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Research paper

Graphene-porphyrin composite synthesis through graphite exfoliation: The electrochemical sensing of catechol

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ABSTRACT

This paper reports for the first time a novel approach for the synthesis of graphene-porphyrin composite (EGr-TPyP) through the electrochemical exfoliation of graphite in the presence of 5,10,15,20-tetra(4-pyridyl)porphyrin (TPyP), in a neutral electrolyte (0.2 M KCl). No exfoliation was observed in the absence of TPyP molecules. The XRD investigation proves that the EGr-TPyP composite consists in a mixture of few-layer (FLG) and multi-layer (MLG) graphene. The mean crystallites size, calculated from the full-width at half-maximum (FWHM) of the corresponding diffraction peak, was found to be 0.73 nm in case of FLG and 6.33 nm in case of MLG. Moreover, the interlayer distance for MLG (0.337 nm) is similar with that of bulk graphite (0.335 nm) while for FLG this number is larger (0.397 nm) suggesting the presence of more wrinkled or disordered graphene sheets. UV–vis and XPS spectroscopy prove that TPyP molecules remained attached to graphene sheets at the end of the exfoliation process. The performances of the EGr-TPyP layer deposited on top of a glassy carbon (GC) electrode were evaluated during the catechol (CAT) detection. In case of EGr-TPyP/GC modified electrode, the CAT redox process is highly accelerated, so the peak currents are significantly higher than those obtained with bare GC substrate. The GC electrode has a low sensitivity towards CAT detection (0.185 $A{\bullet}M^{-1}{\cdot}cm^{-2}$), a narrow linear range (one decade, $10^{-5} - 10^{-4}$ M) and a relatively high detection limit (LOD = 3.03×10^{-6} M). In contrast, the EGr-TPyP/GC electrode has a larger sensitivity (3.22 $A{\bullet}M^{-1}{\cdot}cm^{-2}$), a considerably wider linear range (two decades, $10^{-6} - 10^{-4}$ M) and lower detection limit (LOD = 3.03×10^{-7} M).

1. Introduction

Phenols of anthropogenic origin exist in the environment due to the activity of chemical, pharmaceutical or petrolier industries. Most of the synthetic phenolic compounds are toxic and constitute pollutants in water, food, and soil, therefore their detection is essential. For example, catechol (CAT) is used in photography, cosmetic, dye, rubber, synthetic material and insecticide production [1] and has been identified as one of the most abundant organic products in tobacco smoke [2]. It has been reported that exposure to catechol induces: high-blood pressure and upper respiratory tract irritation, as well as kidney damage and convulsions in high-doses [3]. Due to its high toxicity and harmful effects on the environment and human health, the catechol detection has become of great importance. Many analytical techniques are used to determine catechol, including chemiluminescence [4], high performance liquid chromatography [5], fluorescence, and gas chromatography/mass spectrometry [6]. Conventional methods are expensive, time consuming and quite complicated. Recently, electrochemical methods have been employed for the detection of catechol [7,8]. Since the bare electrodes are not convenient for the detection of catechol due to their poor sensitivity and fouling of signals by the oxidized products, modified electrodes with different materials (hybrid materials, nanomaterials, conductive polymers and biological molecules) have been used for its sensing [9–11]. Among these, graphene modified electrodes were found to be very efficient in the determination of the phenolic compounds [12].

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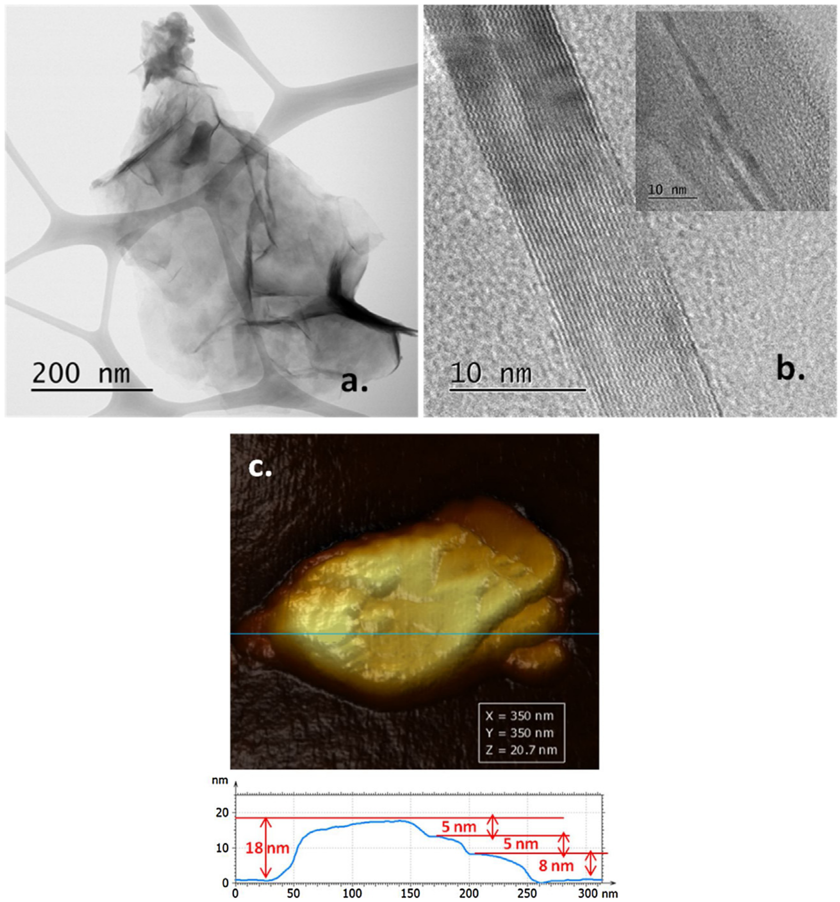

Fig. 1. TEM images of EGr-TPyP sample; scale bar 200 nm (a); HR-TEM images of EGr-TPyP sample, showing MLG and FLG (inset); scale bar 10 nm (b); Topography image at the edge of a graphene sheet (≈ 250 × 300 nm) composed of three overlapped flakes (c) – the thickness of the flakes varies between 5 and 8 nm.

Graphene is currently making an important impact in the electrochemistry field due to its high surface area, high chemical stability, and unique electrical and mechanical properties [13–15]. Various fabrication techniques such as micromechanical cleavage, epitaxial growth, chemical vapor deposition, and thermal/chemical reduction of graphene oxide [16] have been used to obtain graphene nanosheets. Recently, electrochemical exfoliation of graphite has attracted particular attention being an easy, fast and environmentally friendly strategy to produce high quality graphene. Ionic liquids and acidic solutions were mainly used as electrolytes in the electrochemical exfoliation reaction [17]. In our previous work [18] we reported a simple, cost-effective electrochemical approach to produce graphene by electrochemical exfoliation of graphite rods, in acidic electrolytes. X-ray powder diffraction was used as the main technique for graphene structural characterization. Nevertheless, the production of graphene in mild (near neutral) solution by electrochemical exfoliation was rarely reported [19].

Nowadays, there are a greater number of studies focused on the electrochemical exfoliation of graphite in various electrolytes [20–25] compared to the electrochemical production of functional graphene [26,27]. The electrochemical production of functional graphene still remains a non-controllable and a non-optimized process. Aromatic molecules, such as porphyrins, proved to be efficient assistants in the graphite exfoliation producing new hybrids with interesting properties in a single step [28]. Porphyrins are a group of heterocyclic organic compounds composed of four modified pyrrole rings interconnected with methine bridges. They interact with carbon materials through π–π stacking interactions. For this reason, they have been widely used to decorate carbon nanotubes, fullerenes and graphene [29,30]. Until now, graphene sheets with undisturbed networks were prepared via porphyrin exfoliation of graphite in N-methyl-pyrrolidone [31]. Another efficient fabrication of single-layer nanographene hybrid platelets was achieved by graphite exfoliation using a free base porphyrin [28]. Electrodes modified with graphene-porphyrin composites can be used in the field of electrochemical sensors, such as the detection of dopamine [32], glucose [33] or low traces of explosives [34].

In this work we report the assembly of electrochemically exfoliated graphene and 5,10,15,20-tetra(4-pyridyl)porphyrin (TPyP) in aqueous media. To the best of our knowledge, there is no report about the electrochemical exfoliation of graphite in the presence of TPyP in KCl electrolyte. The synergic effect between graphene and porphyrin led to a highly efficient electrocatalytic activity for the catechol oxidation. The novelty of our method lies in the use of a cost effective, non-toxic and environmental friendly electrolyte (0.2 M solution of potassium chloride). Our prepared material consists in a mixture of few layer and multi layer graphene which presents excellent electrocatalytic properties towards catechol detection. In addition the method ensures the preservation of graphene 2D structure, good reproducibility in the number of layers and excellent adherence to the transducer surface (glassy carbon).

2. Experimental

2.1. Chemicals

All reagents were of analytical grade and used without further purification. Catechol, hydroquinone, resorcinol, and ethanol were

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