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Electrochemical properties and electrocatalytic activity of conducting polymer/copper nanoparticles supported on reduced graphene oxide composite

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HIGHLIGHTS

- rGO/CuNPs and polytyramine are prepared by electropolymerization.
- rGO/CuNPs–PT/G shows better capacitance performance.
- rGO/CuNPs–PT/G electrode shows better catalytic performance for methanol oxidation.

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ABSTRACT

Reduced graphene oxide (rGO) was used to support Cu nanoparticles. As electro-active electrodes for supercapacitors composites of reduced graphene oxide/Cu nanoparticles (rGO/CuNPs) and polytyramine (PT) with good uniformity are prepared by electropolymerization. Composite of rGO/CuNPs–PT was synthesized by cyclic voltammetry (CV) methods and electrochemical properties of film were investigated by using electrochemical techniques. The results show that, the rGO/CuNPs–PT/G has better capacitance performance. This is mainly because of the really large surface area and the better electronic and ionic conductivity of rGO/CuNPs–PT/G, which lead to greater double-layer capacitance and faradic pseudo capacitance. Modified graphite electrodes (rGO/CuNPs–PT/G) were examined for their redox process and electrocatalytic activities towards the oxidation of methanol in alkaline solutions. The methods of cyclic voltammetry (CV), chronoamperometry (CA) and electrochemical impedance spectroscopy (EIS) were employed. In comparison with a Cu–PT/G (Graphite), rGO/CuNPs–PT/G modified electrode shows a significantly higher response for methanol oxidation. A mechanism based on the electro-chemical generation of Cu(III) active sites and their subsequent consumptions by methanol have been discussed.

1. Introduction

Conducting polymers such as polypyrrole, polythiophenes or polyaniline represent a group of conjugated π-electron materials which process a combination of various electrical, optical and other semiconductor properties as an organic semiconductors that with respect to electronic energy levels hardly different from inorganic semiconductors. The electropolymerisation of phenol and phenol derivatives has received considerable attention due to their importance in environmental, industrial electrocatalyst and supercapacitor applications [1–5]. Electrochemistry of the phenol derivatives strongly dependent on the type, position and number of substituents as well as on the chosen experimental conditions. [6,7]. For phenol derivatives with amino groups, the reported voltammetric studies have been interpreted by analogy with the well-established aniline oxidation, i.e. a E(CE)n mechanism; the oxidation of o-aminophenol was described as producing a ladder-structured film and reactive intermediates of 2-amino-phenoxazin-3-1 formation in solution. In the case of tyramine (4-(2-aminoethyl)phenol) (Ty), because the amino function is separated from the phenolic ring by two methylene groups, it is expected that only the phenol moiety is oxidized to perform the polymerization [6,7].

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The optimized molecular structure of polytyramine (heptamer) which obtained from quantum mechanical DFT calculations is presented in Fig. 1.

Graphene nanosheet (GN), which is a monolayer of carbon atoms tightly packed into a honeycomb lattice, has opened a new avenue for utilizing two-dimensional (2D) carbon material as a support because of its high conductivity (103–104 S m^{-1}), tremendous surface area (theoretically calculated value, 2630 m^2 g^{-1}), unique graphitized basal plane structure, high thermal and chemical stability, and potential low manufacturing cost [8–10]. These unique structure make graphene a promising additive or supporting component for potential applications in various fields [11–16], such as nanoelectronics [17,18], batteries [19], nanocomposites [20,21], supercapacitors [12], and sensors [22,23] solar cells [24,25] fuel cells [26,27] etc. Especially the metals or metal oxides are distributed onto the surface of graphene or between the graphene layers, as substrates for immobilizing metal or metal oxide catalysts, have been fabricated by restacking graphene sheets in the presence of guest nanoparticles or corresponding precursors. For example, Pt [28], Co_3O_4 [29] nanoparticles supported by chemically converted graphene were found to be an excellent electrocatalyst for oxygen reduction reaction (ORR). Palladium nanoparticles on graphite oxide and its functionalized graphene derivatives showed high catalytic activities for the Suzuki–Miyaura coupling reaction [11]. TiO_2 nanoparticles decorated graphene exhibited high photocatalysis performance [30]. Copper-based and its oxide-based nanomaterials were of great interest for their extensive applications in catalysis, gas sensor, Li ion battery, gas sensor, field-effect transistors and biosensors for a long time [31].

Herein, we describe a simple strategy dispersing of rGO/CuNPs within the conducting polymer matrix by in situ electropolymerization using an ionic surfactant as the supporting electrolyte. The rGO/CuNPs were first dispersed in an aqueous solution containing an ionic surfactant. Then electroactive monomer (Ty) was added into the above mixture and finally electrochemical reaction was preceded at the surface of the graphite electrode. In the present work rGO/CuNPs–PT composite was synthesized by cyclic voltammetry (CV) methods and electrochemical properties of film were investigated by using electrochemical techniques, viz. CV and electrochemical impedance spectroscopy (EIS).

2. Experimental

2.1. Instruments and reagents

All reagents were purchased from the Merck and Aldrich chemical companies and used without further purification. X-ray diffraction measurements were performed with a Philips powder diffractometer type PW 1373 goniometer. It was equipped with a graphite monochromator crystal. Electrochemical studies were carried out in a conventional three electrode cell powered by an electrochemical system comprising of EG&G model 273 potentiostat/galvanostat and Solartron model 1255 frequency response analyzer. The system is run by a PC through M270 commercial software via a GPIB interface. Saturated Calomel Electrode (SCE), a Pt wire and a graphite (G) electrode (0.22 cm^2) were used as the reference, counter and working electrodes, respectively. The X-ray wavelength was 1.5405 Å and the diffraction patterns were recorded in the 2θ range (10–60) with scanning speed of 2°/min. Morphology and particle dispersion was investigated by scanning electron microscopy (SEM) (Cam scan MV2300). The chemical composition of the prepared nanostructures was measured by EDS performed in SEM. All studies were carried out at 298 ± 2 K.

2.2. Preparation of graphene oxide

Graphene oxide was synthesized from commercial graphite by modified Hummers method [32,33]. The commercial graphite powder (10 g) was put into 230 mL concentrated H_2SO_4 that had been cooled to bellow of 20 °C with a circulator. 300 g potassium permanganate ($KMnO_4$) was added with stirring, so that the temperature of the mixture was fixed at bellow of 20 °C. Then, the temperature of the reaction was changed and brought to 40 °C and mixture was stirred at 40 °C for 1 h. 500 mL de-ionized water was added to the mixture, causing an increase in temperature to 100 °C. After that, 2.5 mL H_2O_2 (30 wt. %) was slowly added to the mixture supplementary this solution was diluted by addition lit de-ionized water. For purification, the suspension was washed with 1:10 HCl solution (200 mL) in order to remove metal ions by filter paper and funnel. The suspension was washed with much de-ionized water at several times, until the filtrate became neutral to remove remaining salt impurities. The graphene oxide was characterized by XRD and FT-IR spectroscopy [34].

2.3. Preparation of reduced graphene oxide (rGO)

Chemical reduction of graphene oxide to reduced graphene oxide was done according to a new procedure. Suspension aqueous colloids of GO were prepared from the dried graphene oxide (GO) by mechanical stirring and heat treatment with a circulator. In the experiment, 10 g of graphene oxide was stirred into 1 L of distilled water. This dispersion was stirred using a Fisher mechanical stirring until it became a clear solution with no visible particulate material. After that, the pH of the solution was increased to 10 by adding

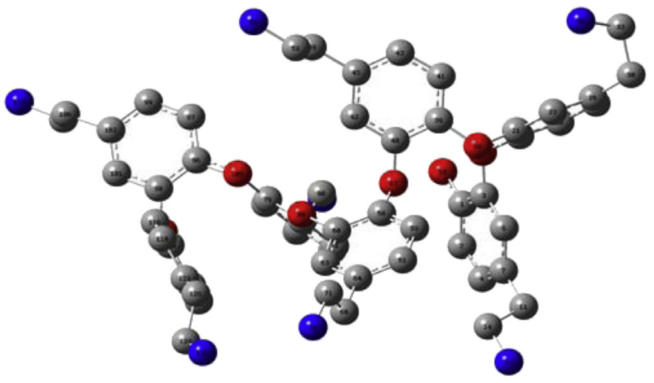

Fig. 1. Optimized molecular structure of heptamer, H atoms has been omitted for clarity.

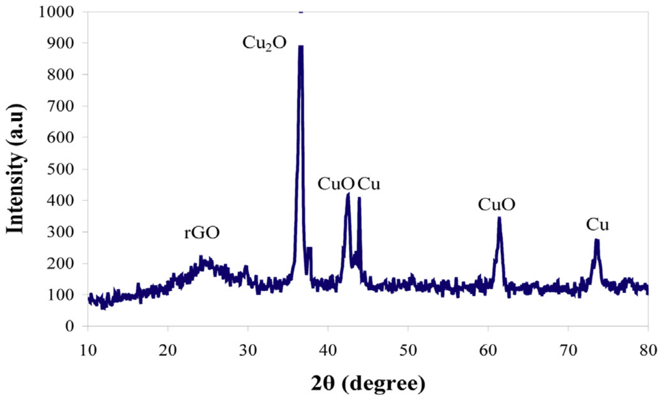

Fig. 2. XRD pattern of rGO/CuNPs.