



Graphene-promoted 3,4,9,10-perylenetetracarboxylic acid nanocomposite as redox probe in label-free electrochemical aptasensor

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ARTICLE INFO

Article history:

Received 21 July 2011

Received in revised form 27 August 2011

Accepted 29 August 2011

Available online 6 September 2011

Keywords:

Graphene

3,4,9,10-Perylenetetracarboxylic acid (PTCA)

Redox-activity

π - π stacking

Electrochemical aptasensor

ABSTRACT

Graphene/3,4,9,10-perylenetetracarboxylic acid (GPD) with three-dimensional porous structure has been successfully synthesized and served as redox probe to construct ultrasensitive electrochemical aptasensor. The GPD nanocomposite shows promoted electrochemical redox-activity of 3,4,9,10-perylenetetracarboxylic acid (PTCA) with an obvious well-defined cathodic peak from -0.7 to 0 V that never been seen from graphene or PTCA, which avoids miscellaneous redox peaks of PTCA in electrochemical characterization, offering a novel redox probe for electrochemical sensors with highly electrochemical active area and conductivity. To the best of our knowledge, this is the first study that utilizes PTCA self-derived redox-activity as redox probe in electrochemical sensors. Moreover, the interesting GPD possesses the advantages of membrane-forming property, providing a direct immobilization of redox probes on electrode surface. This simple process not only diminishes the conventional fussy immobilization of redox probes on the electrode surface, but also reduces the participation of the membrane materials that acted as a barrier of the electron propagation in redox probe immobilization. With thrombin as a model target, the redox probe-GPD based label-free electrochemical aptasensor shows a much higher sensitivity (a detection range from 0.001 nM to 40 nM with a detection limit of 200 fM) to that of analogous aptasensors produced from other redox probes.

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1. Introduction

3,4,9,10-Perylenetetracarboxylic acid (PTCA), an archetypal π -stacking organic perylene dye with outstanding photo and chemical stability as well as desirable organic electronic and optical properties, has been widely recognized as one of the most promising and rapidly emerging research areas for advanced materials (Eremtchenko et al., 2003; Forrest, 1997; Jones et al., 2004; Gregg and Cormier, 2001; Li et al., 2004a). Nevertheless, to the best of our knowledge, few researches have been reported on the application of PTCA-based nanomaterials in electrochemical sensors, besides the exploration of PTCA self-derived redox-activity. In fact, the perylene dye indeed has redox-activity owing to the electronic property, however, there would be miscellaneous redox peaks in electrochemical characterization (e.g. cyclic voltammograms) (Asir et al., 2010), which largely limits its application of redox-activity in electrochemical sensors. The conventional methods to fabricate PTCA based materials for electrochemical sensors are involved in the provision of PTCA just as semiconducting template, for instance, the porous organometallic materials synthesized for

immunosensor in our previous work (Zhuo et al., 2008). In this context, it is significant to improve the property of PTCA with efficient electrochemical redox-activity in the absence of other redox groups for electrochemical sensor.

Graphene, an atomical layer of sp^2 carbon atoms in a densely packed honeycomb two-dimensional lattice, has recently attracted great attention from both the experimental and theoretical scientific communities (Novoselov et al., 2004; Yang et al., 2010b; Tang et al., 2010). Due to its unique properties, such as excellent electronic transport properties, exceptional electrical conductivity, good fracture strength and high aspect ratio properties, graphene has been substantially applied in the areas of electrochemical sensors (Shan et al., 2009; Du et al., 2010a; Yang et al., 2010a; Dong et al., 2010; Zeng et al., 2010). In particular, owing to the fact that nanocomposites can exploit the novel properties of parent constituents, producing a desired material with improved performance, the fabrication of graphene-based nanocomposites is of great interest and importance. Zhang et al. (2010b) for example, developed biocompatible graphene-single stranded DNA nanocomposite and first used as an electrode material for the immobilization and biosensing of redox enzymes. Wang et al. (2010) displayed nitrogen-doped graphene with high electrocatalytic activity for reduction of hydrogen peroxide and fast direct electron transfer kinetics for glucose oxidase. Choi et al.

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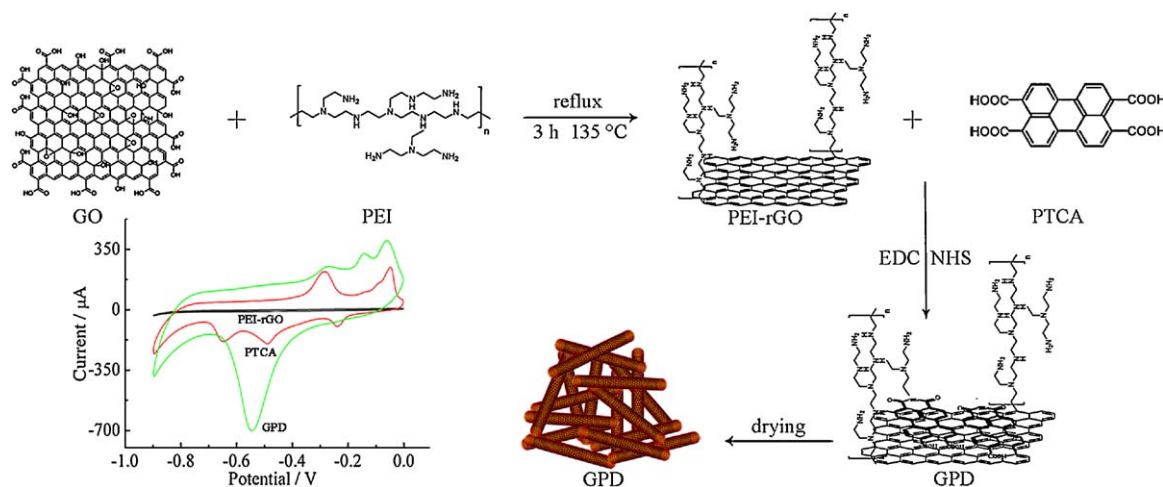


Fig. 1. A schematic diagram of the procedure used to prepare stable GPD nanocomposite.

(2010) reported graphene–nafion nanohybrid films with high-performance for electrochemical biosensing. Although remarkable progress has been made in the fabrication of graphene-based nanocomposites, for electrochemical sensor, utilizing the completely novel functional properties that were produced from the synergistic effect of graphene and organic material has not been reported.

In the present study, we proposed a graphene promoted 3,4,9,10-perylenetetracarboxylic acid nanocomposite (GPD) with three-dimensional porous structure. The planar graphene and perylene dye face-to-face formed a larger delocalized area through π - π stacking, increased the resonance energy and delocalized the charge effectively (Lee et al., 1999). Significantly, the resulting nanocomposite showed enhanced electrochemical activity of PTCA with an obvious well-defined cathodic peak between -0.7 and 0 V that never been seen from the parent constituents (graphene or PTCA) in cyclic voltammetry, which provided a novel redox probe for electrochemical sensors with high electrochemical active area and conductivity. With thrombin aptamer and thrombin as model systems, a redox probe-label-free electrochemical aptasensor composed of GPD as platform and redox probe was constructed. The SEM, XPS, UV–vis, electrochemical characterization, reduction mechanism of the GPD and the performance of the resulted aptasensor are discussed as follows.

2. Experimental

2.1. Materials and reagents

3,4,9,10-Perylenetetracarboxylic acid (PTCA) was purchased from Lian Gang Dyestuff Chemical Industry Co. Ltd. (Liaoning, China). Graphene oxide was obtained from Nanjing xianfeng nano Co. (Nanjing, China). Thrombin, hemin bovine serum albumin (BSA), hemoglobin (Hb), hexanethiol (96%, HT), poly(ethylene imine) (PEI) and gold chloride (HAuCl_4) were obtained from Sigma Chemical Co. (St. Louis, MO, USA). N-hydroxy succinimide (NHS) and N-(3-dimethylaminopropyl)-N'-ethylcarbodiimidehydrochloride (EDC) were acquired from Shanghai Medpep Co. (Shanghai, China). Tris-hydroxymethylaminomethane hydrochloride (tris) was purchased from Roche (Switzerland). Thrombin aptamer (TBA): 5'-(CH₂)₆-GGT TGG TGT GGT TGG-3' was purchased from TaKaRa (Dalian, China). All other chemicals were of reagent grade and used as received. Double distilled water was used throughout this study.

2.2. Apparatus

The UV–vis absorption was recorded with an UV-3600 UV–vis–near infrared (NIR) spectrophotometer (Shimadzu, Japan). The scanning electron micrographs were taken with scanning electron microscope (SEM, S-4800, Hitachi). X-ray photoelectron spectroscopy (XPS) measurements were performed with a VG Scientific ESCALAB 250 spectrometer, using Al K α X-ray (1486.6 eV) as the light source. All electrochemical measurements were performed on a CHI 660C electrochemical workstation (Shanghai Chenhua Instrument, China) with a conventional three electrode system composed of platinum wire as auxiliary, saturated calomel electrode as reference, and a modified gold electrode as working electrode.

2.3. Preparation of graphene/PTCA hybrid nanocomposite (GPD)

The overall process involved in fabricating the GPD is shown schematically in Fig. 1. Briefly, reduced-graphene oxide sheets were firstly prepared according to literature with little modification (Cao et al., 2010). A stable dispersion of exfoliated GO sheets (1 mg/mL, 10 mL) was mixed with PEI (3%, 1 mL) and heated under reflux at 135 °C for about 3 h. The PEI here served as reductant to reduce graphene oxide sheets and provided abundant amino for further association of PTCA. The final black product (PEI-rGO) was collected by centrifugation. Subsequently, EDC and NHS were used as coupling agents which catalyze the formation of amide bond between the carboxyl of PTCA and the amino of PEI-rGO. After centrifugation at 12,000 rpm for 15 min, the sediment of resulted GPD was resuspended in double distilled water and stored at 4 °C for further use.

2.4. Fabrication of the electrochemical aptasensor

The GPD here was served as a redox probe to construct an electrochemical aptasensor. Thrombin, a serine protease that has many effects in coagulation cascade (Rahman et al., 2009), was chosen as model analyte in this work. The stepwise self-assemble procedure of electrochemical aptasensor is shown in Fig. S1 (see Supplementary material). A gold electrode was carefully polished with 1.0 and 0.3 μm alumina powders separately, after rinsing with distilled water the electrode was dried in a nitrogen stream before use. Then, 3 μL as-prepared GPD was coated on the electrode surface and dried at room temperature. Following that, another electrodeposited nano-Au layer was employed for the immobilization of thrombin

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