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AgNWs-PANI nanocomposite based electrochemical sensor for detection of 4-nitrophenol

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ABSTRACT

Silver Nanowire-Polyaniline (AgNWs-PANI) composite modified glassy carbon electrode (GCE) was fabricated for the sensitive electrochemical determination of 4-nitrophenol (4-NP). AgNWs-PANI composite was synthesized in two steps process. The synthesized AgNWs-PANI was characterized by UV–vis, FTIR, SEM and TEM analysis. The electrochemical reduction determination of 4-NP under optimized conditions exhibited a reduction peak at −0.77 V with higher current response compared with bare GCE and AgNWs modified glassy carbon electrode (AgNWs/GCE). Effect of pH and scan rate was investigated to examine the proton transfer number, electron transfer number, electron transfer coefficient and standard rate constant of electrode. Under optimized condition, the reduction peak current and the concentration of 4-NP exhibits the linear relation with the concentration range from 0.6–32 μM, and the limit of detection was determined to be 52 nM (S/N = 3). Although, AgNWs-PANI/GCE were applied to detect the determination the 4-NP in real water samples at the recover ranging from 97.0–101.5%.

1. Introduction

Nitrophenols (NPs), a class of nitro compounds, which are classified as hazardous pollutant and they were widely present in pesticides, pharmaceuticals, and dyes [1]. Among them, 4-nitrophenol (4-NP) was listed as priority pollutant by the US Environmental Protection Agency (EPA) [2,3]. 4-NP can remain in the environment for long time due to its stability and can cause undesirable effects [1]. On the other hands from the industrial products, 4-NP was inevitably released into the environment which may cause a persistent damage to human, animals and plants. US EPA has strictly confined the maximum concentration limit of 4-NP in waste water should be less than 0.14 μM [4,5]. Therefore, it becomes important to develop a simple, efficient, reliable and cost-effective method for the quantitative determination of 4-NP.

During the past decades, a great number of methods were employed for 4-NP detection, such as capillary electrophoresis [6], fluorescence [7], UV–vis spectrophotometer [8], and high-performance liquid chromatography (HPLC) [9] and indirect enzyme-linked immunosorbent assay [10]. Nonetheless, the traditional methods (spectrophotometry) are easily interfered by the other competitive ions present in the real water. In order to overcome the limitations, capillary electrophoresis and HPLC can be preferable choice for the detection of 4-NP, but the high-cost for columns and the high-waste of organic solvents severely restrict the development of these methods. In recent years, electrochemical methods have received much attention for the determination of 4-NP because of their significant advantages, such as high-efficiency, fast response, low-cost and simple operation. In addition, the mechanism of the ongoing electrochemical reaction corresponding to the 4-NP were also elaborated [11,12]. Recently, Giribabu et al. used nitrogen-doped reduced graphene oxide as a modifier for detection of 4-NP [13]. Also other modified electrodes have been reported to demonstrate the determination of 4-NP to name few, nanoporous gold [14], manganese dioxide [15], polyaniline [16,17], silver nanoparticles [18] and carbon nanotubes [19–21]. It is still a serious challenge to explore novel materials for fabrication of a new-type electrode with outstanding electro-catalytic properties.

Nanosilver possess excellent electrical conductivity and can serve as a transparent electrode in electrochemical reactions [22]. Upon scaling down to nanoscale, the one dimensional (1-D) silver nanowires (AgNWs) have received considerable attention in biological/electrochemical sensors [23], due to the unique physical, electrical and chemical properties [24,25]. There are two possi-

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ble pathways that exhibits the excellent property of AgNWs on electrodes: (1) facilitated efficient electron transfer due to the confinement effect (2) effective surface exposure at the electrode-electrolyte interface [26]. Therefore, electrochemical sensors based on AgNWs were reported for the detection of H_2O_2, glucose [27] and cholesterol [28]. Moreover, AgNWs can be used as a template to fabricate nanocomposite for obtaining enhanced electrochemical properties, because of the highly unified morphological feature [29,30]. On the other hand, nanostructured electrically conducting polymers (CPs) were widely applied to the field of electrochemical detection [31]. Polyaniline has unique properties among the other conducting polymers due to its easy preparation, stability and high electrical conductivity which has been demonstrated in many potential electrical devices and sensor applications [32]. However, as a representative of CPs, polyaniline (PANI) have been successfully applied to determination of 4-NP due to the environmental stability, facile doping/dedoping chemistry, and tunable electrical properties [16,33]. In addition, doped PANI with the unique structure and properties offer the capability of interacting with diverse determinants to increase the sensitivity from changing the dynamic factor of electrochemical reaction [34]. Polyaniline-metal nanoparticle composites show better electrical, sensing and catalytic capabilities than that of pure PANI [35]. Unfortunately, during the process of polymerization, the morphology of the doped PANI depends on the type and the mode of doping. In order to easily control the structure of PANI, many researchers combined the PANI with another electrochemical active materials like graphene [17], carbon nanotube [36], hierarchical MoS_2 [37,38], tin oxide nanoparticles [39] and polyaniline nanotube [40] to obtain respective PANI nanocomposite.

Hence, in the present work, a straight forward approach was utilized for the fabrication of AgNWs-PANI nanocomposite to detect 4-NP. The presented sensor exhibited excellent sensitivity and low detection limit in terms of nanomolar levels.

2. Experimental

2.1. Reagents and apparatus

Anhydrous ethylene glycol (≥99.8%), polyvinylpyrrolidone (PVP, MW ~ 1300000), $AgNO_3$ (≥99%), sodium chloride, aniline (≥99.5%) and potassium persulfate were purchased from Sigma-Aldrich (USA), hydrochloric acid solution (Factor: 1.003) was obtained from DAE JUNG Chemicals (Republic of Korea), phosphate buffer solution (pH were carefully adjusted using HCl and sodium hydroxide), 0.01 M 4-NP (Sigma-Aldrich) was prepared by dissolving an appropriate amount of 4-NP in hot distilled water and was stored at 4°C for further use.

2.2. Instrumentation

UV–visible spectra were acquired by an Optical 3220. SEM images were collected using a JEOL JSM-7500F with an acceleration voltage of 15 kV. TEM images were collected using a JEOL 2000 FX microscopy with an acceleration voltage of 200 kV. FTIR data were recorded with Versa STAT3, All the electrochemical detection was carried out by using electrochemical CHI 1103A electrochemical workstation with three electrode system comprising of bare GCE, saturated calomel electrode (SCE) and platinum wire as the working, reference and counter electrode respectively.

2.3. Synthesis of AgNWs

In a typical polyol synthesis procedure that was reported before [41], 3 mM PVP was dissolved in ethylene glycol (20 mL) then ethylene glycol solutions of NaCl (0.5 mL, 0.43 M) and $AgNO_3$ (0.5 mL, 0.43 M) were simultaneously injected into the reaction mixture. The reaction was allowed to proceed under reflux for 30 min. Further, 15 mL of 0.12 M $AgNO_3$ was added to the mixture at the rate of 0.417 $mL\,min^{-1}$ under reflex condition. After this, the reaction mixture was cooled to room temperature and the product was removed by centrifugation. The final product was washed with DI water twice to remove EG and PVP, and finally re-dispersed in DI water for further use.

2.4. Synthesis of AgNWs-PANI nanocomposite

In the typical experiment, aniline monomer (0.1 M) was dissolved in 50 mL of 0.1 M HCl solution and the as prepared Ag nanowires (5 wt% with respect to comonomer) were dispersed in the solution under stirring for 30 min. Then the 50 mL of 0.1 M potassium persulfate was added dropwise and continuously stirred for 12 h. The final product was washed with deionized water and dried in the vacuum oven at 60 °C for 5 h and utilized for further use.

2.5. Fabrication of the AgNWs-PANI nanocomposite to electrode

AgNWs and AgNWs-PANI nanocomposite suspensions were prepared by dispersing the 5 mg AgNWs and AgNWs-PANI into 5 mL of methanol respectively under sonication. Prior to modification, the GCE was polished with alumina powders and then washed with deionized water. Then 15 μL AgNWs and AgNWs-PANI suspensions were dropped onto the surface of GCE and dried in air at room temperature. The modified electrodes were utilized for the electrochemical determination of 4-NP.

3. Results and discussion

3.1. Analytical and morphological characterization

3.1.1. UV–vis spectral analysis and FTIR analysis

The synthesized AgNWs showed two absorption peaks at 350 nm and 390 nm respectively (Fig. 1(a)). The peak at 350 nm and 390 nm can be assigned to the longitudinal surface plasmon resonance (LSPR) transverse plasmon resonance (TSPR) of AgNWs respectively [42]. AgNWs-PANI nanocomposite (Fig. 1(b)) showed the characteristic peak of doped polyaniline at 331 nm, which corresponds to the π-π^* transition within the benzenoid rings of

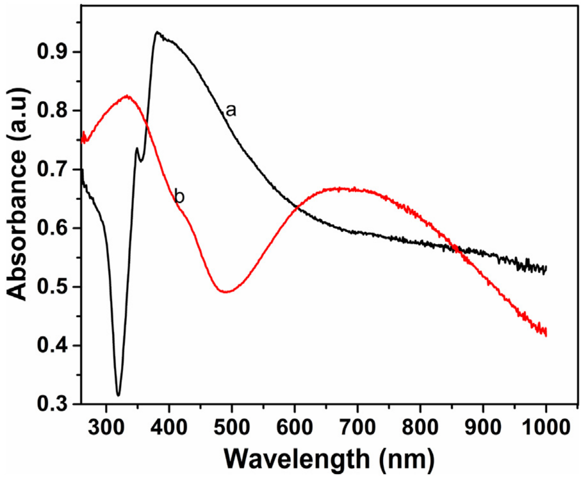

Fig. 1. UV–vis spectra of the (a) AgNWs and the (b) AgNWs@PANI nanocomposite. The AgNWs shows two peak at 350 nm and 390 nm, and the AgNWs@PANI nanocomposite has sharp peak at 331 nm, unconspicuous peak at 400–420 nm and a broad peak at 648 nm.