Simultaneous detection of dopamine and ascorbic acid using silicate network interlinked gold nanoparticles and multi-walled carbon nanotubes

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ABSTRACT

In this manuscript, we report a facile and environmental friendly procedure for the aqueous synthesis of gold nanoparticles (∼3–8 nm) and functionalized multiwalled carbon nanotubes (MWCNT) interlinked through bi-functionalized silicate molecule *N*-[3(trimethoxysilyl)propyl]ethylenediamine (EDAS). The complexes, denoted by MWCNT–EDAS–AuNPs, were then characterized by UV–visible spectroscopy, Fourier transform infrared (FT-IR) spectroscopy, transmission electron microscope (TEM), and atomic force microscope (AFM). In addition, it is also fabricated on glassy carbon electrodes to simultaneously detect ascorbic acid (AA) and dopamine (DA) using an electrochemical technique. MWCNT–EDAS–AuNPs can act as a modified electrode and show a wide linear response for AA and DA in the concentration range of 1×10^{-7}–9×10^{-6} M and 1×10^{-7}–8×10^{-6} M with detection limits of 0.07 and 0.08 μM at $S/N = 3$, respectively. These results have demonstrated that MWCNT–EDAS–AuNPs are a promising candidate as advanced electrode material in electrochemical sensing of AA and DA simultaneously in pharmaceutical samples.

1. Introduction

Since dopamine (DA) has been demonstrated to be a neurotransmitter in the brain, it can shed light on the treatment of disorders of the central nervous system, such as Parkinson's disease. Ascorbic acid has a very important activity as it is involved in the control for metabolism of iron. For example, ascorbic acid AA (vitamin C) has been used for the prevention and treatment of common cold, mental illness, infertility, and cancer. AA is also well known for its antioxidant property and usually coexists with DA in biological samples [1,2]. Both AA and DA are electroactive compounds which can be determined by electrochemical techniques based on anodic oxidation [3]. Starting from the 1970s, electrochemical methods have been used to detect such chemicals [4,5].

However, a major problem is that the oxidation signals of AA and DA show almost at the same potential at bare electrode because the electrochemical anodic peak potentials for ascorbic acid (AA) and DA are similar [6–8]. In addition, the standard electrodes, such as Au, Pt, and glassy carbon electrode (GCE), still suffer from a fouling effect due to the accumulation of oxidized products of DA that can catalyze the oxidation of AA on the electrode surface, resulting in a poor selectivity and sensitivity [9–11]. This research has been focused on how to resolve the potential overlap of voltammetric oxidation of AA and DA with improved intensity.

Metal nanoparticles (MNPs) have attracted much attention because of their unique properties and numerous potential applications [12,13]. In particular, gold nanoparticles (AuNPs) are focused mainly due to their versatile applications in catalysis [14], drug delivery [15], nanoelectronics [16], chemical sensing [17], medical diagnostic tools [18], and complex nanoassemblies as components. Gold nanoparticles in colloidal suspension have been synthesized by using a wide variety of reducing agents, such as sodium borohydride [12,19], sodium citrate [20], and ethanol [21]. Many different types of stabilizers have been used as capping agents to stabilize the nanoparticles, including surfactants [22], polymers [23], dendrimers [24], as well as different types of ligands [25]. Thiol- and

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amine-based sol–gel is one of the most commonly employed functionalized materials, which provides great stability to the attached nanoparticles in both aqueous and organic media [26]. Amine functional groups can exhibit dual functionality in the sol–gel monomers and act as a capping agent to the metal sol and complex the metal ions. Amines have high affinity toward noble metals and they are often used to deposit metallic colloids onto a variety of support materials, such as carbon [27,28], mesoporous silica [29], titania [30], with aminosilanes [31–33].

Carbon nanotubes (CNTs) have been the focus of intense research in the electrochemical detection of biomolecules owing to their unique electronic structures, chemically active surface, high electrical conductivity, high chemical stability, and good biocompatibility [34–36]. Among these areas, CNTs have been used as advanced supporting materials for the dispersion and stabilization of metal nanoparticles, such as Au, Ag, Pt, and Pd [37]. Defects in the graphite structure could cause the non-uniformity of functional groups on the surface of CNTs at both ends and also the sidewalls. Thus, the modification of CNT surface should consider the following points: (a) we need to create homogeneous modification onto the surface; (b) the dispersibility should be enhanced after adding new functional groups; and (c) the structure of CNTs remained unchanged [38]. In particular, Au/CNTs hybrid nanomaterials are advantageous due to the combination of the unique electronic properties and ease of surface modification of CNTs and the biocompatibility of AuNPs. Recent studies demonstrated that the utilization of gold nanoparticles decorated CNT-based electrodes would attain a significant separation of oxidant potential for biological analytes, which could improve the selective sensing of analytes with an enhanced sensitivity [39–41]. Similarly, metal nanoparticle/carbon substrate hybrid structures have been widely used. For example, Huang et al. proposed a palladium nanoparticle (PdNPs)-loaded carbon nanofibers-modified electrode for the electrochemical determination of AA, DA, and UA [42]. Dursun et al. reported that a platinum nanoparticles (PtNPs) decorated multiwall carbon nanotubes-modified electrode for simultaneous determination of AA, DA, and UA in electrochemical methods [43]. Ragupathy et al. synthesized a multiwalled carbon nanotube–silica network–gold nanoparticles-based nanohybrid-modified electrode for the determination of ascorbic acid in the presence of dopamine [44]. Ahmadreza Afraz et al. found Ag nanoparticles (AgNPs)–MWCNT-modified glassy carbon electrode for an analytical sensing of hydrogen peroxide [45]. However, the combined existence of CNTs, sol–gel silica, and AuNPs would provide synergistic effect on the sensor performances.

Therefore in this manuscript, silicate molecule (*N*-[3(trimethoxysilyl)propyl]ethylenediamine and EDAS) capped Au nanoparticles and functionalized MWCNT (MWCNT–EDAS–AuNPs) nanocomposite were synthesized by an environmentally friendly approach, i.e. gold precursor was reduced by EDAS and in addition the latter acted as a capping agent. The structure and composition of EDAS–AuNPs and MWCNT–EDAS–AuNPs were characterized by UV–visible, Fourier transform infrared (FT-IR) spectroscopy, X-ray diffraction pattern (XRD), transmission electron microscope (TEM), and atomic force microscope (AFM). Then the prepared EDAS–AuNPs and MWCNT–EDAS–AuNPs were fabricated as modified electrode to simultaneously determine AA and DA.

2. Experimental method

2.1. Materials and methods

Hydrogen tetrachloroaurate (III) trihydrate (HAuCl$_4$·3H$_2$O, >99.9%), *N*-[3(trimethoxysilyl)propyl]ethylenediamine (EDAS, >98%), multi-walled carbon nanotubes (MWCNT, >90%), dopamine (DA), ascorbic acid (AA), and nafion (5 wt% in alcohol) were purchased from Sigma–Aldrich Inc. Nitric acid (HNO$_3$), sulfuric acid (H$_2$SO$_4$), hydrochloric acid (HCl), potassium dihydrogen phosphate (99%), and dipotassium hydrogen phosphate (99%) were purchased from Merck Inc. and used as received. All other chemicals used were of analytical reagent grade and all aqueous solutions were prepared with double distilled water. All glassware were thoroughly cleaned with aqua regia (3:1 HNO$_3$/HCl (v/v)) and rinsed extensively with double distilled water before use.

2.2. Synthesis of silicate network gold nanoparticles (EDAS–AuNPs)

EDAS–AuNPs were synthesized via the following procedure. 1 mL of 0.01 M HAuCl$_4$·3H$_2$O was mixed with 0.5 mL of 0.1 M EDAS sol in water with vigorous stirring for 15 min. The hydrolysis and condensation were initiated by the addition of 100 μL of 0.1 M HCl and stirred for another 1 h. Then the reaction mixture was made up to 10 mL by adding double distilled water and continuously stirred for another 2 h. A clear yellow color solution was obtained. The solution thus obtained was kept at room temperature overnight, resulting in a color change from yellow to wine red, indicating the formation of EDAS–AuNPs.

2.3. Synthesis of silicate network interlinked gold nanoparticles and multiwalled carbon nanotubes (MWCNT–EDAS–AuNPs)

Before being used, MWCNTs were oxidized by dispersing 20 mg of the as-received MWCNTs in 30 mL of concentrated sulfuric acid and nitric acid mixture (3:1) taken in a 100 mL round bottom flask connected with a condenser. Then the dispersion was heated at 90 °C for 5 h. After that, the resulting dispersion was diluted in water and filtered. The resulting solid was then washed until neutral pH was reached and then the sample was dried in vacuum at 40 °C for 12 h. 3 mL of as-prepared EDAS–AuNPs solution was subsequently mixed with the oxidized carbon nanotubes (0.1–0.3 mg carbon nanotubes) and stirred for 8 h at room temperature to yield homogeneous and well-dispersed solution of the MWCNT–EDAS–AuNPs.

2.4. Characterizations

The absorption spectra were recorded using the Agilent (Specord 600S) diode array UV–visible spectrophotometer. The infrared spectra were recorded by Thermo scientific Nicolet iS5 FTIR spectrometer. The morphology and particle size were analyzed by HRTEM, JEOL JEM2010 model. Energy dispersive X-ray analysis was used to determine the elements present in the nanoparticles. The XRD measurements of gold nanoparticles and MWCNT–EDAS–AuNPs films were carried out by using Rigaku X-ray diffractometer, Japan (Cu-*K*α radiation). Atomic force microscope (AFM) analyses (non-contact mode) were performed on a XE-100 scanning probe microscope, Park systems, South Korea.

2.5. Electrochemical investigation

Electrochemical measurements were performed on a CHI 650C electrochemical workstation (Austin, TX, USA). A conventional three-electrode system was used for cyclic voltammetric (CV), differential pulse voltammetric (DPV), and amperometric studies. A bare or modified glassy carbon (GC) electrode (3 mm diameter) was used as the working electrode, where a Pt wire as the counter electrode and an Ag/AgCl with saturated KCl as the reference electrode were used. The measurements were carried out in a phosphate buffer solution (PBS) with 0.1 M KCl at pH 7.0 and at room temperature.