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Functionalized silver nanoparticles probe for visual colorimetric sensing of mercury

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ABSTRACT

We have investigated the chemical synthesis of gelatin functionalized silver nanoparticles (AgNPs) and their physico-chemical characteristics for sensing of mercury (II) ions (Hg^{2+}). Gelatin functionalized AgNPs were prepared by chemical reduction method. The colorimetric sensing of Hg^{2+} was carried out in three different phases including solution, hydrogel network and paper substrate. AgNPs tend to aggregate upon addition of Hg^{2+} and exhibit a color change from yellow to colorless due to aggregation of AgNPs and leads to the formation of Ag/Hg amalgam. This nanosensor probe exhibited good sensitivity for the detection of Hg^{2+} with detection limit of (LOD) 25 nM. In addition, we have studied the sensing of Hg^{2+} using disposable paper strips and 3D hydrogel matrix. In both cases, the sensor exhibits similar characteristics with respect to sensitivity and selectivity for Hg^{2+} detection under optimized conditions. This gelatin functionalized AgNPs probe is highly versatile and promising for various applications including sensor, antimicrobial coatings, catalysis and food monitoring.

1. Introduction

Silver nanoparticles (AgNPs) possess many unique properties such as optical, mechanical, thermal and biological, compared to other metal nanoparticles, which make them attractive nano-materials for uses in catalysis, sensing, nano-electronics and biomedical applications [1–4]. In general, AgNPs are synthesized by three different routes such as physical, chemical and biological methods [5–8]. Among them, chemical reduction method is demonstrated to be the best method for the preparation of AgNPs due to the advantages of shape, and size control, easy formation and less time-consuming. The steps involved in the chemical reduction methods are (i) reduction of silver nitrate using a reducing agent and (ii) prevention of agglomeration of AgNPs by adding a stabilizing agent [9–12]. A variety of reducing agents have been used for preparation of AgNPs such as, sodium borohydride, tri sodium citrate, glucose and ethylene glycol [13]. Among them, sodium borohydride is a strong reducing agent and it needs very small amount for activation of the reaction. Moreover, it can produce smaller sized nanoparticles [3]. Stabilizing agent plays an important role in the synthesis of AgNPs, and it act as protecting layer for nanoparticles, also it prevents the growth and aggregation of the produced nanoparticles. Aggregation is mainly occurs due to increase in collision and surface tension of nanoparticles and it is controlled through the formation of stable surface layer by using a suitable stabilizing agent around the surface of the nanoparticles. A variety of stabilizers such as citrate, CTAB, gallic acid and SDS [14] are being used for the preparation of AgNPs. However, the most common stabilizer is polymers such as gelatin, chitosan, PVA, PEG, PVP and PMMA [3,15–17]. Among them, gelatin can provide a very good stable capping to silver through the NH—Ag bond and could be used for functionalization for various applications [3].

Heavy metal ions are essential for human health activities but some of the heavy metal ions cause severe health problems to human beings. Among them, Mercury (Hg^{2+}) is the second highly toxic heavy metal with great health risk to living organisms in the world [18]. It highly accumulates in the food chain, especially; marine fishes absorbs more amount of mercury in the form of methyl mercury (a neurotoxin) [19,20]. According to the World Health Organization, the permissible limit of Hg^{2+} in drinking water is 30 nM. Excess intake of Hg^{2+} can create a serious health risks to human body [18]. Hence, monitoring the level of Hg^{2+} in the environment and food system are highly demanding.

Several conventional methods such as atomic absorption/emission/fluorescence (AAS/AES/AFS) [21–23], inductive coupled

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plasma mass spectrometry (ICPMS) [24,25], high-performance liquid chromatography (HPLC) coupled with UV–vis or fluorescence [26], ion selective electrode (ISE) and flame photometry [27] are being used for the determination of Hg^{2+}. However, these methods have limitations with respect to several factors such as time-consuming for sample preparation, complex procedures, and special technical support and needs high cost equipments. Hence, various efforts have been taken for finding the suitable alternative methods. A number of other methods such as Surface Enhanced Raman Scattering (SERS) [28,29], fluorescein quenching/functionalized DNA/DNA enzymes/quantum dots [30–34], electrochemical sensor [35] and colorimetric assays [36–39] have been reported for the sensing of Hg^{2+}. Among them, colorimetric assays enjoys immense attention for the sensing of Hg^{2+} due to the simple, rapid, on-site detection capabilities without the need of sophisticated equipment. Annadhasan et al. [36] reported the green synthesis of Au (gold) and AgNPs using L −tyrosine and utilized for colorimetric sensing of Hg^{2+} and showed a lower detection limits of 16 nM. Chen et al. demonstrated the colorimetric sensing of Hg^{2+} using AuNPs embedded paper electrode with LOD of 50 nM. Similarly, Vinod Kumar et al. [40] and Alam et al. [41] reported AgNPs for Hg^{2+} detection with LOD of ppm and nanomolar levels, respectively. Similarly, Zhang and Huang reported the colorimetric detection and adsorption of Hg^{2+} in aqueous media using modified cellulose substances [42]. Most of the reports involve the AuNPs in the solution phase for Hg^{2+} detection. Limited efforts have been done in the use of AgNPs based affordable colorimetric sensors in solid phase.

In this context, we aimed to establish a new and simple colorimetric sensing probe for Hg^{2+} based on functionalized AgNPs. We evaluated the gelatin functionalized AgNPs in three forms including solution phase, hydrogel and paper substrate. The prepared gelatin functionalized AgNPs tend to form amalgam with Hg^{2+}, which leads to the significant color change from yellow to colorless and as well as in the absorption spectrum. We have also prepared AgNPs loaded paper strips and hydrogel network for similar colorimetric sensing of Hg^{2+}. These paper electrodes and hydrogel networks also showed good sensitivity under optimized conditions. However, it took more time (1 h) for sensing of Hg^{2+} due to the heterogeneous phase reaction and also three dimensional networks. These results suggest that, the gelatin functionalized AgNPs have great potential for applications in sensors, antimicrobial coatings and optoelectronic devices.

2. Experimental section

2.1. Materials

Silver nitrate (99.98%) was acquired from Sigma Aldrich, India. Gelatin (99%) was acquired from Himedia. Sodium borohydride (95%) and metal salts such as $BaCl_2$, $MgCl_2$, $CaCl_2$, $CdNO_3$, Co $(NO_3)_2$, $NiCl_2$, $Cu(CH_3COO)_2$ and $HgCl_2$ were procured from Merck suppliers. Potassium chloride (KCl) was purchased from Rankem chemicals. Lead chloride ($PbCl_2$) was obtained from Loba Chemia suppliers. Sodium hydroxide (NaOH) was acquired from Fisher scientific suppliers. Poly (vinylalcohol) (PVA) was procured from Himedia. Glutaraldehyde was purchased from Merck suppliers. Milli-Q-water was used as solvent for throughout the work. All Chemicals and solvents used in this work were of analytical grade and used without further purification.

2.2. Synthesis of gelatin functionalized AgNPs

Gelatin stabilized AgNPs were prepared and characterized as reported by our group [3]. Briefly, 1 mM of silver nitrate was stirred under ice cold condition for about 30 min to attain the temperature below 10 °C. Then, 1 mM of sodium borohydride solution was added slowly to the above solution. During the addition of reducing agent, the temperature was maintained at ice cold condition. An instant yellow color was observed, indicating the formation of AgNPs as colloidal solution. Finally, 1 wt% gelatin was added to the yellow solution and allowed to stir for 2 h to prevent the agglomeration of AgNPs. The obtained AgNPs colloids were purified and stored at room temperature.

2.3. Characterization methods

Purification of AgNPs was done with help of Sigma 3–30 K high speed cooling centrifuge with the speed of 10,000 rpm for about 20 min at 15 °C. The formation (AgNPs) and the colorimetric sensing studies of Hg^{2+} was carried out using UV–vis absorption spectra with PG spectrophotometer using a 1 × 1 cm quartz cuvette cell in the range of 300–800 nm. The morphological changes of before and after addition of Hg^{2+} to the AgNPs was studied by HR-TEM with JEOL JEM-2100 (Japan make) operated at an accelerating voltage of 200 kV. The incorporation of AgNPs into PVA hydrogel and paper strips were examined by scanning electron microscope (SEM) with aid of Hitachi, Model SN-340064 (USA make). The prepared hydrogel and paper strip samples were mounted on a thin layer of gold alloy using double sided carbon tape and taken an images.

2.4. Visual colorimetric sensing of Hg^{2+} using AgNPs

Gelatin functionalized AgNPs was used as a nanosensor probe for the colorimetric sensing of Hg^{2+} at room temperature. Briefly, the gelatin functionalized AgNPs was diluted to 1 mM with water and the pH of the solution was adjusted by adding acetic acid and sodium hydroxide. Similarly, the stock solution of mercury was prepared by calculated amount of mercury salts in water. Further dilution of 0.5 mM of the Hg^{2+} was achieved by adding necessary amount of water to makeup the solutions up to 5 pM. Different concentrations of Hg^{2+} were added to gelatin functionalized AgNPs and the color change have been observed. The UV–vis spectra were recorded for each sample. In order to study the influence of other metal ions, selectivity studies were carried out towards various other transition metal ions such as $BaCl_2$, $MgCl_2$, KCl, $PbCl_2$, $Co(NO_3)_2$, $NiCl_2$, $CdNO_3$, $Cu(CH_3COO)_2$ and $CaCl_2$ at concentration of 1 mM in aqueous medium. All the samples were observed for color change by visually and monitored the surface plasmon resonance (SPR) band absorption by using UV–vis spectroscopy.

2.5. Preparation of AgNPs incorporated PVA hydrogels for colorimetric sensing of Hg^{2+}

AgNPs/PVA hydrogels were prepared by chemical cross-linking method [43,3]. Typically, 10 wt% of PVA polymer solution was prepared by dissolving calculated amount of polymer in water and kept on stirring at room temperature for 24 h. After getting clear and homogeneous solution, 1 mL of AgNPs (0.5 mM) in water was added to the PVA solution and kept on continuous stirring at room temperature for 2 h to obtain a homogenous phase. In order to achieve the 3D network of hydrogel, glutaraldehyde was used as a cross-linker and it was added to the mixture of AgNPs/PVA. For our experiments, 1 mL of glutaraldehyde was added drop by drop to the AgNPs/PVA mixture at room temperature and gently stirs the solution for another 5 min. Then, the obtained solution was casted in cubic shaped trays and left for gelation. After three days, the formed hydrogels were removed from the trays and washed with distilled water for further sensing studies.