



Polyelectrolyte assisted synthesis and enhanced catalysis of silver nanoparticles: Electrocatalytic reduction of hydrogen peroxide and catalytic reduction of 4-nitroaniline



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ABSTRACT

A facile method was developed for the one-step synthesis of silver nanoparticles (AgNPs), co-stabilized by the polyelectrolyte poly(acrylamide-co-diallyldimethylammoniumchloride) (PADA) and the silicate matrix N1-(3-trimethoxysilylpropyl)diethylenetriamine (TPDT). Here, TPDT acted as reducing agent and both PADA and TPDT served as capping agent for AgNPs. As PADA improved the catalytic properties of AgNPs, its concentration was optimized and the optimum concentration of PADA was found to be 1 wt.% among the concentrations 0.25, 0.5, 1 and 2 wt.%. The AgNPs were characterized using UV–vis absorption spectroscopy, HRTEM, EDX, SAED and FTIR analyses. The PADA(1)-Ag-TPDT NPs showed the better catalytic activity towards electrochemical reduction of H₂O₂ and catalytic conversion of 4-nitroaniline (4-NA) to *p*-phenylenediamine (PPD). The PADA(1)-Ag-TPDT NPs was used to construct the non-enzymatic electrochemical sensor for the detection of H₂O₂. Using the linear sweep voltammetry (LSV) and square wave voltammetry (SWV) techniques, the lowest experimental detection limits attained for H₂O₂ sensing were 5 and 0.2 μM, respectively. Moreover, remarkably a fast conversion of 4-NA to PPD was observed over the PADA(1)-Ag-TPDT NPs catalyst with a rate constant of 0.096 s⁻¹ and the product (PPD) formation was confirmed by ¹H NMR spectroscopy.

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1. Introduction

Nanomaterials with unique physical and chemical properties find extensive applications when compared to their corresponding bulk materials [1]. Challenging issues in the fields of solar energy conversion, catalysis, medicine, and water treatment have been addressed greatly by means of nanoscience and nanotechnology [2,3]. Hence, the novel properties of nanoparticles (NPs) have been exploited in a wide range of potential applications. Among the metal NPs, AgNPs are the interesting materials due to their unique physical, chemical and biological properties [4]. Preparation of promising and cost effective catalyst in a simple and environmentally benign method is a challenging task in the field of catalysis science and technology. Nanoscience and technology showed the way to prepare such catalyst, which finds more than one application for a single material [5–7]. Synthesis of AgNPs with different size and shape in solution phase has been reported earlier [8,9].

Polyelectrolytes capped AgNPs [10,11] and silicate sol-gel (SSG) stabilized AgNPs [5,12] have been reported and widely used.

Effective quantification of hydrogen peroxide (H₂O₂) is very important in the fields of food industry, pharmaceutical, clinical, industrial and environmental analysis and also H₂O₂ is a reactive oxygen species and a by-product in many oxidative metabolic pathways [13]. The quantification of H₂O₂ can be done by various analytical techniques such as titrimetry, fluorescence spectroscopy, UV–vis spectrophotometry, chemiluminescence, chromatography and electrochemical methods. Among them, electrochemical methods are the well-recognized techniques because of its simple instrumentation, high selectivity and high sensitivity [14]. Though, enzyme immobilized electrodes show good selectivity and sensitivity towards H₂O₂, they have several disadvantages such as instability, high cost of enzymes and complicated immobilization procedure [15]. Hence, the development of non-enzymatic electrochemical sensor for the detection of H₂O₂ has great significance.

Nitroaromatic compounds attract much attention over the decades in relation to pollutions, toxicity, mutagenesis, carcinogenesis, therapeutic action and as intermediates in the synthesis of important organic compounds. As far as the nitroaromatic compounds are concerned, the environmental contamination has been

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the major problem [16]. The reduced products of nitroaromatics i.e., aromatic amines are less toxic in nature and are important starting materials for the preparation of many biologically active and pharmaceutical chemicals [17]. Hence, the development of simple, cost effective and efficient catalyst for the conversion of nitroaromatics into corresponding amines being the important field of research.

In the present work, AgNPs were prepared without employing any other external reducing agent in the presence of PADA and TPDT, and were well characterized. The prepared AgNPs were found to be catalytically active for the electrochemical reduction of H_2O_2 and catalytic conversion of 4-NA to PPD in the presence of $NaBH_4$. As PADA improved the catalytic behaviour of AgNPs, its concentration was optimized and 1 wt.% PADA was found to produce catalytically more active AgNPs in combination with TPDT.

2. Experimental section

2.1. Materials and methods

Silver nitrate ($AgNO_3$), poly(acrylamide-co-diallyldimethylammonium chloride) (PADA) and *N*-[3-(trimethoxysilyl) propyl] diethylenetriamine (TPDT) were purchased from Sigma–Aldrich. All other chemicals are analytical grade and were received from Merck. All glassware was thoroughly cleaned with aqua regia (1:3 HNO_3/HCl v/v) (caution: *Aqua regia is a powerful oxidizing agent and it should be handled with extreme care.*) and rinsed extensively with distilled water before use. UV–vis absorption spectra were recorded using Agilent Technologies 8453 spectrophotometer with a 1 cm quartz cell. High resolution transmission electron microscopy (HRTEM), and selected area electron diffraction (SAED) analyses were conducted in a JEOL JEM 2100 and Technai T20 instrument operated at 200 kV. The specimen for the HRTEM analysis was prepared by dropping the colloidal solution onto a carbon coated copper grid and dried at room temperature. Energy dispersive X-ray (EDX) analysis was carried out using JEOL Model JSM-6390LV. Electrochemical characterization of so prepared AgNPs was performed by using a CH Instruments electrochemical workstation (Model–760D). FT-IR analyses were carried out using Shimadzu (8400S). NMR was recorded on Burker 300 MHz instrument using $CDCl_3$ as solvent and the chemical shift values are reported as δ values (ppm) with reference to tetramethylsilane (TMS). Catalytic reduction of 4-NA was carried out by taking 0.1 mL of 2 mM of 4-NA solution in 1.15 mL of water followed by 0.75 mL of 0.056 M $NaBH_4$. To this mixture 10 μ L of prepared AgNPs was added and the reaction progress was monitored by UV–vis spectroscopy.

2.2. Synthesis of PADA(1)-Ag-TPDT NPs

A 5 mL of 1 wt.% PADA solution was mixed with 25 μ L of 1 M TPDT solution and stirred for 15 min. To this solution, 0.1 mL of 0.25 M $AgNO_3$ solution was added and stirred for 48 h. The appearance of yellow color solution confirmed the formation of silver nanoparticles (represented as PADA(1)-Ag-TPDT). Moreover, the prepared AgNPs were stable for more than a month. By following the same procedure, the PADA(0.25)-Ag-TPDT, PADA(0.5)-Ag-TPDT and PADA(2)-Ag-TPDT NPs were prepared with different concentrations of PADA. In the above representation, value in the parenthesis after PADA represents the wt.% of PADA solution used in the preparation. A control experiment was performed to check the formation AgNPs in the presence of PADA alone by adopting the same procedure but the formation of AgNPs was not observed.

2.3. Synthesis of Ag-TPDT NPs

A 25 μ L of 1 M TPDT solution was added to 5 mL of water and stirred for 15 min. To this solution, 0.1 mL of 0.25 M $AgNO_3$ solu-

tion was added and stirred for 48 h. The color of the solution was changed from colorless to yellow confirming the formation of AgNPs.

2.4. Electrochemistry

All the electrochemical experiments were conducted in a single compartment three electrode cell using a CHI760D Electrochemical Workstation, CH Instruments, USA. A GC electrode (3 mm dia) and a platinum wire were used as working and counter electrodes, respectively. Saturated calomel electrode was used as reference electrode. A 5 μ L of the AgNPs solution was drop-casted onto the cleaned GC surface and allowing it to dry for 2 h at room temperature and used for the electrochemical experiments. Phosphate buffer solution (PBS) (pH = 7.2) was used as electrolyte for electrocatalysis and sensor studies. Nitrogen gas was bubbled into the cell solution for 25 min prior to each experiment unless otherwise mentioned.

3. Results and discussion

3.1. Absorption spectral, HRTEM and FTIR studies of AgNPs

The formation of AgNPs in the presence of PADA and TPDT matrix was initially confirmed by noticing the appearance of yellow color of the reaction solution. The slow growth of AgNPs was monitored by recording the absorption spectra at different reaction times (Fig. S1). The intensity of the SPR absorption band of the AgNPs at 413 nm increased gradually over the period of time without any change in the band position, which confirmed the uniform growth of AgNPs in the presence of PADA and TPDT. The absorption spectrum of the PADA(1)-Ag-TPDT NPs (Fig. 1a) showed a sharp SPR band at 413 nm, which suggested the formation of mono-dispersed spherical AgNPs and the Ag-TPDT NPs showed the SPR band at 420 nm (Fig. 1e). The small blue shift observed in the SPR band of PADA(1)-Ag-TPDT NPs in comparison with Ag-TPDT NPs is due to reduced particle size [18], which was evidenced from the HRTEM images (Fig. 2) and also might be due to interaction with PADA. The PADA(0.25)-Ag-TPDT (c), PADA(0.5)-Ag-TPDT (b) and PADA(2)-Ag-TPDT (d) NPs also showed the SPR absorption features of AgNPs at 416, 416 and 421 nm, respectively (Fig. 1). Hence, the absorption band around 410 nm confirmed the formation of AgNPs either in the presence of PADA-TPDT mixture or in the presence of only TPDT. In the present synthesis, no other external reducing agent

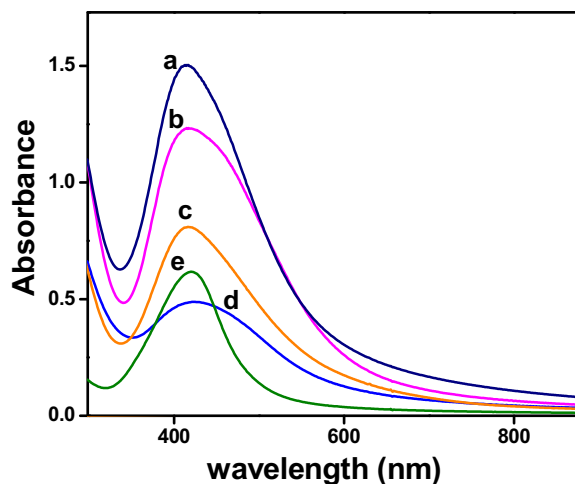


Fig. 1. Absorption spectra of PADA(1)-Ag-TPDT (a), PADA(0.5)-Ag-TPDT (b), PADA(0.25)-Ag-TPDT (c), PADA(2)-Ag-TPDT (d) and Ag-TPDT (e) NPs solutions.

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