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Electrochemically reduced graphene oxide and its capacitance performance

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HIGHLIGHTS

- ERGO is obtained by 1.1 V cathodic reductions in potassium biphthalate buffer solution.
- The role of potassium biphthalate is discussed in the reduction process.
- Most of the oxygen functional groups in GO are successfully removed.
- A maximum specific capacitance of 254.9 F g^{-1} is achieved in pH 13 Na$_2$SO$_4$ solution.

GRAPHICAL ABSTRACT
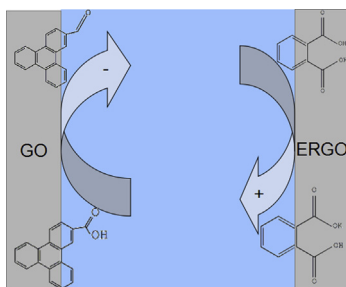
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ABSTRACT

Graphene oxide (GO) is reduced by a rapid cathodic reduction at -1.1 V in 0.05 M potassium biphthalate buffer solution ($C_8H_4O_4H_2/C_8H_4O_4HK$). Potassium biphthalate plays an important role in the reduction process and it is superior to sodium acetate buffer solution (HOAc/NaOAc). The possible reason for this dissimilarity is discussed in detail. The reduced graphene oxide (ERGO) is characterized by Fourier transform infrared spectroscopy (FT-IR), thermogravimetry and differential scanning calorimetry (TGA/DSC), X-ray diffraction spectroscopy (XRD) and transmission electron microscopy (TEM). The results indicate that most of the oxygen functional groups in GO are successfully removed. Electrochemical studies are carried out using cyclic voltammetry, galvanostatic charge/discharge, and electrochemical impedance spectroscopy. A maximum specific capacitance of 254.9 F g^{-1} can be achieved in pH 13 Na$_2$SO$_4$ solution at current density of 1.14 A g^{-1} within the potential window of 1.4 V.

1. Introduction

Graphene obtained by Geim et al. at Manchester University in 2004 [1] is a two-dimensional one-atom-thick sp^2-bonded honeycomb carbon atom sheet [2,3]. It can be rolled flexible into one-dimensional carbon nanotubes or stacked into three-dimensional graphite [4]. It exhibits excellent properties, such as superior thermal conductivity [5], remarkable mechanical strength [6], large theoretical specific surface area of 2630 m^2 g^{-1}, and excellent electrical performance, the electron can transfer on graphene sheet at a constant rate, and the largest mobility of charge carriers exceeds 1.5×10^4 cm^2 V^{-1} s^{-1} even under ambient conditions [12]. So graphene has exhibited great potential in various applications, including energy storage [7,8], polymer composites [9], nanoelectronics [10], and sensors [11] and so on. Supercapacitors are being considered promising power sources for applications due to their high power density and energy density [1–3]. It is well known that the performance of supercapacitors depends on the materials of electrode. Furthermore, the morphology, structure and size of electrode material play important roles on its capacitive properties. Different synthesis methods and even dissimilar reaction

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conditions would produce unusual structures and properties. Till now, several physical and chemical approaches have been developed to produce graphene, including chemical vapor deposition [13], chemistry reduction [14–16], flame reduced [17], and electrochemical reduction [18–20] etc. And various morphologies of graphenes have been obtained, comprising two dimensional graphene nanosheets (GNSs), one-dimensional graphene nanoribbons (GNRs) [21–23], and zero-dimensional graphene quantum dots (GQDs) [24,25]. The most exciting fact is the properties of graphene can be tuned by their size and edges [26]. The more attractive practices lead to the more enthusiasm to research on it. It is worth to do more study on graphene for its promising application in supercapacitors. In this paper, we report a facile and fast approach to synthesize high quality graphene, which is reduced from graphene oxide (GO) by cathodic reduction at −1.1 V in 0.05 M potassium biphthalate solution (pH = 4). The mechanism of electrochemical reduction is discussed. As far as we know the reduction of GO in the potassium biphthalate buffer solution has not been reported before.

In 2011 Peng [27] et al. reported a specific capacitance of 128 F g^{-1} by reducing GO with constant potential reduction at −1.2 V in 0.5 M NaNO$_3$ solution. Jiang [28] et al. prepared electrochemically reduced graphene oxide (ERGO) by cyclic voltammetry from 0.0 to −1.5 V (vs. SCE) in PBS (Na$_2$HPO$_4$/NaH$_2$PO$_4$, N$_2$-purged, 0.05 M, pH 5.0) solution. The specific capacitance of ERGO is 223.6 F g^{-1}. Considering the relative stability of buffer solution, and the character of GO, i.e. there are plenty of oxygen function groups, we choose potassium biphthalate buffer solution (pH = 4) as the electrolyte in reducing process. In our present work, the specific capacitance of ERGO is up to 254.9 F g^{-1}, which is higher than literature 27 and 28. And most oxygen functional groups have been eliminated after the reduction process.

2. Experimental

2.1. Synthesis of graphene oxide

Graphene oxide (GO) is obtained from reagent grade graphite powder (99.85%, shanghai colloid chemical industry, china) by using a modified Hummer's method. 2.0 g graphite powder is mixed with 50 ml 98% H$_2$SO$_4$ solution in ice bath and keeping stirred for 30 min at 0–10 °C. Following that, 0.3 g KMnO$_4$ is put into the mixture to pre-oxide 3 min. Then 6 g KMnO$_4$ is added in 3 batches to keep the reaction temperature below 20 °C. After that the ice bath is removed. The mixture remains at 35 °C for 2 h. Follow on, 90 ml deionized water is slowly added to the paste to make the temperature reach 90 to 100 °C. By then bright yellow deposition is obtained. Finally, 280 ml warm deionized water and 20 ml 30% H$_2$O$_2$ are added in 10 min to terminate the reaction. All the above processes are finished under keeping vigorously stirred. The as-prepared products are filtered and washed with 1% HCl solution and deionized water in turn to remove metal ions. The depositions GO is transferred to the watch glass and dried in vacuum at 70 °C for 24 h.

2.2. Electrochemical reduction of GO

GO and two drops of conductive adhesive (PELCO colloidal graphite) are mixed evenly and pasted on a Ni foam substrate. After compressed at 20 Mpa and vacuum dried for 24 h at 70 °C, working electrode is obtained. Platinum sheet is used as counter electrode and saturated calomel electrode (SCE) is used as reference electrode. With a CHI 660D electrochemical workstation (Chenhua Instrument Co., Shanghai, China), graphene is obtained by constant potential reduction at −1.1 V in a 3-electrode configuration in 0.05 M potassium biphthalate buffer solution (pH = 4). According

to the reduced time 0.5 h, 1 h, 2 h and 4 h, the electrochemical reduced graphene oxide (ERGO) are recorded as ER05, ER1, ER2, and ER4 (the mass is all about 1 mg), respectively. To compare the effect of different electrolytes on the graphene oxide reduction, GO is also electrochemical reduced in acetate buffer solution. ERGOs reduced 0.5 h, 1 h, 2 h and 4 h in acetate buffer solution are recorded as H05, H1, H2 and H4, respectively. The other experiment conditions are the same as that of in potassium biphthalate solution. The ERGO electrodes with different mass, 0.6, 0.8, 1.0, 1.2, 1.4, 1.6, 1.8 mg, are labeled as M1, M2, M3, M4, M5, M6, and M7, respectively. The geometric surface area of each electrode is 1 cm^2.

2.3. Structural characterization

ER05, ER1 are removed from foam Ni by dispersing in absolute ethyl alcohol and vacuum dried for 12 h at 70 °C. And FT-IR adsorption spectra (KBr) of ER1, graphite, and GO are carried out using 510PFT FT-IR. Thermogravimetry and differential scanning calorimetry are tested by TGA/DSC. The graphite, GO and ER1 samples are heated in a nitrogen atmosphere from room temperature to 900 °C at a heating rate of 10 °C min^{-1}. The transmission electron microscope of GO and ER1 are obtained using JEOL-2100F at acceleration voltage of 200 kV. X-ray diffraction analysis of GO, ER05 and ER1 are carried out using PW3040/60.

2.4. Electrochemical performance

The electrochemical properties of materials are investigated by cyclic voltammograms (CV), galvanostatic charge/discharge (CP) and electrochemical impedance spectroscopy (EIS) at room temperature in pH 13 Na$_2$SO$_4$ solution (NaOH solution is added to adjust pH value). The specific capacitance is calculated with CP curves according to Eq. (1):

$$C = \frac{it}{mV} \tag{1}$$

where i is the current density, t is the discharge time, m is the mass of materials and V is potential window.

3. Results and discussion

3.1. Characterization of ERGO

FT-IR spectroscopy is used to indicate the degree of removing the oxygen functional groups.

Fig. 1 shows the FT-IR spectra of pristine graphite (a), GO (b) and ER1 (c). In Fig. 1(a) and (b), the peak at 3424 cm^{-1} is due to O–H
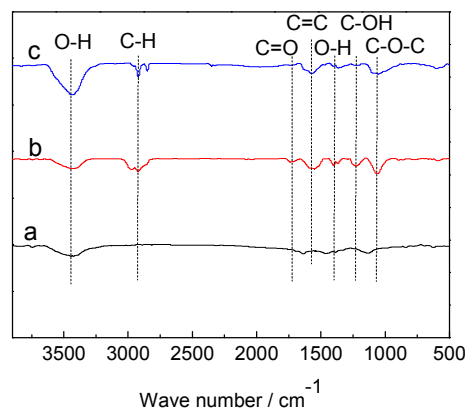

Fig. 1. FT-IR spectrum of graphite (a), GO (b) and ER1 (c).