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A sensitive electrochemical nitrate sensor based on polypyrrole coated palladium nanoclusters

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ABSTRACT

This study examines the synthesis and characterization of polypyrrole coated palladium nanocluster (Pd NCs-PPy) composites and their application in nitrate detection at pH = 7.0. The synthesis was performed via the direct reduction of an aqueous solution of Pd $(CH_3COO)_2$ in the presence of pyrrole monomers in NaOH. X-ray diffraction and field emission scanning electron microscopy observations showed that the Pd cations were completely reduced to Pd with the formation of Pd NCs-PPy cluster morphology, respectively. Electrochemical properties of the Pd NCs-PPy electrode were studied by differential pulse voltammetry (DPV), cyclic voltammetry and electrochemical impedance spectroscopy. From the DPV results, the estimated limit of detection, limit of quantification (S/N = 3) for the two linear segments (lower and higher concentration of nitrate) are 0.7444, 2.4815 and 0.4535, 1.5117 μM, respectively. The sensitivity of these two linear segments is 0.124 and 0.204 $\mu A\ \mu M^{-1}\ cm^{-2}$, respectively. Results from the reproducibility experiments show that the Pd NCs-PPy is feasible for the quantitative determination of certain concentration ranges of nitrate.

1. Introduction

Polypyrrole (PPy), an electroactive polymer, has wide applications in various fields of research due to its excellent properties [1]. Recent investigations have shown that PPy or its composites with metal oxides and metals such as silver and palladium are useful for the fabrication of different type of devices, due to their good conductivity and reductive ability [2–7]. On the other hand, recent results have confirmed the effects of size and morphology of the nanocomposites on the catalytic properties [8,9]. It is clear that the catalyst efficiency can be increased with the increase of the surface area. Therefore, based on this important factor, the most important research is focused on the synthesis of electroactive polymer in the presence of noble metal or metal oxide nanoparticles [10,11]. On the other hand, the cost and the type of metal or metal oxide nanoparticles are other important factors which must be considered.

Recently, it is clearly recognized that nitrate pollution of water sources is a huge problem for the society. Several techniques have been proposed for the efficient removal of nitrate, but such applications are limited by their expensive cost [12–16]. On the other hand several methods such as spectrophotometry, chromatography and electrochemistry have been used for nitrate reduction or sensing [17]. Among these different methods, electrochemistry has numerous advantages such as low cost, simplicity, high sensitivity and selectivity. A viable method for the detection of nitrate is based on its electroreduction in the presence of metallic or bimetallic catalyst [18–21,17]. A noble metal such as palladium or its alloy can be used as a catalyst for the reduction and sensing of nitrate. Recent reports have shown that palladium and bimetallic catalyst such as copper–palladium, or other metal catalysts can be used for nitrate electroreduction in acidic [22–24] and basic [25,26] media, although the majority of ground and drinking waters are close to neutral pH. Therefore, the focus on the type of catalysts for the sensing or electroreduction of nitrate without any pretreatment is an interesting area of research. Most of the reports on nitrate electroreduction or sensing in neutral media gave very small ranges of nitrate concentrations [23,27]. In this

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work, we report a facile synthetic method for the fabrication of polypyrrole coated palladium nanocluster (Pd NCs-PPy) composites via a direct reduction of palladium cations in the presence of pyrrole monomers. The performance of these new nanocomposites toward nitrate sensing at pH = 7.0 is investigated.

2. Experimental methods

2.1. Synthesis of polypyrrole coated palladium nanocluster (Pd NCs-PPy) composites

Palladium (II) acetate (98%) was procured from Sigma-Aldrich (St. Louis, MO, USA). The pure pyrrole monomer (reagent grade, 98%, Malaysia) was stored in the dark, prior to synthesis. In this synthesis process, 1 mL of 0.1 M $(CH_3COO)_2Pd$ was added to 30 mL, 7 M NaOH solution in a reaction vessel; the reaction was allowed to occur at room temperature with continuous stirring at 500 rpm with a mechanical stirrer. After 20 min, 0.5 mL pyrrole monomer was added and the color of the solution turned from light grey to black. The reaction between the pyrrole monomer and Pd^{2+} occurred for 30 min. This was followed by the solvothermal reduction process with the addition of 0.01 mL hydrazine monohydrate into the reaction mixture and rising the temperature to 60 °C at a rate of 1.5 $°C\ min^{-1}$. This process was continued for another 60 min until the completion of the reaction. In the final step, the reaction mixture was centrifuged at 4000 rpm for 10 min to separate the Pd NCs-PPy from the solution, followed by drying in a vacuum oven at 60 °C for 12 h.

2.2. Electrode preparation

The synthesized Pd NCs-PPy (1 mg) was dispersed in DMF (1 ml) with ultra-sonication for 1 h to obtain a homogenous suspension. Then, 5 μL of the homogenous suspension was dropped on the surface of a polished glassy carbon electrode (GCE) and dried at room temperature. The current density was calculated based on the active area of GCE (0.07 cm^2) which was covered with the synthesized Pd NCs-PPy.

2.3. Apparatus and characterizations

The morphology of the Pd NCs-PPy was studied using field emission scanning electron microscopy (FESEM, Quanta 200F). The sample was dropped on the ITO surface and dried at room temperature before the FESEM characterization. X-ray diffraction (Siemens D5000) with Cu Kα radiation measurements was used to analyze the structure and phase composition of the prepared Pd NCs-PPy. The FT-IR spectrum was obtained using a Spectrum 400 (FT-IR/FT-FIR spectrometer). Electrochemical impedance spectroscopy (EIS) measurements were performed at 0 V potential in 1 mM $Fe(CN)_6^{3-/4-}$ (1:1) solution with 0.1 M KCl supporting electrolyte (Potassium ferricyanide $K_3Fe(CN)_6$, 99.2%, Sigma-Aldrich and potassium ferrocyanide $K_4Fe(CN)_6 \cdot 3H_2O$, Fischer Scientific). The impedance spectra were obtained over a frequency range of 100 kHz–0.1 Hz, with an acquisition of 10 points per decade and signal amplitude of 5 mV around the open circuit potential. The analysis of the impedance spectra was done by fitting the experimental results to equivalent circuits using the non-linear least-square fitting procedure. A potentiostat/galvanostat from Autolab, PGSTAT-302N (Ecochemie, Netherlands), controlled by a USB IF030 (MetrohmAutolab) interface card with the FRA.EXE software (version: 409.007, distributor: Metrohm Malaysia) installed in a PC was used to perform these experiments.

3. Results and discussions

The Pd NCs-PPy nanocluster morphology is confirmed by the FESEM images (Fig. 1a–b). The images show Pd nanoparticles which are bundled together with the PPy. This structure is clearly confirmed by a higher magnification of the FESEM image in Fig. 1b. The FESEM results show available surface area of the Pd NCs-PPy which can be utilized as a catalyst for nitrate reduction.

The XRD pattern of Pd NCs-PPy is shown in Fig. 2. The intensity of the (111), (200) and (220) peaks in the diffractogram are related to the Pd-PPy (Ref. code: 00-001-1201 and JCPDS card no. 05-0681). A broad amorphous diffraction peak between $2\theta = 5–25°$ in the XRD diagram of the Pd NCs-PPy is attributed to the scattering from the bare polymer chains at the interplanar spacing [28,29]. The XRD result clearly confirms that Pd^{2+} was converted to Pd element in the presence of pyrrole monomers during the synthesis of Pd NCs-PPy. Two conclusions can be drawn from the XRD and FESEM results of the Pd NCs-PPy. First, the pyrrole monomers are able to reduce Pd^{2+} to Pd, which alone undergoes oxidative polymerization to PPy, and second, the polymerized PPy encapsulates the surface of Pd nanoparticles forming a nucleus for further growth, via the Ostwald ripening process [30–32], which acts as a barrier against the corrosive NaOH environment. In addition, the surface energy and capping effect are considered as the major driving force for the nanoparticle formation [33].

The FTIR spectra of Pd NCs-PPy are shown in Fig. 3. The peak at 3454 cm^{-1} is attributed to the N–H bond, while the peak at 1682 cm^{-1} is attributed to the C–N–C bond or the C=O group,

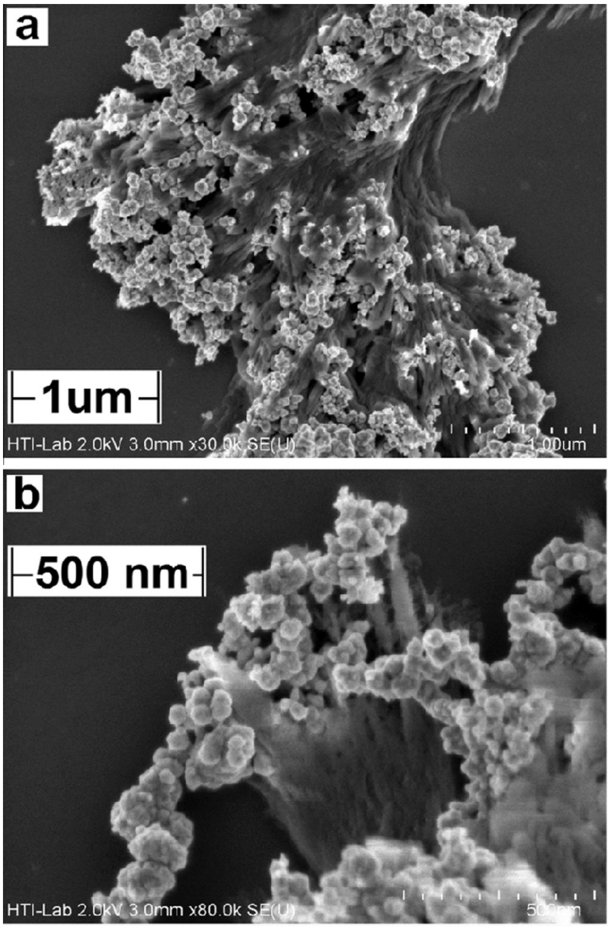

Fig. 1. (a) FESEM images of the Pd NCs-PPy and (b) a higher magnification image of (a).