



Facile and on-line colorimetric detection of Hg^{2+} based on localized surface plasmon resonance (LSPR) of Ag nanotriangles



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ABSTRACT

A rapid and sensitive colorimetric detection method for the determination of Hg^{2+} has been successfully developed in this research. Citrate-functionalized silver nanotriangles (AgTrngs) were synthesized via one-pot sodium borohydride method with the edge-length range of 30–40 nm. The obtained AgTrngs were fully characterized using UV-Vis spectrophotometry, transmission electron microscopy (TEM), energy dispersed spectroscopy (EDS) and X-ray diffractometer. The efficiency of the developed sensor was optimum at pH = 8 due to interfering effect of H^+ ions for Hg^{2+} under acidic conditions. The successful detection of mercury in aqueous solutions in the concentration range of 10 nmol L^{-1} – $50 \mu\text{mol L}^{-1}$ indicated the applicability of the developed sensor for effective monitoring and controlling the level of Hg^{2+} in industrial effluents. The ability of Hg^{2+} ion to interact with Ag and form the Hg–Ag alloy (amalgam) over the surface of AgTrngs resulted in an obvious color change from blue to violet. UV-Vis spectrophotometry showed that the sensor has the limit of detection (LOD) value of as low as 4 nmol L^{-1} which was below the safety level of Hg^{2+} ions (10 nmol L^{-1}) in drinking water. The proposed method can be used for on-line determination of Hg^{2+} in the complex aqueous solutions.

1. Introduction

Extensive agriculture, unintended mining and metal-based operations, as the consequences of industrialization, are the main sources of environment contamination by the heavy metals. The presence of heavy metallic ions in water, water pollution, causes negative effects on the living organisms. Among the heavy metallic ions, mercury ion (Hg^{2+}) is severely hazardous due to accumulation in body cells and it causes several diseases in nervous and endocrine systems, brain and kidneys [1,2]. The Environmental Protection Agency (EPA) highly restricts the safety level of Hg^{2+} as low as 10 nmol L^{-1} in drinking waters [3] indicating the seriousness of sensitive and accurate detection of Hg^{2+} in aqueous media. Despite the availability of conventional techniques for the detection of Hg^{2+} , including atomic absorption/emission spectrometry (AAS/AES), inductively coupled plasma atomic emission spectroscopy (ICP-AES) and high-performance liquid chromatography (HPLC), they are costly and time consuming analyses [4–7].

In the last decade, extensive effort has been devoted for developing sensitive and easily applicable metallic ion sensors by many analytical researches; e.g. the sensors based on oligonucleotides [8], DNA [9], fluorophores or chromophores [10,11] and nanoparticles [12–14]. Recently, the colorimetric sensors based on plasmonic nanoparticles

have turned into an interesting approach for detection various chemical and biochemical species [15–20]. The main advantage of the sensors based on surface plasmon resonance (SPR) of nanoparticles, is their high sensitivity. Extraordinary extinction coefficient (in the order of $10^{10} \text{ mol}^{-1} \text{ L cm}^{-1}$) of the plasmonic nanoparticles, with acceptable limit of detection (LOD) values, makes them highly sensitive to any physical/chemical changes such as adsorption of species, dielectric properties of the medium, size and shape of the particle.

In the case of Hg^{2+} detection, different morphologies (shape and size) and compositions of plasmonic nanostructures have been proposed. For instance, the Au@Ag core-shell nanoparticles functionalized by monolayer of 2,5-Dimercapto-1,3,4-thiadiazole (DMcT) have been employed as a label-free probe with a LOD as low as 10 pmol L^{-1} [21]. In addition, Karthiga et al. [22] have reported the ability of Ag nanorods and Ag nanotriangles for the detection of Hg^{2+} ; the morphological features of both nanostructures dramatically change due to the Hg^{2+} ability to oxidize Ag. Also, Kim et al. [23] have conducted a comprehensive study on the shape-dependent properties of Ag nanostructures for detection of metallic ions; i.e. the rod-shaped nanostructures can effectively respond to a specific analyte but the spherical-shaped nanostructures, with the same composition, cannot. It is worthy of note that most of the published literature on the Hg^{2+}

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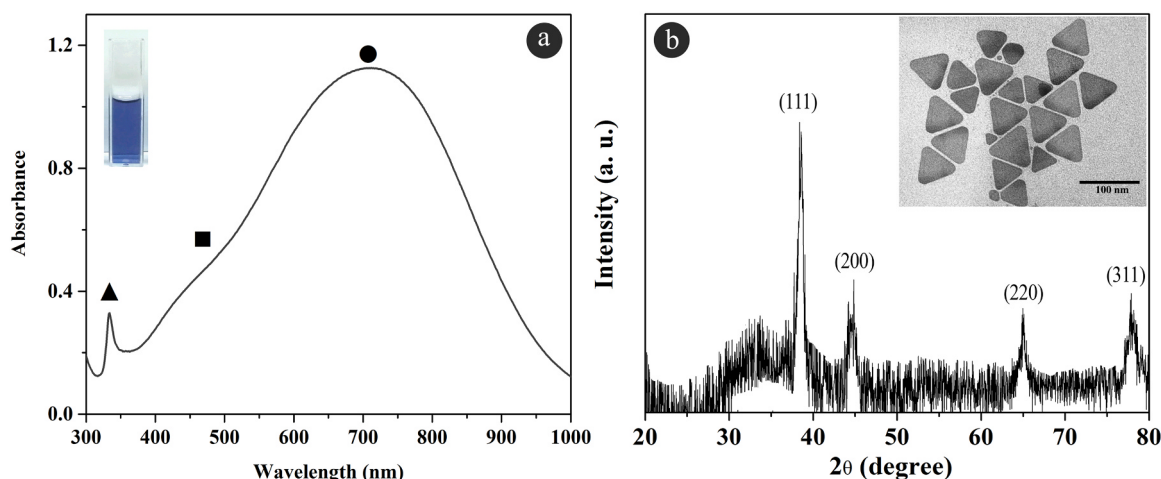


Fig. 1. UV-Vis spectra (a) and XRD pattern (b) of synthesized AgTrngs. Inset in (b) shows the TEM image of synthesized AgTrngs.

detection have employed the spherical nanostructures [24–33]; in addition, almost all of them indicate that the morphology of Ag nanostructure changes in the presence of Hg^{2+} .

In this paper, the triangular shaped silver nanostructures was simply synthesized; by the functionalizing the Ag nanotriangles with trisodium citrate, we could successfully detect the Hg^{2+} in aqueous media. The prepared silver nanotriangles (AgTrngs) with the distinctive in-plane dipole, in-plane quadrupole and out-plane quadrupole resonances showed sensitive response to Hg^{2+} . In order to increase the confidence level of Hg^{2+} sensing, the ratio of absorbance at in-plane dipole resonance to absorbance at out-plane quadrupole resonance were employed. Formation of Ag–Hg nano-alloy was responsible for the observed changes in the spectrum of silver nanotriangles. The short response time (10 s) together with the low detection limit (4 nmol L^{-1}) of the developed sensor, indicates the efficient determination of Hg^{2+} in aqueous media.

2. Experimental

2.1. Chemicals

Silver nitrate (AgNO_3 ; Scharlau), trisodium citrate dehydrated ($\text{TSC}\cdot\text{H}_2\text{O}$; Merck), polyvinylpyrrolidone (PVP–K30; Daejung chemicals), hydrogen peroxide (H_2O_2 ; Merck) and sodium borohydride (NaBH_4 ; Daejung chemicals) were the essential chemicals for synthesis of AgTrngs. Also, Mercury chloride (HgCl_2), the precursor of analyte, was purchased from Merck. Sodium hydroxide (NaOH) and hydrochloric acid (HCl), Sigma–Aldrich, were employed for pH adjustment. NaCl , for the study of ion concentration, was purchased from Merck. For the preparation of solutions throughout the experiments, Milli–Q purification system (Branstead, USA) was used.

2.2. Apparatus

UV–Vis spectra of the samples were recorded by a Shimadzu 160 AUV–vis spectrometer. Dynamic light scattering (DLS) studies were conducted using a Malvern (Zetasizer 3000 HSA). A Metrohm 632 was used for pH adjustment/measurement. X–ray diffraction (XRD), unit Unisantis XMD–300, was employed for phase analysis. Transmission electron microscope (TEM)–Zeiss, EM10C, 80 kV – was used for characterizing the morphological features of the synthesized nanostructures.

2.3. Synthesis of AgTrngs

A modified Mirkin method [34] was employed for the synthesis of

AgTrngs. In a typical synthesis run, mixture of 50 ml of AgNO_3 (0.1 mmol L^{-1}) and 3 ml of TSC (30 mmol L^{-1}) was vigorously stirred in a 100 ml Erlenmeyer flask. Then, 3 ml of PVP (0.7 mmol L^{-1}) and $120 \mu\text{l}$ of H_2O_2 (30%) were added into the system under ambient conditions. After 10 min, $300 \mu\text{l}$ of ice-cooled NaBH_4 (100 mmol L^{-1}), as the reducing agent, was injected into the solution and left stirring at 600 rpm. Right after the addition of NaBH_4 color of the solution changed from colorless to pale yellow indicating the formation of Ag nanostructures. After around 30 min, color of the solution changed from an initial color of dark yellow to orange, red, indigo and a final color of violet/blue, successively. The appearance of violet/blue color was an indicative of the formation of silver nanotriangles. All of the experiments were conducted under ambient conditions. The prepared nanostructures were then washed with acetone and deionized water in a 4000 rpm centrifuge and re-dispersed in water for further experiments.

2.4. Hg^{2+} detection

AgTrngs were used as probe for colorimetric detection of Hg^{2+} . Different concentrations of Hg^{2+} , in the range of 10 nmol L^{-1} – $50 \mu\text{mol L}^{-1}$, were added to AgTrngs colloidal system and the resulted UV–Vis spectral were recorded. The absorbance ratio, defined as the ratio of in-plane dipole resonance (DR) to out-plane quadrupole resonance (QR), was used for calibration.

2.5. The effects of pH and ion concentration

Effects of ion concentration and pH on the surface charge and optical properties of AgTrngs were also studied by adding NaCl and NaOH/HCl into the system and recording the corresponding changes in UV–vis spectra. The range of pH and NaCl concentration were within the ranges of 3.0–10.0 and 50–100 (mmol L^{-1}), respectively.

3. Results and discussions

3.1. Characterization of synthesized AgTrngs

According to Fig. 1, UV–Vis spectra (a) and XRD pattern (b) of the synthesized AgTrngs together with the TEM image (inset in (b)), the symmetrical AgTrngs could be successfully obtained. According to the XRD pattern, the four peaks at $2\theta = 38.3, 44.4, 64.5,$ and 77.4 degrees can be assigned to the (111), (200), (220), and (311) planes of the face-centred cubic (FCC) Ag nanostructures, respectively (JCPDS File No. 04-0783). In addition, the synthesized Ag nanostructures exhibit a (111) crystal texture on their surface, inherited from the abundant

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