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Biosensing applications of titanium dioxide coated graphene modified disposable electrodes

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ABSTRACT

In the present work, preparation of titanium dioxide coated graphene (TiO_2/graphene) and the use of this nanocomposite modified electrode for electrochemical biosensing applications were detailed. The nanocomposite was prepared with radio frequency (rf) rotating plasma method which serves homogeneous distribution of TiO_2 onto graphene. TiO_2/graphene was characterized with scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS) and X-ray diffraction (XRD) analysis. Then, this nanocomposite was dissolved in phosphate buffer solution (pH 7.4) and modified onto disposable pencil graphite electrode (PGE) by dip coating for the investigation of the biosensing properties of the prepared electrode. TiO_2/graphene modified PGE was characterized with SEM, EDS and cyclic voltammetry (CV). The sensor properties of the obtained surface were examined for DNA and DNA-drug interaction. The detection limit was calculated as 1.25 mg L^{-1} (n=3) for double-stranded DNA (dsDNA). RSD% was calculated as 2.4% for three successive determinations at 5 mg L^{-1} dsDNA concentration. Enhanced results were obtained compared to the ones obtained with graphene and unmodified (bare) electrodes.

1. Introduction

Graphene is a two-dimensional (2D) carbon-based nanomaterial (sp^2 hybridized carbon) which has unique properties such as good thermal, electrical, optical and mechanical properties, having high specific surface area and ultrahigh carrier mobility [1,2]. The invention of graphene has been one of the milestones in nanotechnology. Nowadays composites of graphene have attracted great attention for the use in diverse areas. In this regard, titanium dioxide (TiO_2)/graphene composites hold an attractive position since TiO_2 is a nontoxic, highly stable and a good catalyst material with a large surface area. TiO_2/graphene composites have been synthesized by various techniques such as atomic layer deposition, electrospinning, blending graphene oxide sheets with a titanium hydroxide-based ionic salt and reduction of graphene oxide in the presence of TiO_2 nanoparticles [3–6]. During the TiO_2 growth on graphene, graphene can help for controlling the morphology of TiO_2 in terms of nucleation [7]. These composites have utilized in important applications including photocatalysis, lithium-ion batteries, supercapacitors, dye-sensitized solar cell photoanodes, fuel cells, and sensors [8–10]. William et al. have prepared TiO_2/graphene nanocomposites via UV-assisted photocatalytic reduction of graphene oxide [11]. How and his colleagues have synthesized TiO_2 with highly exposed {001} facets with a solvothermal method and they have decorated the surface using reduced graphene oxide sheets. The prepared nanocomposite has been modified onto a glassy carbon electrode in order to perform electrochemical dopamine sensing [12]. The prepared electrode has showed enhanced electrocatalytic activity towards the oxidation of dopamine and ascorbic acid compared to unmodified glassy carbon electrode. The differential pulse voltammetric studies has exhibited sensitivity and selectivity for the detection of dopamine in the presence of ascorbic acid. A lactate biosensor based on TiO_2 nanoparticles and reduced graphene has been prepared by Casero et al. [13]. The bionanocomposite has been mixed with laccase oxidase and immobilized on the surface of a glassy carbon electrode. The sensor has been exhibited higher sensitivity and better detection limit compared to the biosensor without TiO_2 nanoparticles. Nafion/TiO_2/graphene composite films have been used for the electrochemical detection of L-tryptophan and L-tyrosine. TiO_2/graphene nanocomposite has been prepared by a hydrothermal procedure [14]. The nanocomposite film has been modified onto a glassy carbon electrode and its voltammetric response to L-tryptophan and L-tyrosine has been examined. The incorporation of TiO_2 nanoparticles with graphene significantly has improved the electrocatalytic activity compared to electrode

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modified with Nafion/graphene. Direct electrochemistry of hemoglobin on graphene and TiO_2 nanorods composite modified electrode has been performed by Sun et al. [15]. The graphene-TiO_2-hemoglobin composite modified carbon ionic liquid electrode has been constructed through a simple casting method with Nafion. Direct electron transfer of quasi-reversible redox waves have obtained in the study. Gao et al. have developed an electrochemical DNA biosensor based on graphene, TiO_2 nanorods and chitosan nanocomposite modified carbon ionic liquid electrode [16]. Mixture of graphene, TiO_2 and chitosan has been obtained by sonication. The prepared electrode has been used for the detection of the transgenic soybean sequence of MON89788. By using methylene blue as hybridization indicator for monitoring the hybridization with different single-stranded DNA (ssDNA) sequences, the differential pulse voltammetric response of methylene blue has been compared. The electrochemical response of methylene blue has been improved. TiO_2/graphene nanocomposite has been prepared by hydrolysis of titanium isopropoxide in colloidal suspension graphene oxide and in situ hydrothermal treatment [17]. Electrochemical detection of adenine and guanine has been performed in the study. The presence of TiO_2 nanoparticles significantly improved electrocatalytic activity and voltametric response have been obtained towards adenine and guanine.

However, there is no data about the synthesis of TiO_2/graphene composites by using rotating plasma method and application of the composite. To the best of our knowledge this is the first to synthesize this nanocomposite with radio frequency (rf) rotating plasma method and to present its application as an electrochemical DNA and DNA-anticancer drug interaction biosensing by using disposable and low-cost electrode technology. Another excellent carbon-based nanomaterial, carbon nanotubes, have been decorated with metal clusters (nickel) to form nanohybrids by plasma treatment which offers ideally controlled nanostructures [18]. In addition there are some attempts to dope graphene with nitrogen [19], chlorine [20] and fluorine [21] by plasma technique. In the current work, we detailed the preparation of TiO_2/graphene nanocomposite by rf rotating plasma which serves homogeneous distribution of TiO_2 onto graphene for the first time in the literature. Later on electrochemical DNA and DNA-anticancer drug (Mitomycin C) interaction sensing applications were performed in order to build up novel, fast, low cost and reliable analysis methods. In each work, the comparison of the performance of the TiO_2/graphene modified PGE was made with the performance of the graphene modified and unmodified (bare) ones.

2. Experimental

2.1. Chemicals

Graphene powder (99.9%) and $TiCl_4$ (99.0%) were purchased from Aldrich. Fish sperm double-stranded DNA (dsDNA) was obtained from Serva. Mitomycin C (MC) was from Sigma. Other chemicals were in analytical grade and supplied from Sigma and Merck.

2.1.1. Preparation of solutions

All solutions were prepared with ultra pure water. Stock solutions of dsDNA (2000 mg L^{-1}) were prepared with Tris-EDTA buffer solution (10 mM Tris-HCl, 1 mM EDTA, TE, pH 8.00). More diluted solutions of DNA were prepared with 50 mM acetate buffer containing 20 mM NaCl (ABS, pH 4.8). Stock solutions of MC (500 mg L^{-1}) was prepared in ultra pure distilled water. More diluted solutions of MC were prepared with 50 mM phosphate buffer solution (PBS, pH 7.4) containing 20 mM NaCl.

Table 1
Elemental compositions of the samples.

Sample/element, weight %	C	O	Ti
Graphene	93.27	6.73	–
Graphene/TiO_2	55.47	35.98	8.55

2.2. Apparatus

Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) techniques were performed with AUTOLAB-PGSTAT 204 analysis system supported with a NOVA software package (Metrohm, The Netherlands). A three electrode system consists of a pencil graphite working electrode (PGE), a Ag/AgCl reference electrode (BASi, West Lafeyette, IN USA) and a platinum (Pt) wire counter electrode (BASi, West Lafeyette, IN USA) was used in the experiments. The connector of the PGE (0.5 mm HB Tombow) was a Tombow pencil.

2.3. Preparation of rf plasma coating of $TiCl_4$ onto graphene powders

The plasma modification process was carried out in a capacitively coupled, 13.56 MHz rf rotating plasma reactor [22]. In order to modify dry graphene powder, vapor of the dopant agent of $TiCl_4$ was sent into the rotating chamber and plasma was created through 50 W rf power. Steady state plasma coating parameters were applied for both modification during 1 h and the base pressure of 20–30 mTorr.

2.3.1. Surface characterization

Surface morphology and elemental analysis of the samples were examined using scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDS) with FEI Quanta FEG 250 scanning electron microscope.

2.3.2. X-ray diffraction (XRD) analysis

XRD analysis of the samples were performed with Bruker AXS D8 Advance Model X-ray Powder Diffraction System.

2.4. Modification of the working electrode with TiO_2/graphene

0.25 mg mL^{-1} TiO_2/graphene was dissolved in 50 mM pH 7.4 phosphate buffer solution. The solution was sonicated at least 30 min before experiments. A bare pencil tip was dipped into the sonicated solution for 30 min 0.25 mg mL^{-1} graphene was dissolved in the same way and used for the comparison experiments. No pretreatment step was used for the electrodes.

2.4.1. Surface characterization

Surface morphology of the electrodes were examined using scanning electron microscopy-energy dispersive X-ray spectroscopy with FEI Quanta FEG 250 scanning electron microscope.

2.5. Immobilization of dsDNA onto TiO_2/graphene modified PGE

TiO_2/graphene modified PGE was held at 0.0 V vs. Ag/AgCl for 180 s in order to accumulate dsDNA. Same procedure was applied for graphene modified PGE. TiO_2/graphene nanocomposite on the PGE surface was positively charged and therefore negatively charged dsDNA was immobilized electrostatically onto the electrode surface [12].

2.5.1. Interaction of MC with dsDNA immobilized TiO_2/graphene modified PGE

The prepared electrode was immersed into vials containing

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