface functionalities which make them good candidates for specific applications [5]. The noble metal–biomolecule conjugates find widespread applications as colorimetric sensor for detection of molecules [6] or metal ions [7].

Various groups have focused their research on the interaction between biomolecules and nanometal surfaces using different

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spectroscopic techniques [8–10]. In an ongoing study of amino acid functionalized Ag NPs, we had reported the comparison of histidine functionalized silver NPs prepared by two different methods [11] with potential sensor application. Several investigators have studied the interaction of molecules containing a thiol group with gold and silver NPs [12,13]. Generally, these molecules interact with the Au or Ag nanometal surface via the sulphur atom resulting in the formation of the Au–S or Ag–S bond respectively [14,15]. Adsorption of this ligand via the carboxylate group has also been observed [16]. The stability of these nanometal–biomolecule conjugates depends on several factors like ligand concentration, temperature and pH [17]. Podstawka et al. [18] studied different amino acid-stabilized silver nanoparticles and established that cysteine molecules interacted with the Ag NPs through the carboxylate, the  $-NH_2$  and the  $-CS$  groups.

Mercury is a widespread heavy metal in the environment with high toxicity and has a severe adverse effect on human health. Mercury pollution comes from diverse sources including both natural and human activities [19]. The water soluble divalent mercuric ion ( $Hg^{2+}$ ) is one of the most common and stable forms of mercury pollution [20]. Environmental monitoring of aqueous  $Hg^{2+}$ , using a simple colorimetric sensor for on-site and real-time metal ion detection, is desirable. Colorimetric methods can be easily monitored with the naked eye, does not require any advanced instruments and is cost effective.

Ravindran et al. [21] showed that cysteine functionalized silver nanoparticles could be used as sensors to recognise  $Cr^{2+}$  ion. Li et al. [22] utilised cysteine capped Ag in the presence of  $Hg^{2+}$  to detect histidine. Few groups reported the colorimetric detection of  $Hg^{2+}$  in the presence of cys-gold NPs [7,12]. The spectral and colorimetric detection of  $Hg(II)$  ions were carried out using the synthesised  $SiO_2/Ag$  NPs by Rameshkumar et al. [23]. Colorimetric and fluorescent detection of  $Hg^{2+}$  were carried out using rhodamine derivative-modified filter papers [24]. Liu et al. used fluorescent Ag clusters in the detection of  $Hg^{2+}$  [25].

Cysteine, a common amino acid possesses a terminal thiol moiety, and can bind onto the surface of Ag NPs through Ag–S bond to form the cysteine functionalized silver NPs. Exploiting this property, we describe a new, facile colorimetric sensor for the detection of  $Hg^{2+}$ . This is a much simpler and more cost-effective method as compared to the existing methods which involve the preparation of  $Hg^{2+}$  assay or dye derivatives [24,25]. Through this approach, aqueous  $Hg^{2+}$  can be detected by the naked eye in a simple way.

The effect of pH on the cysteine–Ag nanoparticles (cys–Ag NPs) using UV–Vis absorption spectrum is investigated. Zeta potentials at different pH are used to determine the stability of cysteine capped silver NPs. The crystallographic structure was confirmed by the XRD pattern and the morphology analysed through the TEM outputs. The binding site of the molecule on the silver surface was identified through the SERS measurements and the cys–Ag NPs used as a colorimetric sensor to detect  $Hg^{2+}$  without using any other conjugate molecule.

## Experimental

### Materials

Silver nitrate,  $AgNO_3$ , of 99.8% purity (NICE) was used as a precursor, L-cysteine ( $C_6H_9N_3O_2$  99.0% – HIMEDIA) as the capping agent and sodium borohydride ( $NaBH_4$   $\geq 95\%$  MERCK) as the reducing agent. Nitric acid ( $HNO_3$ ) and sodium hydroxide ( $NaOH$ ) were used to adjust the pH and accelerate the oxidation and reduction reaction in water. All chemicals were of analytical grade and used as purchased without further purification. Millipore water was used throughout the experiments.

### Synthesis

#### Synthesis of silver nanoparticles

Silver sol was prepared according to Creighton's method [26]. In brief 20 ml of silver nitrate solution (1 mM) was added drop-wise to 60 ml of sodium borohydride solution (1 mM) with vigorous stirring. Before mixing, both solutions were chilled to ice temperature. After the complete addition of  $AgNO_3$ , a yellow solution (silver sol) was obtained which was stable for more than 6 months.

#### Optimisation of cysteine capped Ag NPs

L-Cysteine was added drop-wise to  $AgNO_3$  which was constantly stirred with a magnetic stirrer. This solution was added drop by drop to  $NaBH_4$  solution with vigorous stirring. The addition of aliquots L-cysteine showed a distinguishable range of colour depending on the cysteine concentration (Fig. 1). The samples prepared with varying concentrations of cysteine (Table 1) were stored at 5 °C and observed each day. Sample 3 alone (1 mM) was found to be stable and was used for further studies.

### Characterisation

A Double beamed spectrophotometer (Helios alpha) was used for absorption spectra measurements. In every case Millipore water was taken as the blank solution. To obtain the TEM images the colloid was drop casted on a carbon coated Cu grid and the solvent evaporated. The specimen was examined on a FEI-Tecnai 30G<sup>2</sup>S-Twin Transmission Electron Microscope at 300 kV.

The zeta potential of the synthesised Ag NPs and the L-cysteine capped silver (Cys–Ag) NPs were determined by a Zetasizer (Malvern instruments) with 173° backscattered detection angle equipped with a He–Ne laser of wavelength 632.8 nm and beam diameter 0.63 nm.

X-ray diffraction (XRD) analysis of the drop-casted films on glass substrates from cys–Ag sample was carried out on a Model X'Pert, PRO, PW 3050/60 using Cu  $K\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ).

The Raman spectrum was recorded by back scattering geometry using He–Ne laser with an excitation of 633 nm and 16 mW power coupled with a LABRAM-HR 800 micro-Raman spectrometer

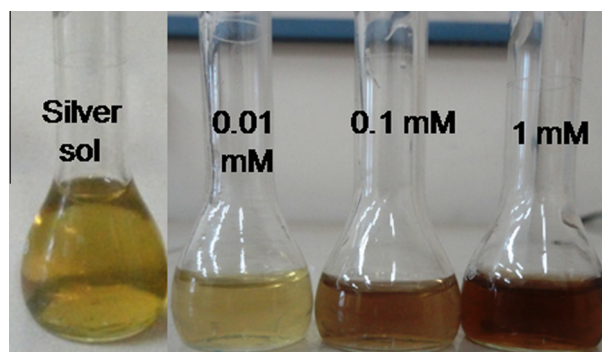


Fig. 1. (a) Silver colloid and (b–d) cys–Ag sol with cysteine concentration 0.01 mM, 0.1 mM and 1 mM respectively.

Table 1

Sample composition, colour and stability of cysteine capped Ag NPs [ $AgNO_3$ ] = [ $NaBH_4$ ] = 1 mM.

Samples	[Cysteine] (mM)	Observation
1	0.01	Colour became pale. Particles settled down
2	0.1	Colour changed from yellow to brown to grey. Remained stable for two days
3	1	Honey coloured. Remained stable for four months

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