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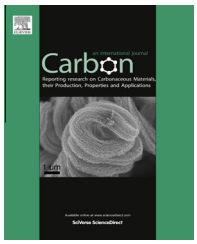

The evolution of surface charge on graphene oxide during the reduction and its application in electroanalysis

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ABSTRACT

A series of reduced graphene oxide (RGO) colloids with different amounts of surface charges was prepared. The change in surface charge at different pH values was detected by zeta potential measurement, and the evolution of oxygen-containing functional groups attached to the RGOs was analysed by Fourier-transform infrared spectroscopy and ultraviolet-visible absorption spectroscopy. Results showed that the edge phenolic hydroxyl and carboxyl groups made more contributions to the negative surface charge compared with the basal-plane hydroxyl and epoxy groups. Electrical impedance spectroscopy results proved that the surface charge of RGOs significantly affected their electrochemical properties. Furthermore, GO and RGOs (graphene oxide materials) were also used to construct electrochemical sensors for quantitive measurement of Cu^{2+} by differential pulse anodic stripping voltammetry. The results revealed that the increase in negative surface charge on RGO enhanced its electrocatalytic activity for Cu^{2+} reduction. Thus, considering that studies on the properties of graphene oxide materials can be simplified by the surface charge, its analysis is an important means of material characterisation.

1. Introduction

Graphene, a two-dimensional layer of graphitic carbon, has been the focus of recent experimental and theoretical studies because of its unique nanostructure and physicochemical properties [1–6]. In particular, the extraordinary electronic transport properties and high electrocatalytic activities of graphene make it a promising material for electrochemical applications, such as energy storage [7], transparent electronics [8], electrochemical supercapacitors [9] and ultrasensitive chemical sensors [10]. The chemical reduction of graphene oxide (GO) has been commonly used to mass-produce graphene, often called chemically reduced graphene oxide (RGO) [11], since GO was easily prepared from graphite with Hummers method [12]. Great efforts [11,13,14] have been directed to understanding the chemical structure of GO and RGO (graphene oxide materials). Many structure models have been proposed for GO. Among them, the most well-known one is

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Lerf–Klinowski model [15–17], which depicts that GO sheets are terminated with hydroxyl and carboxyl groups while epoxy and hydroxyl groups are attached on their basal planes. However, even to these days no unambiguous models of graphene oxide materials exist, and more efforts will be made to investigate their chemistry of surface functional groups [18,19]. To study the surface oxygen-containing functional groups in detail, researchers have used many characterisation methods, including Fourier-transform infrared (FT-IR), ultraviolet–visible (UV–vis) absorption, X-ray photoelectron (XPS) and nuclear magnetic resonance (NMR) spectroscopy analyses and so on [17,20,21]. Sometimes, these characterisation methods must be combined with one another to analyse functional groups qualitatively or quantitatively, which is very cumbersome and easily leads to ambiguous results [22]. Actually, investigating their surface functional groups in detail aims to determine their properties for specific applications because the oxygen-containing functional groups can remarkably affect the electronic and chemical properties of graphene oxide materials [23,24]. Therefore, an easy method for evaluating the performance of graphene oxide materials instead of investigating their surface functional groups in detail should be developed.

Surface charge, which consists of inherent and variable charges, is determined by the material structure. Inherent charge is mainly generated by isomorphous replacement [25], whereas variable charge is mainly caused by the ionisation and reaction of surface functional groups when materials are dispersed in water or other solutions. The latter can vary with the surface groups and solvent conditions. The zeta potential, which results from the arrangement of surface charges and balance among counter-ions in solution, is used widely to study surface charge on a variety of carbons materials [26,27]. Li et al. [28] found that the zeta potential of GO is more negative than that of RGO at the same pH value, and assumed that the surface negative charge mainly results from the ionisation of oxygen-containing functional groups. Si et al. [29] and Liu et al. [30] have respectively reported the similar findings that the zeta potential of GO decreases after the removal of oxygen-containing functional groups. Considering the close relationship between oxygen-containing functional groups and the properties of graphene oxide materials, surface charge may be able to evaluate the performance of graphene oxide materials on the whole. Furthermore, the evaluation of surface charges by zeta potential measurement is easier than the detailed determination of surface functional groups. However, there are few reports on the effect of surface functional groups on the surface charge of RGO during the reduction.

In this work, a series of homogeneous RGO colloids with various quantities of surface negative charges was prepared by a chemical reduction method. The evolution of surface charge on RGO during the reduction was evaluated by zeta potential measurement. And the change in oxygen-containing functional groups was detected by FT-IR and UV–vis methods. Subsequently, the surface morphologies and structures of the as-prepared RGOs were investigated by transmission electron microscopy (TEM) and X-ray diffraction (XRD). The electrochemical properties of RGOs with various quantities of surface charges were measured by electrical impedance spectroscopy (EIS) in potassium chloride (KCl) supporting electrolyte containing $Fe(CN)_6^{3-/4-}$. What's more, the influence of surface charge on the performance of RGOs in the electrochemical reduction and detection of Cu^{2+} was investigated by CV and differential pulse anodic stripping voltammetry (DPASV). The results showed that the surface negative charge of RGOs contributed to the electroreduction of positively charged Cu^{2+} ions.

2. Experimental

2.1. Chemicals and materials

Natural graphite flakes (99.8 wt.%, 325 mesh) were purchased from Alfa Aesar (Tianjin, China). Chemically pure hydrazine hydrate (80 wt.%) and ammonia water (28 wt.%) were purchased from Beijing Chemical Works (Beijing, China). Polishing slurries (10 wt.% aqueous suspensions of 0.5 μm and 50 nm α-Al_2O_3) were purchased from Tianjin Aida Hengsheng Technology Co. Ltd. (Tianjin, China). All other chemicals were analytical grade or better and used as received. All solutions used were prepared with ultrapure water (18.2 MΩ cm^{-1}, Milli-Q, Millipore). Cu^{2+} solutions with different concentrations were prepared by diluting a 0.1 M aqueous solution of $Cu(NO_3)_2$. Britton–Robison (BR) buffer with the required pH was prepared by mixing appropriate amounts of H_3BO_3, CH_3COOH, H_3PO_4 and NaOH followed by diluting with ultrapure water to the appropriate volume.

2.2. Synthesis of GO and RGOs

GO was synthesised with a modified Hummers method [12,28]. In a typical procedure, 3 g of graphite was placed in an 80 °C solution of concentrated sulphuric acid (12 mL), $K_2S_2O_8$ (5 g) and P_2O_5 (5 g) for 4.5 h. The mixture was cooled to room temperature, diluted with 1 L of water, and left undisturbed overnight. The mixture was then passed through a 0.22 μm Nylon Millipore filter and washed with water to remove residual acid, and the product was dried in air. The obtained powder and $KMnO_4$ (15 g) were cautiously mixed with concentrated sulphuric acid (120 mL) in a round-bottom flask at 35 °C for 2 h. The suspension was diluted with 1 L of water in an ice bath, and then 25 mL of 30 wt.% hydrogen peroxide was added. Finally, the mixture was washed and centrifuged five times with 10% (v/v) HCl solution and ultrapure water sequentially. The bottom sediment was resuspended in water, and a brown–yellow colloid (0.25 wt.%) was formed. After this colloid was sonicated in water (300 W, 50% amplitude) for 60 min and centrifuged at 5000 rpm for 15 min to remove the unexfoliated graphite oxide particles, a GO aqueous solution was obtained.

RGO homogeneous colloids were prepared by the chemical reduction method with hydrazine. As-prepared GO aqueous solution (400 mL) was adjusted to pH 10 with 1 M ammonia water, and hydrazine solution (300 μL, 80 wt.% in water) was added under stirring. The hydrazine added solution was kept at 35 °C in a water bath with refluxing. Several liquid samples were extracted with a syringe at 0, 1, 2, 6 and 12 h and marked as GO, RGO-1, RGO-2, RGO-6 and RGO-12, respectively. Part of each sample was washed and dried for FT-IR and XRD

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