



Bimetallic Au/Ag nanorods embedded in functionalized silicate sol–gel matrix as an efficient catalyst for nitrobenzene reduction

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ABSTRACT

A simple method for the preparation of bimetallic gold/silver nanorods embedded in amine functionalized silicate sol–gel matrix (Au/Ag–TPDT NRs) in aqueous medium and their application towards the catalytic reduction of nitrobenzene is reported. The Au/Ag–TPDT NRs are prepared by using *N*¹–[3-trimethoxysilyl)propyl]diethylene triamine (TPDT) as a reducing as well as stabilizing agent. The catalytic activity of the Au/Ag–TPDT NRs is evaluated by studying the catalytic reduction of nitrobenzene to aniline upon the addition of NaBH₄ in an aqueous solution. The Au/Ag–TPDT NRs was found to be a good catalyst when compared to the Au–TPDT NRs and Au NRs for the reduction of nitrobenzene to aniline at room temperature. The enhanced catalytic activity of Au/Ag–TPDT NRs is due to the synergistic effect of Au and Ag present in the bimetallic Au/Ag–TPDT NRs. The reaction rate constants (*k*) are estimated to be 0.4050, 0.2515 and 0.1235 min^{−1} for Au/Ag–TPDT NRs, Au–TPDT NRs and Au NRs, respectively. The electrocatalytic reduction of nitrobenzene at pH 7 using the Au/Ag–TPDT NRs modified electrode is also investigated and compared with the Au–TPDT NRs. The higher electrocatalytic activity of Au/Ag–TPDT NRs is due to the synergistic effect of Au and Ag present in the bimetallic Au/Ag–TPDT NRs. The results of the study demonstrate that the Au/Ag–TPDT NRs are efficient catalyst for the catalytic reduction of nitrobenzene.

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1. Introduction

Gold nanorods (Au NRs) are elongated nanoparticles which possess two principal plasmon absorption bands *viz.*, a transverse plasmon band, corresponding to light absorption and scattering along the short axis of the nanoparticles located in the visible region of the spectrum around 520 nm and the longitudinal plasmon band, corresponding to light absorption and scattering along the long axis of the nanoparticles and this can be tuned from the visible to the near-IR region of the electromagnetic spectrum by changing the aspect ratio of the Au NRs [1–5]. The preparation of various aspect ratios of Au NRs has been widely reported [6,7]. The preparation of bimetallic Au/Ag core–shell and alloy bimetal NRs have attracted much attention in recent years due to their characteristic electronic, optical and catalytic properties differ from those of the Au NRs and they exhibit stronger extinction coefficients and blue shift in their longitudinal surface plasmon resonance (LSPR) band [8–13] and these properties find applications in metal ions sensing [14], biomolecules sensing [15] and surface-enhanced Raman scattering [16]. The silica-coated Au nanoparticles resulted in large pore

size, high surface area, good stability and biocompatibility [17–20]. The silica-coated Au NRs was found to be a novel biocompatible nanocomposite material and find applications in colorimetric sensing [4,20] and electrocatalysis [21,22]. The Au/Ag core–shell NRs embedded in functionalized silicate sol–gel matrix found applications in electrochemical sensors [23]. The silica-coated Au/Ag core–shell NRs exhibited applications in targeting of cancer cells [24].

The catalytic reduction of nitroaromatics is studied extensively in recent years [25–31]. The bimetallic Au/Ag NRs prepared with different structures showed good catalytic activity towards 4-nitrophenol reduction [32]. Nitrobenzene shows their detrimental effects on human health and on environment as toxic and mutagenic substances [33,34]. The reduction of nitrobenzene has generated significant interest in the creation of secure environment and in other applications [35]. The oxidation of nitrobenzene may produce toxic dead-end products like picolinic acid [36] but however, reductive technologies have attracted more attention than oxidation [37]. The electrochemical reduction of nitrobenzene yields a variety of products, including aniline, phenylhydroxylamine, azoxybenzene, azobenzene, nitrosobenzene, etc., which depends on the pH and type of electrodes. One of the products, aniline exhibits the lowest toxicity and best biodegradable property while the remaining products are toxic compared to aniline

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[38]. Hence, it becomes highly relevant to develop a method which can selectively reduce nitrobenzene to aniline.

In the present study, the bimetallic Au/Ag NRs embedded in amine functionalized silicate sol–gel matrix (Au/Ag–TPDT NRs) are prepared using N^1 -[3-(trimethoxysilyl)propyl]diethylene triamine (TPDT) silane as reducing agent and stabilizing agent. This catalyst was characterized by UV–vis spectroscopy, transmission electron microscopy (TEM), energy-dispersive X-ray spectroscopy (EDS), selected area electron diffraction (SAED), X-ray diffraction (XRD) and cyclic voltammetry. The prepared Au/Ag–TPDT NRs are used as a model catalyst for the catalytic reduction of nitrobenzene to aniline in the presence of NaBH_4 . The encapsulation of bimetallic Au/Ag NRs by TPDT functionalized silicate sol–gel enhances the preconcentration of nitrobenzene around the Au/Ag NRs thus promoting the reduction upon the addition of NaBH_4 . The catalytic activity of Au/Ag–TPDT NRs is compared with the Au–TPDT NRs and Au NRs catalysts towards the reduction of nitrobenzene to aniline in the presence of NaBH_4 . The electrocatalytic reduction of nitrobenzene at the Au/Ag–TPDT NRs modified electrode was studied. The results were also compared with the performance of Au–TPDT NRs modified electrode.

2. Experimental

2.1. Chemicals

Cetyltrimethylammonium bromide (CTAB) was purchased from Sigma. N^1 -[3-(trimethoxysilyl)propyl]diethylene triamine (TPDT), hydrogen tetrachloroaurate(III) hydrate, silver nitrate and sodium borohydride were purchased from Aldrich. Nitrobenzene was purchased from Merck. All other chemicals, unless otherwise specified, used in the present work were of analytical grade. All glassware were thoroughly cleaned with *aqua regia* (1:3 (v/v) HNO_3/HCl) (Caution: *Aqua regia* is a powerful oxidizing agent and it should be handled with extreme care) and rinsed extensively with distilled water before use.

2.2. Preparation of Au NRs

The Au NRs were prepared according to seed mediated growth method reported by Nikoobakht and El Sayed [7]. Briefly, CTAB solution (5 mL, 0.2 M) was mixed with 5 mL of 5×10^{-4} M HAuCl_4 and stirred. To this solution, 0.6 mL of ice-cold 0.01 M NaBH_4 was added with constant stirring, which resulted in the formation of a brownish yellow seed solution. Vigorous stirring of this solution was continued for another 2 min. Then the solution was kept at 25 °C in the absence of stirring. For the preparation of growth solution, CTAB (5 mL, 0.2 M) was added to 0.15 mL of 4×10^{-3} M AgNO_3 solution at 25 °C. To this solution, 5 mL of 1×10^{-3} M HAuCl_4 was added, and after gentle mixing of the solution 70 μL of 0.0788 M ascorbic acid was added. After the addition of ascorbic acid, the color of the growth solution changed from dark yellow to colorless. The final step was the addition of 12 μL of seed solution to the growth solution at 27–30 °C. The solution color gradually changed within 10–20 min. Finally, the temperature of growth medium was kept at around 27–30 °C. This pathway produced Au NRs with an aspect ratio of ~ 3.5 .

2.3. Synthesis of Au/Ag–TPDT NRs

A volume of 0.8 mL of the as prepared Au NRs solution ($[\text{Au}] = 0.5 \times 10^{-3}$ M) was added to 4 mL of water and then 50 μL of 1 M TPDT silane solution was added to the solution. The as-prepared Au NRs solution still contains Ag and Au ions [11,15]. The reaction was kept for 1 day to complete the formation of Au/Ag–TPDT NRs.

The TPDT silane acts as a reducing agent as well as stabilizing agent. The final color of the Au/Ag–TPDT NRs solution was changed.

2.4. Preparation of Au/Ag–TPDT NRs modified electrodes

The GC electrode (diameter = 3 mm, CH Instruments) was polished twice using alumina powder (0.05 μm) followed by sonication in distilled water for 3 min. The cleaned GC electrode was dried in air for 5 min at room temperature. A known volume of the Au/Ag–TPDT NRs or Au–TPDT NRs was coated on the surface of the GC electrode and then allowed to dry at room temperature for 2 h (represented as GC/Au/Ag–TPDT NRs or GC/Au–TPDT NRs). The modified electrodes were then kept in water for 10 min and then used for the electrochemical experiments. Nitrogen gas was purged through the electrolyte solution for 30 min before each experiment.

2.5. Catalytic reduction of nitrobenzene

The catalytic reduction of nitrobenzene was carried out in the standard quartz cuvette with a 1 cm path length. In a typical reaction, 2 mL of aqueous solution of nitrobenzene (0.4×10^{-3} M) was added to the quartz cuvette under magnetic stirring. To this solution 0.4 mL of freshly prepared aqueous solution of NaBH_4 (0.2 M) was added and finally Au/Ag–TPDT NRs or Au–TPDT NRs or Au NRs (0.075 mL, 0.08×10^{-3} M) were added to the quartz cuvette. The UV–visible absorbance spectra were recorded at regular time intervals to monitor the progress of the reaction.

2.6. Characterization and electrochemical studies

The UV–visible absorption spectra and *in-situ* absorption spectral changes with time were recorded using an Agilent 8453 diode array spectrophotometer. The morphological feature and elemental composition of Au/Ag–TPDT NRs were analyzed using high resolution transmission electron microscopy (HR-TEM) equipped with energy dispersive spectrum (EDS) using JEOL JEM 2100 instrument with an operating voltage of 200 kV. The Au/Ag–TPDT NRs solutions were centrifuged at 9000 rpm for 10 min to remove excess amounts of CTAB before the TEM analysis. The sample for TEM measurement was prepared by placing a drop of sample solution on a carbon-coated copper grid and then dried at 25 °C. The X-ray diffraction (XRD) analysis was carried out using Bruker AXS D8 advance X-ray diffractometer with monochromatized $\text{Cu K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$). The sample for XRD was prepared by casting the Au/Ag–TPDT NRs solution on a glass plate and allowed to dry at 25 °C. The electrochemical experiments were conducted using a CHI760D Electrochemical Workstation, CH Instruments, Inc., USA. Electrochemical measurements were performed using a three-electrode cell with a glassy carbon (GC) working electrode (electrode area = 0.07 cm^2), a Pt wire counter electrode and an Ag/AgCl reference electrode at 25 °C.

3. Results and discussion

3.1. UV–visible spectral studies of Au/Ag–TPDT NRs

The UV–visible spectra obtained for the Au NRs, Au–TPDT NRs and Au/Ag–TPDT NRs showed that the optical properties of the Au NRs were influenced by the Ag on the Au NRs (Fig. 1). The deposition of Ag on the surface of the Au NRs showed about a blue shift in the longitudinal plasmon band when compared to the Au NRs. The as-prepared Au NRs showed a transverse plasmon band at 511 nm and a longitudinal plasmon band at 796 nm (Fig. 1(a)). The Au–TPDT NRs showed a transverse plasmon band at 511 nm and a longitudinal plasmon band at 766 nm (Fig. 1(b)) and the Au/Ag–TPDT NRs showed a transverse plasmon band at 501 nm and a longitudinal

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