

Carboxymethylagarose-AuNPs generated through green route for selective detection of Hg²⁺ in aqueous medium with a blue shift

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ABSTRACT

We report here a facile, rapid, cost-effective method *via* a green route for the selective detection of Hg²⁺ in aqueous media. In this study carboxymethylagarose (CMA) is used to generate gold nanoparticles and subsequently to act as a stabilizer for the CMA-functionalized gold nanoparticles (CMA-AuNPs). The resulting CMA-AuNPs was characterized by UV–visible, X-ray diffraction, transmission electron microscopy (TEM), dynamic light scattering (DLS), atomic force microscopy (AFM) and zeta potential measurements. Zeta potential value (~ -73 mv) of CMA-AuNPs in the aqueous medium shows its higher stability. When CMA-AuNPs were exposed to an aqueous Hg²⁺, a blue shift for its localized surface plasmon resonance absorbance (LSPR) band is observed along with significant colour change of the solution. The probe enables to detect Hg²⁺ in the range of 0.01–100 ppm even in spiked lake water samples. This study offers a sustainable and eco-friendly route for selective detection of Hg²⁺ in aqueous solution and may find potential application towards water purification.

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1. Introduction

Mercury, a well-known highly toxic and dangerous environmental pollutant routinely released from small scale gold mining, coal-based power plants, metal refining plants, oceanic and volcanic emissions *etc.* The long atmospheric residence time of Hg (0) vapour and its oxidation to soluble inorganic Hg²⁺ provide a pathway for contaminating surrounding environment including water and soil. Bio-organism like bacteria living in an aqueous environments transform inorganic Hg²⁺ into methyl mercury, which is a powerful neurotoxin that concentrates through the food chain in the tissues of fishes and marine mammals. Subsequent ingestion of methyl mercury by humans from sea-food and other dietary sources is connected to the many serious problems such as sensory, motor, and cognitive disorders. The higher levels of Hg²⁺ can be dangerous to the brain, heart, lungs *etc.* of humans. According to an estimate the total mercury released into the environment reaches to ~ 7500 t/year (Hoyle & Handy, 2005). The United Nations ratified

a new Convention on Mercury Control on January 19, 2013, following multinational dialogues that began on January 2013. Because toxic mercury ion contamination normally accumulates in existing organisms and slowly progresses over time, therefore timely detection of low concentrations of Hg in environmental water is a key issue for the researchers. Thus it is very important to develop an extremely high sensitivity, cost-effective and bio-based Hg²⁺ sensor that can provide real-time determination of Hg²⁺ levels in the environment, water, and food (Darbha, Ray, & Ray, 2007). A great effort has been exerted to detect Hg²⁺ using various detection techniques, including optical spectroscopy (Jiang *et al.*, 2012; Lim, Escobedo, Lowry, Xu, & Strongin, 2010; Rusin *et al.*, 2003; Wang *et al.*, 2005; Wang, Heon Lee, & Lu, 2008), electrochemical methods (Liu, Nie, Jiang, Shen, & Yu, 2009; Spătaru, Sarada, Popa, Tryk, & Fujishima, 2001), high-performance liquid chromatography (Chen, Chen, Jin, & Wei, 2009; Lu, Zu, & Yam, 2007), inductively coupled plasma mass spectrometry, and so forth (Chen *et al.*, 2009; Li *et al.*, 2006). However, most of these techniques require expensive instrumentation and complicated sample preparation in certain cases, which make them inappropriate for point of use applications. To overcome these drawbacks, a variety of colorimetric sensors based on gold nano particles (AuNPs) have been attempted for the simple and rapid detection of Hg²⁺ (Kumar & Paul, 2014; Lee, Ulmann, Han, & Mirkin, 2008; Maity, Kumar, Gunupuru, & Paul, 2014; Xue, Wang, & Liu, 2008; Yu & Tseng, 2008; Zhang, Xu, Yuan, Yang, & Yang, 2011).

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The utilization of nontoxic chemicals, environmentally benign solvents and renewable materials are some of the key issues that merit important consideration in a green synthesis strategy (Poliakoff & Anastas, 2001; DeSimone, 2002; Raveendran, Fu, & Wallen, 2003). In literature natural polymers like starch and chitosan are reported to stabilize silver nanoparticles (Raveendran et al., 2003; Huang & Yang, 2004b).

Nanoparticles have potential applications in medical diagnosis and therapeutics like detection of genetic disorders by using gold nanoparticles, (Boisselier & Astruc, 2009; Cao, Jin, & Mirkin, 2002; Taton, Mirkin, & Letsinger, 2000) colour-coded fluorescent labelling of cells using semiconductor quantum dots (Chan & Nie, 1998) and drug delivery (Sandhu, McIntosh, Simard, Smith, & Rotello, 2001), are reported in literature. Therefore use of biologically compatible materials for nanoparticles synthesis and stabilization will undoubtedly play a crucial role in this area. In addition, physical properties of gold nanoparticles are actually different from other nano scale particles such as ability to display brilliant colours, which further made them extremely smart objects of study for researchers (Dreaden, Alkilany, Huang, Murphy, & El-Sayed, 2012). Biopolymers like chitosan, carboxymethyl chitosan, heparin and hyaluronan are also reported in the literature for synthesis and stabilization of silver and gold nano particles (Huang & Yang, 2004a; Huang & Yang, 2004b; Kemp et al., 2009). Gold nanoparticles in both colloidal solutions and films respond to elemental mercury with blue shifts in localized surface Plasmon resonance (LSPR) wavelength (Chen et al., 2009; Jiang et al., 2012; Li et al., 2006; Lim et al., 2010; Liu et al., 2009; Lu et al., 2007; Rusin et al., 2003; Spătaru et al., 2001; Zhang et al., 2011). The above reports indicates that there are no reports on the synthesis and stabilization of gold nanoparticles (AuNPs) using carboxymethylagarose.

The present study described the use of carboxymethylagarose (CMA) for the synthesis and stabilization of gold nanoparticles for the first time. Subsequently, CMA-AuNPs was successfully used as colorimetric probe for selective detection of Hg^{2+} ions at room temperature in neutral aqueous medium.

2. Experimental

2.1. Materials

Carboxymethylagarose (CMA) was synthesized by the process described in our previous work (Chaudhary, Kondaveeti, Gupta, Prasad, & Meena, 2014), using agarose extracted from *Gracilaria dura* as described in our previous work (Meena et al., 2014). Hydrogen tetrachloroaurate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$), NaBH_4 , mercuric perchlorate, lead perchlorate, cadmium perchlorate, manganese perchlorate, silver perchlorate, nickel perchlorate and copper perchlorate, zinc perchlorate, chromium perchlorate, were purchased from Sigma-Aldrich and used without further purification. HNO_3 was purchased from S. D. Fine, India.

2.2. Characterizations

UV-visible absorption spectra were recorded on Varian Cary-500 (Shimadzu UV 3600) spectrophotometer. Transmission electron microscope (TEM) images were recorded on a HR-TEM (JEOL GEM 2100) instrument operated at an accelerated voltage of 200 kV. Powder XRD was recorded on a model Empyrean powder XRD (Cu-K α radiation) supplied by PAN analytical Netherland. AFM analysis was carried out using NTEGRA, TS-150 instrument by Table stable Ltd., USA. DLS measurement was carried out using Malvern instrument UK at a scattered angle of 90° at 30°C . The incident light was the 488 nm of Argon laser GSL 3110. Surface charge

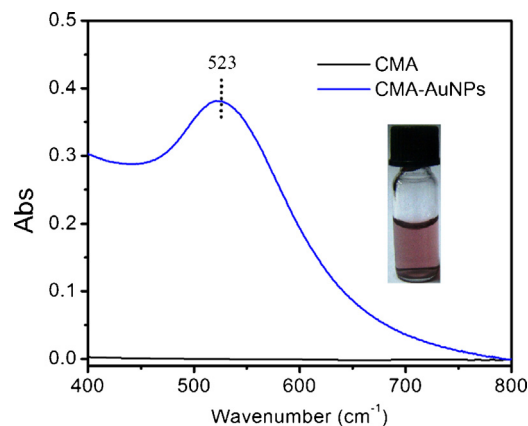


Fig. 1. UV-visible absorption spectra of CMA-AuNPs.

on the CMA-AuNPs was monitored by zeta potential measurements using Malvern Instruments, U.K.

2.3. Preparation of CMA-AuNPs

In a typical synthetic procedure, 0.5 mL of 0.01 M $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ and 0.5 mL of 0.1% w/v CMA in water were added to 14 mL of deionized H_2O under stirring at room temperature. Then 0.5 mL freshly prepared 0.1 M NaBH_4 was added under stirring, and the colour of solution was changed from colourless to purple, stirring was stopped, and whole solution was washed with methanol to remove the excess NaBH_4 . The resulting CMA-AuNPs were dispersed in Milli-Q water and left undisturbed for 12 h. Finally whole solution was stored in refrigerator for further study.

3. Results and discussion

3.1. Selectivity of metal ions with CMA-AuNPs

Fig. 1 shows the UV spectra of the CMA and CMA-AuNPs. The LSPR absorption maximum observed at 523 nm confirmed the formation of CMA-AuNPs (Radhakumary & Sreenivasan, 2011). The size of CMA-AuNPs obtained in the present study ranges from 5 to 7 nm and exhibited an absorption maximum at 523 nm and was in good agreement with those reported in literature (Huang & Yang, 2004b; Pal, Esumi, & Pal, 2005; Watthanaphanit, Panomsuwan, & Saito, 2014). To investigate the interaction of different metal ions with CMA-AuNPs, 100 ppm aqueous solutions of metal ions (e.g. Hg^{2+} , Pb^{2+} , Cd^{2+} , Ag^+ , Ni^{2+} , Cu^{2+} , Zn^{2+} , Co^{2+} , Fe^{3+} , and Cr^{3+}) were prepared from their respective salts. The absorption maxima of the CMA-AuNPs before and after addition of 100 ppm of each metal ions solution was recorded (Fig. 2A and B). The absorption maxima of CMA-AuNPs did not show any significant blue shift on interacting with all the cations except Hg^{2+} (obtained blue shift from 523 nm to 512 nm) revealed selective interaction with mercury ions (Fig. 2A and B). Interestingly on the addition of 100 ppm of Ag^+ ions in the CMA-AuNPs solution causes a slight red shift in LSPR maxima was obtained (Fig. 2A). These results revealed that CMA-AuNPs prepared in this study had a high selectivity towards Hg^{2+} ions and could be employed as colorimetric probe for Hg^{2+} .

3.2. Optimization for detection of Hg^{2+}

Effect of pH of aqueous media on the detection capability of this probe is shown in Fig. S1. This study revealed that this probe is highly suitable for aqueous media with pH 7 as maximum blue shifting of 11 nm (from 523 nm to 512 nm) was observed. Furthermore, To optimized the incubation time for interaction of Hg^{2+}

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