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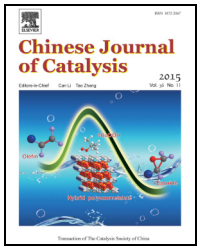

Article

Electrochemically reduced graphene oxide with enhanced electrocatalytic activity toward tetracycline detection

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ABSTRACT

An electrochemically reduced graphene oxide sample, ERGO$_{-0.8V}$, was prepared by electrochemical reduction of graphene oxide (GO) at –0.8 V, which shows unique electrocatalytic activity toward tetracycline (TTC) detection compared to the ERGO$_{-1.2V}$ (GO applied to a negative potential of –1.2 V), GO, chemically reduced GO (CRGO)-modified glassy carbon electrode (GC) and bare GC electrodes. The redox peaks of TTC on an ERGO$_{-0.8V}$-modified glass carbon electrode (GC/ERGO$_{-0.8V}$) were within 0–0.5 V in a pH 3.0 buffer solution with the oxidation peak current correlating well with TTC concentration over a wide range from 0.1 to 160 mg/L. Physical characterizations with Fourier transform infrared (FT-IR), Raman, and X-ray photoelectron spectroscopies (XPS) demonstrated that the oxygen-containing functional groups on GO diminished after the electrochemical reduction at –0.8 V, yet still existed in large amounts, and the defect density changed as new sp^2 domains were formed. These changes demonstrated that this adjustment in the number of oxygen-containing groups might be the main factor affecting the electrocatalytic behavior of ERGO. Additionally, the defect density and sp^2 domains also exert a profound influence on this behavior. A possible mechanism for the TTC redox reaction at the GC/ERGO$_{-0.8V}$ electrode is also presented. This work suggests that the electrochemical reduction is an effective method to establish new catalytic activities of GO by setting appropriate parameters.

1. Introduction

Tetracyclines (TTCs) are one of the most extensively used veterinary medicines for their broad antibacterial spectrum and low production cost. Currently, TTCs are increasingly applied in personal care products. The large consumption of this antibiotic inevitably leads to the existence of the unmodified parent compounds or metabolized products in surface water, groundwater and sewage treatment plants, which can be directly toxic or spread drug-resistant genes [1,2]. So far, several techniques and methods have been developed for the determination of TTC, including immunoassay, microbiological meth-

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ods, and chemical-physical techniques (e.g., high-performance liquid chromatography/glass carbon electrode and capillary zone electrophoresis) [3,4]. However, these are expensive, time-consuming, or demand complicated sample pre-treatments. Most importantly, they are not suitable for in-situ or routine analysis.

Electrochemical methods are proposed to be promising for pollutant detection owing to their simple and reliable procedure, low cost, fast investigation, and high sensitivity [5,6]. It has been reported that TTC can be electrochemically oxidized by several materials, especially carbon nanotubes [7–11].

As a competitor to carbon nanotubes, graphene has exhibited superior performance in electrochemical sensor application [12]. However, graphene oxide (GO), as a precursor of graphene, has many oxygen-containing functional groups on the basal plane and the sheet edge, which lead to its insulation and disorder. These functional groups provide the unique chemical functionality of GO owing to its heterogeneous electronic structure, which contains a mixture of sp^2- and sp^3-hybridized carbon atoms [13]. Owing to some unique characteristics, interest among researchers has increasingly shifted from investigating GO as a precursor for graphene to determining the properties of GO. It has been found that the oxygen-containing functional groups on the basal plane and sheet edge allow GO to interact with a wide variety of organic and inorganic materials. Furthermore, a more efficient reduction treatment for GO could result in further interesting properties by the creation of new sp^2 clusters and the adjustment of surface functional groups through the removal of oxygen [14]. It is known that the electrochemistry of a variety of compounds is sensitive to surface defects and surface functional groups. Therefore, reduced GO may be potentially used as an electrocatalyst in various electrochemical reactions [12,15–18]. However, investigations on the development of graphene-based materials/devices for electroanalysis and electrocatalysis are still limited [15].

Among the different techniques in reduction chemistry, electrochemical reduction provides a green and fast method for GO reduction, and shows promise for controlling the extent and process of reduction [6,12,19,20]. Moreover, electrochemically reduced GO (ERGO) has shown a better performance than chemically reduced GO (CRGO) in several previous reports [5,6,17,18,21]. The tunability of the sp^2 and sp^3 fractions by the electrochemical reduction is a powerful way to tune its bandgap and transform GO from an insulator to a semiconductor [15]. The obtained functionalized graphene material has an abundance of structural defects and functional groups, which are beneficial for electrochemical applications [22,23]. Researchers have reported that the ERGO exhibits enhanced activity for the electrocatalytic reduction of O_2 and H_2O_2, and higher electrochemical capacitance for the potential application in ultracapacitors [18] or other applications [24–26]. Most electrochemical reduction is performed at the potential of –1.0 to –1.5 V, where a variety of the oxygen-containing functional groups can be removed [6,16,27]. However, the electrocatalytic activity of GO may also disappear along with the functional groups.

In this work, the electrochemical reduction of GO was applied through cyclic voltammetry to adjust the surface defects and surface functional groups. The obtained ERGO shows unique electrocatalytic activity toward TTC detection compared with GO and CRGO. The structural features of ERGO, GO, and CRGO were investigated by Raman, Fourier transform infrared (FT-IR), and X-ray photoelectron spectroscopy (XPS) techniques, and were correlated with their electrochemical behavior toward TTC detection. The possible electrocatalytic mechanism of ERGO toward TTC oxidation was proposed.

2. Experimental

2.1. Materials and instruments

Graphite powder (99.95% purity) was purchased from Aladdin (Shanghai, China). TTC was obtained from Sigma-Aldrich. Other chemicals, such as hydrazine hydrate and *N,N*-dimethylformamide (DMF), were all of analytical grade and obtained commercially. All the solutions were prepared using double-distilled water.

A whirlpool mixer (QL-901, Haimen Kylin-Bell Lab Instruments Co., Ltd) was employed to disperse TTC in 0.10 mol/L sodium tartrate solutions (pH = 3.0). The cyclic voltammetric (CV) experiments were performed on a CHI 760D electrochemical workstation (Chenhua Co., Shanghai, China) in a conventional three-electrode system, including a modified glassy carbon electrode (GC, 3 mm in diameter) as a working electrode, an SCE as a reference electrode, and a platinum plate (1 cm×1.5 cm) as an auxiliary electrode. All the potential values were reported against SCE.

2.2. Preparation of the modified electrode

GO was synthesized from graphite powder (99%, 40 nm, Aladdin) by Hummers' method [28]. CRGO was obtained by the chemical reduction of GO, where GO was reduced by ammonia water and hydrazine hydrate. GO (50 mg) was first dispersed in 250 mL of water by ultrasonication. Consequently, 250 μL of 25% ammonia water and 250 μL of hydrazine hydrate were added to the solution. The solution was maintained at 95 °C in a water bath for 1 h, followed by filtration and washing with water.

The GO-modified GC (GC/GO) electrode was prepared with a 5-μL GO aqueous dispersion solution (0.05 wt%) dropped on the electrode, and then dried in air. A similar method was used to prepare the GC/CRGO electrode, with a 5-μL CRGO DMF dispersion solution (0.05 wt %) dropped on the electrode. Prior to use, each of the modified electrodes was carefully rinsed with water to remove the loosely attached materials.

The $GC/ERGO_{-0.8V}$ electrode was obtained by electrochemical reduction of the GC/GO electrode. CV was applied to the GC/GO electrode in 0.1 mol/L sodium tartrate buffer solutions in the potential range of –0.8 to +1.4 V at a scan rate of 10 mV/s for five cycles, until the cyclic voltammetric curve was stable. The $GC/ERGO_{-1.2V}$ electrode was obtained by applying a potential in the range of –1.2 to +1.4 V to the GC/GO electrode under