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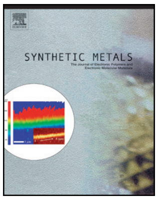

Fabrication of silver nanoparticles–polypyrrole composite modified electrode for electrocatalytic oxidation of hydrazine

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ABSTRACT

An electrochemical sensor was fabricated by electrodeposition of silver nanoparticles on pre-synthesized polypyrrole (PPy) nanofiber, forming a silver nanoparticle/PPy composite matrix on glassy carbon electrode (Ag/PPy/GCE). The electrochemical behavior and electrocatalytic activity of Ag/PPy/GCE were characterized by cyclic voltammetry. As an electrochemical sensor, the Ag/PPy/GCE exhibited strong catalytic activity toward the oxidation of hydrazine. The morphology of electrodes was characterized by scanning electron microscopy (SEM). The kinetic parameters such as the electron transfer coefficient (α) and the catalytic rate constant (k_{cat}) for the oxidation of hydrazine were determined. The diffusion coefficient (D) of hydrazine in solution was also calculated by chronoamperometry. The detection limit of hydrazine was found to be 0.2 μM. Moreover, the sensor showed excellent sensitivity, selectivity, and stability.

1. Introduction

Hydrazine is extensively used as a raw material in manufacturing of agricultural chemicals, a powerful reducing agent in fuel cells [1], and also as an intermediate in industrial preparation of pesticides, plant growth regulators, polymerization catalysts, corrosion inhibitors and antioxidants [2]. However, hydrazine is toxic and can cause irreversible cellular damage. Hydrazine has adverse health effects on the liver and brain [3], damages DNA [4], induces blood abnormalities, and causes irreversible deterioration of the nervous system [2]. Thus, it is of practical importance to accurately determine the concentration of hydrazine in a sample in an affordable manner [5]. So far, various analytical methods have been reported for determination of hydrazine, such as flow injection analysis (FIA) [6,7], ion chromatography [8], chemiluminescence (CL) and various types of spectroscopy [9–11]. However, many of these methods include sophisticated processes, and the linear ranges obtained in the methods are relatively narrow with low precision. Fortunately, electrochemical techniques are accompanied by many advantages, such as cost-effectiveness, sensitivity, simple operation and the ease of miniaturization [12–14]. However, hydrazine exhibits irreversible oxidation, requiring large overpotential at conventional electrodes. Several inorganic and organic materials have been used in development of chemically modified electrodes (CMEs) for the detection of hydrazine, which can considerably lower the overpotential and increase the electron transfer rate [15–19].

In this regard, there has been much interest in potential use of conducting polymers for some applications such as battery electrodes [20], corrosion protectives [21], and biosensors [22,23]. Among the several conducting polymers, polypyrrole (PPy) has attracted much notice due to its high conductivity, thermal and environmental stabilities, and relative ease of synthesis [24–26]. Nonetheless, since PPy-based conducting polymers exhibit poor physical and mechanical properties and are not soluble in common solvents, a few utilizations have been reported for them.

Polymer nanocomposites have attracted considerable attention in recent years and have become key substances in modern nanotechnology.

Recently, metal nanoparticles (Me-NPs), which have large surface area and greater catalytic activities than the corresponding bulk metals, have attracted a lot of interest because of their possible application in many technologically relevant applications. In particular, it has been reported that immobilization of the Me-NPs in a conducting polymer matrix serve as a convenient electrocatalyst for oxidation and reduction reactions of various redox species [27]. Among many nanoparticles, silver nanoparticles have been the most sought-after (nano) material. This is mainly due to their unique electrical [28–32], optical [33–35], catalytic [36–38], and, particularly, antimicrobial properties [39,40]. Furthermore, owing to their ability in attaching bio-molecules, being used in biosensors is one of their potential applications [41,42]. Electrochemical

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immobilization of metal is a convenient and fast method for preparation of metallic nanocrystallites on large areas of conductive substrates. The classical deposition technique from solution is not so useful, as the homogeneity in particle size and spatial particle distribution is probably disappointing when compared with the tip-directed SPM routes [43–46] or techniques using deposition into nanotemplates [47]. It is proposed that the double-pulse method is a convenient approach for controlling electrodeposition of nanoparticles, if the pulse parameters are carefully chosen and adjusted to the desired particle structure [48].

In this work we synthesize an Ag/PPy nanocomposite matrix by two steps. The first step is the electropolymerization of pyrrole with nanofiber structure on a glassy carbon electrode, while the second step is the electrochemical deposition of silver nanoparticles on the surface of the polypyrrole nanofibers. The silver nanoparticles were immobilized on the PPy matrix and also well dispersed onto the surface of the polymer. The Ag/PPy nanocomposite matrix provides a porous structure with large effective surface area and high electrocatalytic activity toward the oxidation of hydrazine.

2. Experimental

2.1. Chemicals

Pyrrole (Fluka) was purified by distillation under nitrogen atmosphere before use, stored at low temperature and protected from light. Hydrazine, $K_3Fe(CN)_6$, $LiClO_4$, $HClO_4$, $AgNO_3$ and $NaNO_3$ were purchased from Merck. Double distilled water was used throughout this research. All experiments were carried out at ambient temperature.

2.2. Apparatus and characterizations

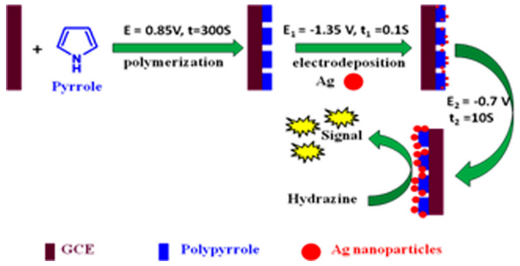
All electrochemical measurements were performed using an electrochemical system analyzer (Sama Instruments, Iran). A three-electrode cell with a glassy carbon electrode (GCE) as the working electrode, a saturated calomel electrode (SCE) as the reference electrode and a platinum (Pt) wire as the counter electrode was used.

The morphology studies were carried out with scanning electron microscope (SEM, model EM 3200, KYKY).

2.3. Preparation of PPy nanofiber and PPy/Ag nanocomposite modified electrodes

A bare GCE was polished successively with 0.05 μm alumina slurry on a synthetic cloth, rinsed with pure water, and sonicated subsequently in 1:1 double distilled water and ethanol for 5 min. Before the polymerization, electrolyte solutions were desecrated thoroughly with pure nitrogen. Electrochemical deposition of PPy on GCE was performed at ambient temperature and potentiostatically 0.85 V vs. SCE in aqueous solution containing 0.15 M pyrrole, 0.10 M $LiClO_4$ and 0.10 M carbonate. Freshly prepared PPy nanofiber electrodes were usually conditioned in 0.10 M $HClO_4$ solution for 24 h to remove the carbonate ions.

The PPy nanofibers modified electrode was treated at 0.85 V for 300 s in 0.15 M NaOH solution. The silver nanoparticles were then electrochemically deposited on the prepared PPy nanofiber in aqueous solution containing 1.0 mM $AgNO_3$ and 0.1 M $NaNO_3$ by a double pulse technique. The double pulse technique involves applying of two pulses; the first, the nucleation pulse E_1 and the second, the growth pulse, E_2. The pulse parameters were chosen carefully to avoid degrading the polymer. The pulse parameters were determined as follows: $E_1 = -1.35$ V, $t_1 = 0.1$ s and $E_2 = -0.70$ V, $t_2 = 10$ s (Scheme 1).



Scheme 1. Steps for preparation of AgNPs/PPy/glassy carbon modified electrode.

3. Results and discussion

3.1. Characterization of the modified electrode

The surface morphologies of PPy/GCE and Ag/PPy/GCE were investigated by SEM, as shown in Fig. 1. Fig. 1A shows well-defined PPy nanofibers. These PPY nanofibers are very uniform with 90–100 nm in diameter and up to several micrometers in length, and are interconnected together to form netlike nanostructures. It can be seen in Fig. 1B that many of the Ag nanoparticles were deposited onto the surface of the PPy nanofibers. Moreover, the size of Ag nanoparticles is small, with diameters of about 50–100 nm; therefore, the available surface area of Ag nanoparticles that were deposited onto the surface of the PPy nanofibers is high.

In order to further study the electrochemical properties of the modified electrodes, the cyclic voltammograms of the Ag/GCE (curve a) and Ag/PPy nanocomposite electrode (curve b) were

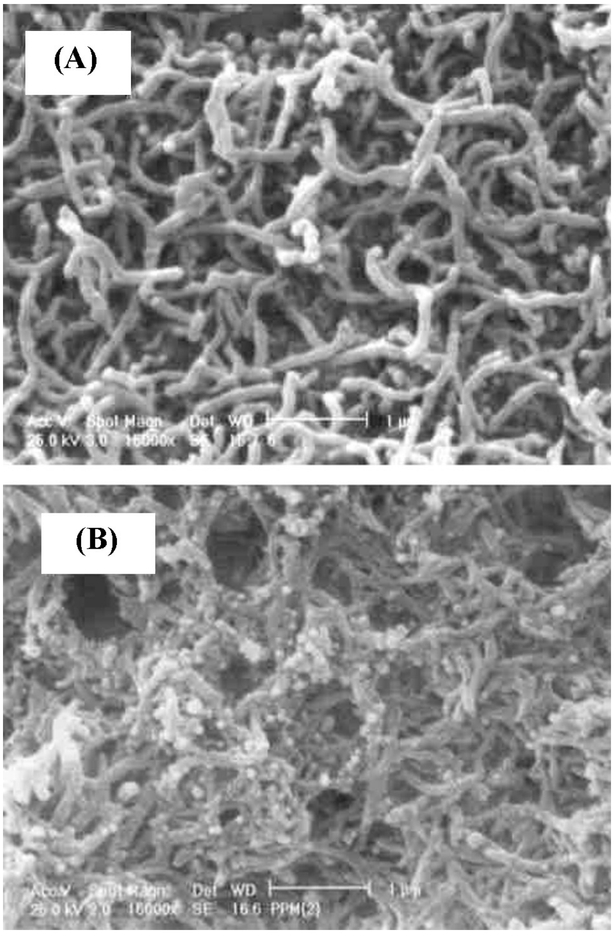


Fig. 1. SEM pictures of PPy/GCE (a) and Ag/PPy/GCE (b).