



Electrochemical determination of nanomolar levels of isoniazid in pharmaceutical formulation using silver nanoparticles decorated copolymer



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ABSTRACT

A copolymer of methyl methacrylate and 2-acrylamido-2-methylpropane sulfonic acid (P(MMA-co-AMPS)) and silver nanoparticles (Ag NPs) incorporated P(MMA-co-AMPS) (Ag-P(MMA-co-AMPS)) are used to construct efficient electrochemical sensing platforms (ESPs) to quantitatively determine isoniazid (INZ) at neutral pH conditions. Cyclic voltammetry, amperometry and electrochemical impedance spectroscopy are used as diagnostic tools for INZ determination at these ESPs in pH 7.0 phosphate buffer solution. It has been found that P(MMA-co-AMPS) copolymer facilitates the INZ oxidation with improved electrochemical behaviors. At Ag-P(MMA-co-AMPS), electrochemical characteristics of INZ is much improved than at P(MMA-co-AMPS) due to the interaction of INZ with Ag NPs. Based on the linear increase in oxidation current, a sensitive INZ electrochemical sensor is constructed. The sensor displays a linear calibration range from 50.0 nM to 150.0 μ M for INZ determination. Detection limit (based on three times standard deviation of the blank) and sensitivity of this sensor is 10.0 nM and 197 nA μ M⁻¹ cm⁻², respectively. Further, P(MMA-co-AMPS) and Ag-P(MMA-co-AMPS) materials are successfully applied for analysis of INZ in presence of other biologically important molecules and also in a pharmaceutical formulation. The obtained results are very much consistent with the INZ amount originally present in the pharmaceutical formulation.

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1. Introduction

Numerous studies have been carried out in the past two decades on polymeric film/composite modified electrodes because of their advantageous features like good stability/adherence on electrode surfaces and defending metal nanoparticles (MNPs) from aggregation [1–3]. Incorporating MNPs into polymer matrix offers the possibility to synthesize hybrid materials which combine the properties of polymers as well as MNPs [4]. A large variety of polymers and copolymers have been used to stabilize MNPs and subsequently used for various applications [5–9]. On the other hand, catalysts based on Ag NPs is known to facilitate several electron transfer reactions and used as electrochemical sensing platforms to determine various biomolecules, environmental pollutants, etc [6–8].

INZ (pyridine-4-carboxylic acid hydrazide) is an organic compound and widely used in prevention and treatment of pulmonary tuberculosis along with pyrazinamide and rifampicin

[10–13]. However, overdose/regular uptake of INZ may cause hepatotoxicity and other adverse effects on human body [13]. Therefore, it is highly essential to monitor the INZ level in biological fluids for medical diagnosis throughout the treatment as well as in pharmaceutical preparations for quality control. This urged the scientists to develop cheap/low-cost methods (including electrochemical methods) to quantitatively determine INZ [14–28]. However, major problems associated with electrochemical methods are the requirement of large overpotential and poor sensitivity because of sluggish electron transfer kinetics at bare electrodes for the oxidation of INZ. To resolve these problems, various modified electrodes have been used. For example, Bergamini et al. used poly-L-histidine modified screen-printed carbon electrode for INZ determination in urine [18], Yang et al. used poly(amidosulfonic acid) (PASA) for INZ determination in pharmaceuticals [22], Satyanarayana et al. used multiwall carbon nanotube ensembled biopolymer electrode for selective INZ determination *in vitro* [23], Cheemalapati et al. used electrochemically modified rhodium electrode for the electrocatalytic oxidation of INZ [24], Raj and coworkers reported nano-Au decorated sol-gel based Au electrodes for the amperometric detection of INZ [25], Gao et al. used (ferrocenylmethyl) trimethylammonium

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((FcM)-TMA) to electrocatalyze the INZ oxidation [26], Shahrokhian et al. investigated thionine immobilized multiwall carbon nanotube based electrodes for the determination of INZ [27] and Yan et al. reported INZ oxidation and its amperometric detection at ordered mesoporous carbon modified electrode [28]. However, most of the above said modified electrodes suffer with one or more disadvantages like high oxidation overpotential, low sensitivity, high detection limit, electrode fouling effects, acidic/basic conditions, etc. Thus, there is still need to search for new materials which exhibit low oxidation overpotential, high sensitivity, low detection limit and fast electron transfer kinetics for INZ determination in pH 7.0. Hence in this paper, we are proposing new nano-structured materials based on copolymer of methyl methacrylate (MMA) and 2-acrylamido-2-methylpropane sulfonic acid (AMPS) (abbreviated as P(MMA-co-AMPS)) and silver nanoparticles (Ag NPs) incorporated in P(MMA-co-AMPS) (abbreviated as Ag-P(MMA-co-AMPS)) for the very first time to construct high quality electrochemical sensor for INZ determinations in a pharmaceutical formulation. This newly synthesized copolymer stabilizes the Ag NPs and it is expected to carry the properties of both the monomers. The sulfonic acid group of the copolymer can interact with amine group, $-NH_2$ of INZ [14]. Therefore, the mediating ability of the copolymer (because of the favorable interaction of the copolymer with INZ) and Ag NPs-copolymer (due to the interaction between amine groups of INZ with Ag NPs) can be advantageously used for the INZ determination.

2. Experimental

2.1. Chemicals and materials synthesis

Isoniazid from Himedia, silver nitrate and *N,N*-dimethylformamide (DMF) from Merck were obtained and used without further purification. MMA was procured from S.D. Fine Chemicals (Mumbai, India) and it was purified to remove the inhibitor by washing with 30% sodium hydroxide solution. AMPS was procured from Sigma-Aldrich (India). All other chemicals were analytical grade and used without further purification. Triple distilled water was used throughout all experiments and 0.1 M phosphate buffer solution (PBS) of pH 7.0 was prepared by mixing appropriate amount of aqueous K_2HPO_4 and KH_2PO_4 solutions. P(MMA-co-AMPS) and Ag-P(MMA-co-AMPS) materials were prepared as reported in our previous work [29]. Briefly, P(MMA-co-AMPS) was prepared by mixing intended amount of MMA and AMPS in water in presence of N_2 . This mixture was further purged with N_2 under refluxing condition for 45 min and then $K_2S_2O_8$ was added as initiator. After polymerization, the formed copolymer was precipitated by ethanol and washed with distilled water to remove the residual AMPS and MMA monomers. The copolymer was then

dried at 60 °C for 12 h and then pulverized. Ag-P(MMA-co-AMPS) was prepared by mixing 0.1 wt% $AgNO_3$ and 1.0 wt% of P(MMA-co-AMPS) copolymer in DMF under constant stirring at 40 °C for 24 h.

2.2. Instrumentation

Electrochemical experiments were performed at room temperature with CHI-660C (CH instruments, USA) using a conventional three electrodes system with a cleaned glassy carbon (GC) electrode (area = 0.071 cm²) or modified GC as working electrode, saturated calomel electrode (SCE) as reference electrode and Pt wire as counter electrode. Electrochemical impedance spectroscopy (EIS) was measured between the frequency ranges 0.1 Hz to 100 KHz using 5 mV amplitude. Diffusion coefficient is calculated from chronoamperometric measurements. Prior to each electrochemical study, solution was purged with high purity N_2 for 10–20 min to remove the dissolved O_2 . Transmission electron microscope (TEM) images of Ag-P(MMA-co-AMPS) were obtained from TECNAI 12 G² FEI microscope (Netherlands), operating at 120 kV. For TEM analysis samples were prepared on 300-mesh carbon coated copper grid by dropping colloidal dispersion of the sample and drying at room temperature. UV–vis spectra were measured with a 2802 PC UV–vis absorption spectrophotometer (Unico, USA).

2.3. Preparation of electrochemical sensing platform

GC electrode surface were polished mechanically, with 0.05 μ m neutral alumina powder, rinsed thoroughly with triply distilled water and then sonicated in ultrasonic cleaning bath for 15 min. After ultrasonication, the electrode was rinsed with triply distilled water again and allowed to dry at room temperature. To prepare the electrochemical sensing platform (ESP), dry and clean GC electrodes were coated with calculated amount of prepared Ag-P(MMA-co-AMPS) material and air dried (denoted as GC/Ag-P(MMA-co-AMPS)). To obtain the constant current response between the successive cycles, the GC/Ag-P(MMA-co-AMPS) electrodes were continuously swept between -0.6 to 1.2 V in 0.1 M pH 7.0 PBS. When the GC/Ag-P(MMA-co-AMPS) electrodes show constant current (normally after 5–10 cycles), the potential sweeping is stopped and used for further electrochemical studies. Similarly, GC electrode coated with P(MMA-co-AMPS) was also used as ESP (denoted as GC/P(MMA-co-AMPS)) for comparative studies.

2.4. Sample preparation

Commercially available tablet (R-Cinex, Lupin, India) of composition 300 mg INZ and 450 mg rifampicin was procured from the local medical store. One tablet was dissolved in 25 mL of

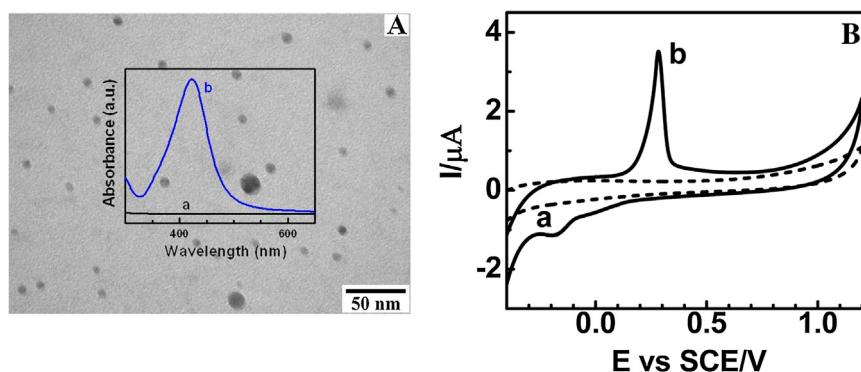


Fig. 1. (A) TEM image of Ag-P(MMA-co-AMPS). Inset shows UV–vis spectra of (a) P(MMA-co-AMPS) and (b) Ag-P(MMA-co-AMPS) materials. (B) CV curves of (a) GC/P(MMA-co-AMPS) and (b) GC/Ag-P(MMA-co-AMPS) electrodes in 0.1 M PBS (pH 7.0) at 20 mVs⁻¹.

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