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Hydrazine oxidation at gold nanoparticles and poly(bromocresol purple) carbon nanotube modified glassy carbon electrode

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ABSTRACT

Bromocresol purple monomers were polymerized electrochemically at carbon nanotube modified glassy carbon electrode surface and obtained electrodes were donated as poly(BCP)/CNT/GCE. After electrochemical polymerization, Au nanoparticles were doped on the polymer film carbon nanotube modified glassy carbon electrode surface by electrochemical reduction from their acidic solutions. Modified electrodes are characterized with electrochemical impedance spectroscopy (EIS), scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX), and X-ray photoelectron spectroscopy (XPS) techniques. The electrochemical behavior of hydrazine oxidation was investigated at gold nanoparticles modified poly(BCP)/CNT electrodes in pH 10.0 phosphate buffer solution. The obtained results were compared with other modified electrodes. The best catalytic activity was obtained at AuNPs/poly(BCP)/CNT/GCE due to the shift of oxidation peak to more negative values than other electrodes with a higher current value. The peak potential and current oxidation of hydrazine were obtained at AuNPs/poly(BCP)/CNT/GCE (−28 mV, 205 μA) and poly(BCP)/CNT/GCE (427 mV, 80 μA). Under optimal conditions, the calibration curves for hydrazine were obtained over the range of 5.0×10^{-7}–1.0×10^{-3} M. The limit of detection for hydrazine was calculated as 1.0×10^{-7} M for AuNPs/poly(BCP)/CNT/GCE.

1. Introduction

Hydrazine (N_2H_4) is a small inorganic molecule. It is a water-soluble volatile colorless liquid and is the simplest unique diamine in its class because of the N—N bond. Hydrazine is used in certain rockets and spacecraft; for example, as fuel in space shuttles [1]. Hydrazine is also an ideal fuel for a direct fuel cell system since its fuel electro-oxidation process does not suffer any poisoning effects [2]. Hydrazine and its derivatives have found application in industry, agriculture, and other fields including production of metal films, photographic chemicals, explosives, insecticides and blowing agents for plastics. Hydrazine is also a toxic material. It has carcinogenic and hepatotoxic effect and can be absorbed through skin, affects blood production, causes liver and kidney damage [3]. A large number of methods for the determination of hydrazine have been reported for the development of electroanalytical [4,5] and spectrophotometric biosensors [6–8]. Methods for the determination of hydrazine which have been reported in literature are spectrophotometric [9], spectrophotometric flow injection [10,11], liquid chromatography [12], gas chromatography–mass spectrometry [13], and Raman spectroscopy [14]. However, the processes involved in many of these methods are extremely complex, and the linear ranges are relatively narrow and have low precision. Electrochemical techniques offer an opportunity for portable, economical, sensitive, and rapid methodologies. On the other hand, the electrooxidation of hydrazine at carbon electrodes is kinetically slow and require high overpotentials. Modification of the electrode surface is an approach to enhance the rate of electron transfer and minimize its overpotential.

Carbon nanotubes (CNTs) are suitable materials for electrode modification and support in biosensor applications because of their large accessible surface area, low electrical resistance, extremely high mechanical strength and stiffness, outstanding charge-transport characteristics, and high chemical stability [15]. They can be used to promote electron transfer reactions when applied as electrode materials in electrochemical devices [16].

Moreover, various chemically modified electrodes have been used in the determination of hydrazine, including polyNi(II) complex modified electrodes [17], chlorogenic acid modified glassy carbon electrodes [18], hybrid hexacyanoferrates of copper and cobalt film [19], modified-CNT paste electrode [20], pyrocatechol violet (PCV) [21], cobalt phthalocyanine [22], ethylenediamine cellulose immobilized palladium nanoparticles [23], bismuth

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hexacyanoferrate-modified carbon ceramic electrodes [24], catechin film on a glassy carbon electrode [25], coumestan modified carbon paste electrode [26], electrodeposited nano-scale islands of ruthenium oxide [27], and sol–gel derived carbon ceramic electrode modified with CNT [28]. Various electrocatalytic active metal NPs-modified electrodes containing Pd [29,30], Pt [31], Ag [32] and Au [1,33] have been used for determination of hydrazine.

Noble metals such as Pt, Pd, Ru, and Au have been reported to be efficient catalysts for most fuel cell anodes [34]. However, the cost of these materials is still a big drawback for full commercial application of fuel cells. To date, several studies have sought to find an abundant, inexpensive, stable and efficient electrocatalytic material as a substitute for noble metal catalysts [35,36].

Conducting polymer films have been widely studied for applications in chemical sensors and biosensors. Bromocresol purple (BCP) is a pH indicator. It is also used as a dye to measure albumin in medical laboratories. Its electropolymerization at the electrode surface and its function as an electrocatalyst have been reported in literature [37]. The poly (BCP) modified electrode possesses a larger actual surface area, π—π conjugated bond, a great deal of active sites and better conductivity, which led to the dissimilar conjugation effect of the purine derivatives on the electrode interface [37]. Various poly(BCP) modified electrodes have been applied in the determination of ascorbic acid [38] and cadmium [39].

In this work, we developed an electrochemical method for detection of hydrazine. Bromocresol purple monomers were polymerized electrochemically at carbon nanotube modified glassy carbon electrode surface and obtained electrodes were donated as poly(BCP)/CNT/GCE. After electrochemical polymerization, gold nanoparticles were doped on the surface of poly(BCP)/CNT/GCE by electrochemical reduction from their acidic solutions. Poly(BCP)/CNT/GCE and AuNPs/poly(BCP)/CNT/GCE were fabricated, a process which has never been reported before. These electrodes were characterized by SEM-EDX and XPS techniques. The prepared modified electrode has several advantages including high surface-charge-transfer rate constant, wide linear dynamic range, and good sensitivity for hydrazine.

Finally, gold nanoparticle modified poly(BCP)/CNT/GC electrode has been used for LSV detection of hydrazine in a micromolar unit. The electrochemical reversibility of the oxidation of hydrazine may be greatly improved in the presence of the poly(BCP) film by accelerating the rate of electron transfer, indicating that the poly(BCP) film had excellent electrocatalytic activity for oxidation reaction of hydrazine at the surface of the modified electrode.

2. Experimental

2.1. Chemicals

All reagents were of analytical grade and were used as received. Bromocresol purple was obtained from Sigma–Aldrich. Hydrazine ($N_2H_4{\cdot}H_2SO_4$) was obtained from Merck. All solutions were prepared with ultra pure water. Daily prepared BCP and hydrazine solutions were used prior to measurements. A 1.0 mM $HAuCl_4$ was prepared by diluting the concentrated Au solution with 0.1 M HCl after dissolving the Au wire (99.999% in purity) in HNO_3:HCl (1:3). Multi-walled carbon nanotubes (CNTs) were purchased from Aldrich (purity > 95% diameter 110–170 nm, length 9 μm). N,N-dimethyl formamide (DMF), HNO_3 and HCl were purchased from Merck and all were in ultrapure grade. Phosphate buffer solution (PBS) was prepared with 0.1 M H_3PO_4 and pH was adjusted with 3 M NaOH. All solutions were prepared using ultrapure water (Milli-Q 18.2 MΩ cm, Millipore System Inc.).

2.2. Apparatus

Autolab PGSTAT101 and PGSTAT 128N voltammetric analyzer with a three electrode system involves a working electrode (bare GCE with a diameter of 3 mm and a geometric area of 0.0707 cm^2), a platinum wire counter electrode, and an Ag/AgCl (sat. KCl) reference electrode for voltammetric measurements. The surface characterization was examined by using Thermo K-Alpha-Monochromated high-performance XPS spectrometer and Philips XL 30 SFEG SEM.

2.3. Pre-treatment of CNT and preparation of poly(bromocresol purple)/CNT/GCE

GCE was cleaned by polishing on a synthetic cloth with Al_2O_3 slurry, followed by ultrasonication of the electrode for 3 min each in ethanol and pure water, respectively. Purification and activation procedures were applied to untreated CNTs by the following procedure: 0.1 g CNT was boiled in an adequate amount of HNO_3 and then acid-treated CNTs were rinsed with ultrapure water for multiple times [40]. Finally the black colored suspension was obtained by dispersing 30 mg of purified CNT in 4 mL DMF. CNT/GC electrode was prepared by dropping the 10 μL sample from CNT suspension on the pre-conditioned GCE and letting the solvent (DMF) of the suspension on the GCE surface evaporate at 60 °C.

The poly(BCP)/CNT/GC electrode was prepared by electrochemical polymerization of bromocresol purple (BCP) on a CNT/GCE

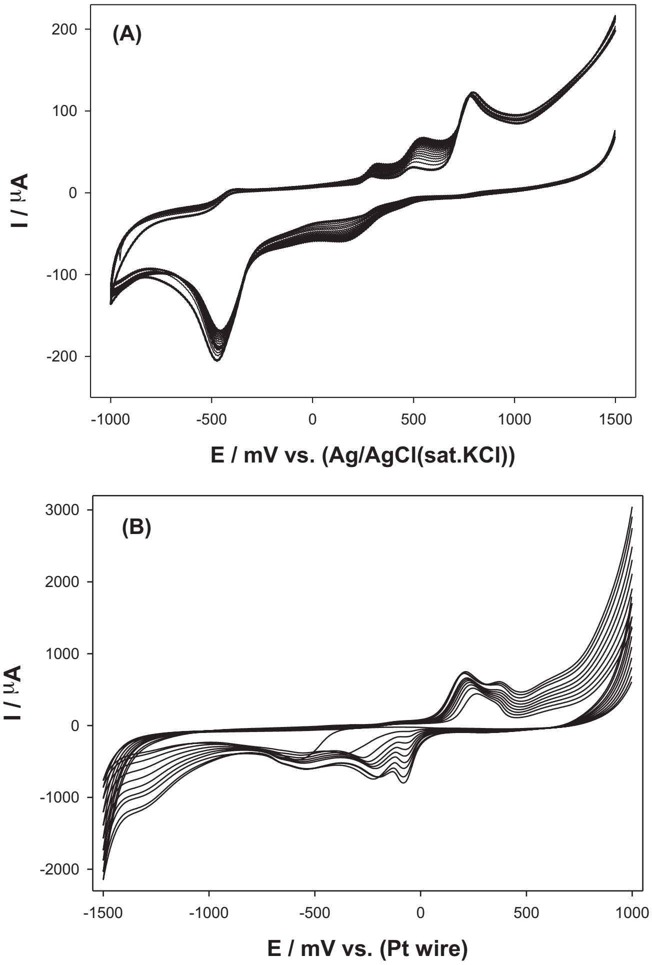

Fig. 1. Cyclic voltammograms for, (A) electrochemical polymerization for 2.0 mM BCP in 0.1 M KNO_3, (B) Au nanoparticle deposition from $HAuCl_4$ solution containing 3.0 mM Au^{3+}.