Materials Science and Engineering C 49 (2015) 640–647

Contents lists available at ScienceDirect

Materials Science and Engineering C

journal homepage: www.elsevier.com/locate/msec

A bisphenol A sensor based on novel self-assembly of zinc phthalocyanine tetrasulfonic acid-functionalized graphene nanocomposites

Keyu Hou [a,b,c], Lei Huang [b,c], Yongbo Qi [b,c], Caixia Huang [a,b,c], Haibo Pan [a,b,c,*], Min Du [a]

[a] Fujian Key Lab of Medical Instrument & Pharmaceutical Technology, Yishan Campus, Fuzhou University, Fuzhou, Fujian 350002, China
[b] Institute of Research for Functional Materials, Yishan Campus, Fuzhou University, Fuzhou, Fujian 350002, China
[c] College of Chemistry, Qishan Campus, Fuzhou University, Fuzhou, Fujian 350116, China

ARTICLE INFO

Article history:
Received 21 September 2014
Received in revised form 2 December 2014
Accepted 17 January 2015
Available online 19 January 2015

Keywords:
Graphene
Self-assembly
π–π stack
Bisphenol A detection
Metallophthalocyanine

ABSTRACT

In this work, a novel zinc phthalocyanine tetrasulfonic acid (ZnTsPc)-functionalized graphene nanocomposites (f-GN) was synthesized by a simple and efficient electrostatic self-assembly method, where the positive charged GN decorated by (3-aminopropyl) triethoxysilane (APTES) was self-assemblied with ZnTsPc, a two dimensional (2-D) molecules. It not only enhanced its stability for the hybrid structure, but also avoided the reaggregation of ZnTsPc or f-GN themselves. Based on layered ZnTsPc/f-GN nanocomposites modified glassy carbon electrode, a rapid and sensitive sensor was developed for the determination of bisphenol A (BPA). Under the optimal conditions, the oxidation peak current increased linearly with the concentration of BPA in the range of 5.0×10^{-8} to 4.0×10^{-6} M with correlation coefficient 0.998 and limits of detection 2.0×10^{-8} M. Due to high absorption nature for BPA and electron deficiency on ZnTsPc/f-GN, it presented the unique electron pathway arising from π–π stackable interaction during redox process for detecting BPA. The sensor exhibited remarkable long-term stability, good anti-interference and excellent electrocatalytic activity towards BPA detection.

1. Introduction

Bisphenol A (BPA, 2,2-bis(4-hydroxyphenyl)propane) is a highly versatile hydrocarbon molecule that forms major feedstock in the production of epoxy resins and polycarbonate plastics [1–3]. BPA is readily enriched in the human body through environment and the food chain [4,5]. As an endocrine disrupting chemical, BPA is capable of disturbing the normal endocrine function, influencing sexual development and reproductive capability. In consideration of several laborious and time-consuming steps in mass spectrometry, gas chromatography (GC) and liquid chromatography (LC) for detecting BPA, main attention is recently devoted to electroanalysis techniques [6–9], which are rapid, sensitive, inexpensive and suitable for on-site monitoring.

As organic molecules including of a planar π-conjugated skeleton similarity in structure to the biological molecules (chlorophyll, hemoglobin) [10–13], metallophthalocyanine derivatives (MPcs) exhibit great thermal and chemical stability, and an efficient biomimetic catalysts for redox reactions. Zinc phthalocyanine tetrasulfonic acid (ZnTsPc, the molecule structure in Scheme 1), as electronic donor–acceptor coordination complexes, should contribute to electrocatalysis related with redox reaction. Generally, MPcs commonly suffer from hydrophobicity and aggregation (especially in aqueous solutions) owing to large π-conjugated systems. Although many water-soluble MPcs have been synthesized by introducing hydrophilic moieties and sulfonic groups, it is highly aggregated in water.

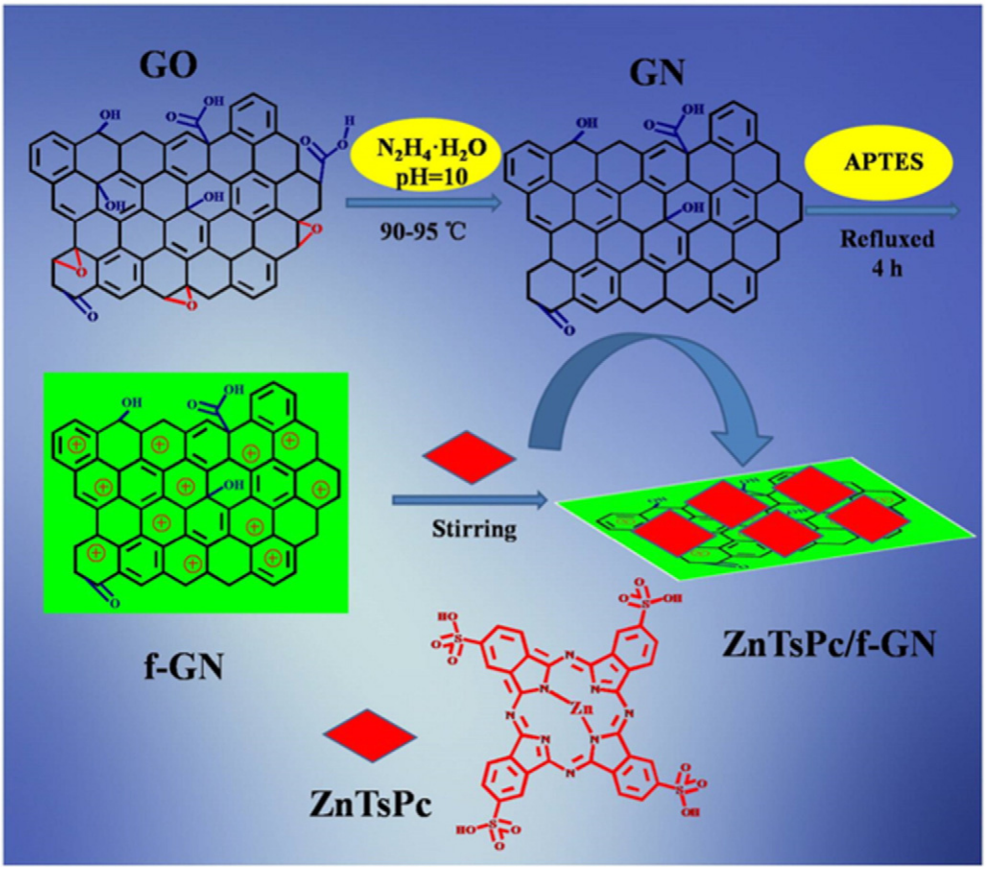
Graphene (GN), 2-D monolayer comprising sp^2-hybridized carbon atoms with the huge surface-to-volume ratio, fast charge carrier mobility, high thermal conductivity, and strong Young's modulus, has attracted wide attention for both fundamental science and application. For instance, some recent works related with the excellent ability of GN in electrochemical biosensors have come to our sight [14–16]. Recently, the GN modified with MPcs is under intensive exploitation, and few reports were published in synthesis and characterization of MPcs on GN [17–20], where MPcs combine with GN covalently or coordinatively.

In present work, we developed a novel approach to combine the positively charged functionalized nanoscale graphene (f-GN) with negatively charged ZnTsPc by a simple and efficient electrostatic self-assembly method (Scheme 1), where GN was decorated by (3-aminopropyl) triethoxysilane (APTES) at first. Note that they would form strong noncovalent π–π conjugated composite (ZnTsPc/f-GN)

---

* Corresponding author at: Fujian Key Lab of Medical Instrument & Pharmaceutical Technology, Yishan Campus, Fuzhou University, Fuzhou, Fujian 350002, China.
E-mail address: hbpan@fzu.edu.cn (H. Pan).

http://dx.doi.org/10.1016/j.msec.2015.01.064
0928-4931/



Scheme 1. Schematic illustration for electrostatic self-assembly of ZnTsPc/f-GN nanocomposites.

through the π–π stackable interaction [21]. And also, it exhibited charming characteristics in electrocatalysis feature by their synergetic combination of two components. Owing to the above advantages, an alternative electrochemical sensor for the selective and sensitive detection of BPA was realized by ZnTsPc/f-GN modified glassy carbon electrode (GCE). The redox mechanism on ZnTsPc/f-GN/GCE was raised further in BPA. For confirming its practical application, the determination of BPA in real samples was also fulfilled by using differential pulse voltammetry (DPV).

2. Experimental

2.1. Materials and reagents

Natural graphite (FP 99.95% pure) and APTES ($C_9H_{23}NO_3Si$,) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). ZnTsPc ($C_{32}H_{16}N_8O_{12}S_4Zn$) was obtained from J&K Scientific Ltd. (Beijing, China). 3,3′,5,5′-tetrabromobisphenol A (TBBPA) was obtained from Alfa Aesar Company (Tianjin, China). BPA was purchased from TCI (Shanghai) Chemical Industry Co. Ltd. and its stock solution (2 mM) was prepared with ethanol. The working solutions were prepared by diluting the stock solution with phosphate buffer saline (PBS, 0.1 M, pH 7.0). All other chemicals were of analytical grade and used as received without any further purification. Deionized (DI) water obtained from a Milli-Q plus water purification system (Millipore Co. Ltd., USA, 18 MΩ·cm) was used throughout the study.

2.2. Apparatus

Zeta-potential value measurement was recorded on Zeta Sizer 3000 Laser Particle Size and Zeta Potential Tester (Malvern Corporation, UK), and DI water was used as a dispersant. Fourier transformed infrared spectroscopy (FT-IR) were performed on a Nicolet Nexus 670 FT-IR spectrophotometer at a resolution of 4 cm^{-1}. UV–vis spectra were measured with a UV–vis absorption spectrometer (PerkinElmer Lambda 900). The morphologies of samples were observed by AFM (Agilent 5500, USA). High-resolution transmission electron microscope (HRTEM) image was obtained using Tecnai G2 F20 S-TWIN, 200 kV (FEI Company, USA). All the electrochemical measurements were carried out on a CHI660D electrochemical workstation (Shanghai Chenhua Instrument Co. Ltd., China) with a conventional three-electrode system. Glass carbon electrode (3 mm diameter) loaded different materials was used as working electrode. The surface of GCE was polished with 0.3 and 0.05 μm alumina slurries, ultrasonicated in water and ethanol, sequentially. Then the bare GCE was dried under pure N_2. Finally, these materials were dropped on the surface of bare GCE, and dried under room temperature.

2.3. Preparation of graphene nanosheets

Graphene oxide (GO) was synthesized from natural graphite powder using modified Hummers' method. Typically, 1 g of graphite powder was put into a mixture of 6 ml of concentrated H_2SO_4, 1.25 g of $K_2S_2O_8$, and 1.25 g of P_2O_5. The solution was heated to 80 °C in an oil-bath kept stirring for 24 h. It was carefully diluted with 300 ml of DI water, filtered, and washed until pH ~7. The pre-oxidized graphite powder was added to a mixture of 60 ml of concentrated H_2SO_4 and 30 ml HNO_3 under vigorous stirring at 0 °C. Then, 8 g $KMnO_4$ was added gradually under stirring and the temperature of mixture was kept to be below 20 °C by cooling. Successively, it was diluted with 500 ml of DI water in an ice bath to keep the temperature below 50 °C for 2 h. After further dilution with 500 ml of DI water, 20 ml of H_2O_2