



## Electrochemically reduced fullerene–graphene oxide interface for swift detection of Parkinsons disease biomarkers



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### ABSTRACT

We are reporting first-time synthesis of the novel water-soluble fullerene–graphene oxide (C<sub>60</sub>–GO) conjugate by 1,3-dipolar cycloaddition reaction between fullerene (C<sub>60</sub>) and azide functionalized graphene oxide (GO–N<sub>3</sub>). The synthesized fullerene–graphene oxide (C<sub>60</sub>–GO) conjugate was characterized by fourier transform infrared spectroscopy (FTIR), Ultraviolet–visible (UV–vis) spectroscopy, electrochemical and field emission electron microscopy (FESEM). The C<sub>60</sub>–GO conjugate was immobilized on surface of glassy carbon electrode (GCE) using surface bound diazonium salts as an impact strategy. The nitrophenyl modified GCE (GCE–Ph–NO<sub>2</sub>) was fabricated by electrochemical reduction of nitrophenyl diazonium salt (N<sub>2</sub><sup>+</sup>Cl<sup>–</sup>–Ph–NO<sub>2</sub>). The GCE–Ph–NO<sub>2</sub> modified electrode was reduced to phenylamine-modified electrode (GCE–Ph–NH<sub>2</sub>) by sodium borohydride/gold–polyaniline (NaBH<sub>4</sub>/Au–PANI) system. The surface phenylamine groups of GCE–Ph–NH<sub>2</sub> were converted to diazonium groups (GCE–Ph–N<sub>2</sub><sup>+</sup>Cl<sup>–</sup>) which upon electrochemical reduction in an aqueous C<sub>60</sub>–GO conjugate solution causes successful immobilization of C<sub>60</sub>–GO conjugate to give phenyl modified fullerene–graphene oxide interface (C<sub>60</sub>–GO–Ph–GCE). The C<sub>60</sub>–GO–Ph–GCE interface upon electrochemical reduction in 1.0 M potassium hydroxide (KOH) solution produces highly conductive electrochemically reduced (ERC<sub>60</sub>–GO–Ph–GCE) interface. The electrocatalytic activity of developed (ERC<sub>60</sub>–GO–Ph–GCE) interface originates from the synergetic effects of electrochemically reduced fullerene (ERC<sub>60</sub>) and graphene oxide (ERGO) species that makes the conjugate (C<sub>60</sub>–GO) film highly conductive. The (ERC<sub>60</sub>–GO–Ph–GCE) interface was applied for determination of the homovanilic acid (HVA; a biomarker for Parkinsons disease) over a concentration range from 0.1–7.2 μM with a detection limit of 0.03 μM. The developed (ERC<sub>60</sub>–GO–Ph–GCE) interface shows good sensitivity that makes it suitable for detection of HVA in biological fluids (urine).

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### 1. Introduction

Fullerenes and graphene are representative allotropes of carbon having unique physiochemical properties due to their structural design [1]. Fullerene (C<sub>60</sub>) is a closed-cage structure considered as powerful building blocks in material and biological science [2]. Graphene oxide (GO) is an important derivative of carbon decorated by carboxyl groups resulting in polar surface properties and has shown potential applications in electronic and sustainable energy storage devices [3–5]. In recent years, hybrid structures

combining two different forms of carbon nanostructures have been prepared to generate multifunctional nanomaterials with enhanced properties [6–8]. However, most of the hybrid materials are insoluble in aqueous medium limiting their applications. In the present work, we are reporting first-time synthesis of water-soluble fullerene–graphene oxide (C<sub>60</sub>–GO) conjugate by 1,3-dipolar cycloaddition reaction between fullerene (C<sub>60</sub>) and azide functionalized graphene oxide (GO–N<sub>3</sub>). The present approach for direct conjugation of fullerene (C<sub>60</sub>) with GO–N<sub>3</sub> is more efficient than reported methods that involves comparatively more number of steps for the synthesis of fullerenes derivatives (pyrrolidine fullerene and C<sub>60</sub>–CNH) followed by conjugation with functionalized graphene oxide [9,10]. The current method for synthesis of

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water-soluble fullerene–graphene oxide ( $C_{60}$ –GO) conjugate will open new windows for its applications in biomedical research.

Most applications of hybrid carbon nanomaterials require their immobilization at the solid surfaces as thin films for understanding their chemistry at the interface. Currently electrochemical reduction of aryldiazonium salts become one of the most realistic interface for immobilization of the nanomaterials [11–13]. This method involves electrochemical grafting of aryldiazonium ions to produce stable grafted organic layers on many conductive and semi-conducting surfaces. The diazonium salts are easy to prepare by simply mixing of aromatic amines with sodium nitrite in an ice-cold aqueous acidic solution. The grafting involves one electron electrochemical reduction of aryldiazonium salt liberating nitrogen gas and form aryl radical that instantaneously reacts with the surface. Recently Svorc et al. reported grafting of nitrophenyl diazonium salt at boron-doped diamond electrodes and the terminal nitrophenyl groups were electrochemically reduced to phenylamine groups [14]. However, electrochemical reduction of grafted nitrophenyl to phenylamine groups is not an efficient method to produce major product as phenylamines due to quasi-reversible nature of the electrode process [15]. This method produces less concentration of phenylamine groups at electrode surface responsible for further formation of diazonium salts that will effectively immobilize the carbon nanomaterials. Therefore, there is a need of an alternative method that can efficiently reduce grafted nitrophenyl to phenylamine groups.

Gold nanoparticles (AuNPs) have attracted considerable attention due to their various inherent advantages such as ease of synthesis, high chemical stability and catalytic properties for reduction of the aromatic nitro compounds to amine derivatives [16,17]. Among conducting polymers, polyaniline (PANI) has become a particular focus of interest because of its environmental stability and controllable electrical conductivity. Gold–polyaniline (Au–PANI) nanocomposite materials with synergetic chemical and physical properties have received great attention worldwide from both academic and industrial point of view due to the enhanced catalytic properties of gold nanoparticles (AuNPs) and large surface area of polyaniline (PANI) [18–20]. The present work reports synthesis of high-aspect ratio worm-like polyaniline (PANI) coated gold nanorods (Au–PANI) by in situ polymerization of aniline using chloroauric acid ( $HAuCl_4$ ) as an oxidizing agent and citric acid (CA) acts as a capping agent for gold nanorods (AuNRs). Polyaniline (PANI) doped during acidic conditions become hydrophilic that enhances solubilization of the gold–polyaniline (Au–PANI) nanocomposite in an aqueous solution. The present study reports novel applications of sodium borohydride/gold–polyaniline ( $NaBH_4$ /Au–PANI) system for catalytic reduction of the nitrophenyl (GCE–Ph– $NO_2$ ) to phenylamine groups (GCE–Ph– $NH_2$ ) attached to the solid interface (glassy carbon electrode).

Parkinsons disease (PD) is a neurodegenerative disorder causes dysfunction, cognitive, sensory symptoms and sleep disturbances [21]. The identification of Parkinsons disease biomarkers is mainly observed in cerebrospinal fluid (CSF) and biological fluids (plasma and urine) [22]. Dopamine undergoes catabolism by monoamine oxidase and catechol–O–methyl transferase to give homovanillic acid (HVA) and 3, 4-dihydroxyphenylacetic acid (DOPAC) as metabolites that appears to be attractive biomarkers for Parkinsons disease [23]. Monitoring of the HVA in patients suffering from Parkinsons disease is highly demanding and therefore there is a need to develop simple, rapid and low-cost methods for routine analysis of the HVA in excreted urine samples. Reported methods for determination of HVA are capillary electrophoresis [24] and enzyme-linked immunosorbent assay (ELISA) [25]. However, cross reactivity of immunoassay methods often makes analysis semi-quantitative and expensive nature of monoclonal antibodies limits

their applications. Electrochemical methods are useful to provide a possible route for quick measurement of biomarkers in biological fluids.

Fullerene ( $C_{60}$ ) and graphene oxide (GO) are non-conducting materials that upon electrochemical reduction (ER) produce highly conductive films at electrode surface that shows electrocatalytic properties [26,27]. The aim of the present work is to synthesize and characterize water-soluble fullerene–graphene oxide ( $C_{60}$ –GO) conjugate and then electrochemically reduce the conjugate ( $C_{60}$ –GO) at glassy carbon electrode (GCE) to produce highly conductive film. The fullerene–graphene oxide ( $C_{60}$ –GO) conjugate was immobilized on the surface of glassy carbon electrode (GCE) using surface bound diazonium salts to give phenyl modified conjugate interface ( $C_{60}$ –GO–Ph–GCE). This  $C_{60}$ –GO–Ph–GCE interface was electrochemically reduced in an aqueous solution of potassium hydroxide (1.0 M KOH) to produce highly conductive electrochemically reduced (ERC $_{60}$ –GO–Ph–GCE) interface that shows electrocatalytic properties for detection of homovanillic (HVA) acid.

## 2. Experimental

### 2.1. Chemicals and instrumentation

All the chemicals used in this work were of analytical grade and used without further purification. Pristine fullerene ( $C_{60}$ ) with purity 99.5%, pristine graphite powder, gold (III) chloride trihydrate ( $HAuCl_4 \cdot 3H_2O$ ), tetrabutylammonium hexafluorophosphate (TBAPF<sub>6</sub>), sodium borohydride ( $NaBH_4$ ), aniline, sodium nitrite ( $NaNO_2$ ), potassium hydroxide (KOH), citric acid (CA), *p*-nitroaniline (PNA) and homovanillic acid (HVA) were obtained from Sigma-Aldrich Chemie, Germany. A stock solution of 0.1 mM HVA was prepared in Millipore water. Supporting electrolytic solutions (1.0 M KOH and 0.1 M TBAPF<sub>6</sub>) were prepared in Millipore water and acetonitrile, respectively. Phosphate buffer solution (PBS) of pH 7.0 was prepared by mixing appropriate amounts of Potassium orthophosphate ( $KH_2PO_4$ ) and dipotassium phosphate ( $K_2HPO_4$ ).

Electrochemical measurements were performed using potentiostat (Gamery Instruments, USA) connected to a conventional three electrode cell consists of glassy carbon electrode (GCE), platinum wire and Ag/AgCl (saturated KCl) used as working, counter and reference electrodes, respectively. The electrochemical impedance (EIS) measurements were conducted over a frequency range from 0.1 Hz to 100 kHz at amplitude of 5 mV. The Fourier transform infrared (FTIR) spectroscopic analysis was recorded at Carry FTIR-660 instrument (Agilent) using potassium bromide (KBr) pellets of samples. Ultraviolet–visible (UV–vis) spectra of samples was recorded on UV-1800 (Shimadzu) fitted with 1.0 cm diameter of quartz cell. The surface morphological characterization was studied using both Field emission scanning electron microscopy (FESEM, Tescan Lyra-3) and Scanning electron microscopy (SEM: JEOL–JSM 840-A, Japan). The Energy dispersive X-ray spectroscopy (EDX) analysis was performed using JEOL–JSM 840-A.

### 2.2. Synthesis of fullerene–graphene oxide ( $C_{60}$ –GO) conjugate

The graphene oxide (GO) was synthesized by modified Hummers method [28]. The first step for synthesis of fullerene–graphene oxide ( $C_{60}$ –GO) conjugate involves acyl-functionalization of graphene oxide (GO) by refluxing 100 mg of GO in 40 mL of thionyl chloride ( $SOCl_2$ ) and 1.0 mL of dimethyl formamide (DMF) at 70 °C for 24 h under argon atmosphere. The excess  $SOCl_2$  was evacuated under reduced pressure and product was washed with anhy-

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