Materials Science and Engineering B 193 (2015) 37–40

Contents lists available at ScienceDirect

Materials Science and Engineering B

journal homepage: www.elsevier.com/locate/mseb

An economic route to mass production of graphene oxide solution for preparing graphene oxide papers

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ARTICLE INFO

Article history:
Received 23 April 2014
Received in revised form 28 October 2014
Accepted 8 November 2014
Available online 18 November 2014

Keywords:
Graphene oxide solution
Graphene oxide paper
Separation
Thermal storage

ABSTRACT

Graphene oxide paper (GOP) is a composite material fabricated from graphene oxide (GO) solution. In addition, it can be a novel and potential material for application on the separation of water vapor from gaseous steam or larger alkali ions from aqueous solution. GOP could be used as electricity and thermal storage materials. The preparation of GO commonly uses high purity natural or artificial graphite. It is difficult to prepare GOP from artificial graphite powder due to the cost of $1,450 US/ton. In this study, we tried to prepare GOPs from homemade graphene sheets containing carbon materials (GSCCMs) and evaluate the thermal properties of GSCCM derived GOPs. Results show that GSCCM derived GOPs have a higher phase transition temperature, and the average mesophase phase change enthalpy is 9.41 J/g, which is 2.87 times higher than graphite derived GOP. Therefore, to prepare GOP from GSCCMs could highly reduce the cost.

1. Introduction

Graphene oxide paper (GOP) is a composite material fabricated from graphene oxide (GO) solution. In addition, it could be a novel and potential material for application on the separation of water vapor from gaseous steam or larger alkali ions from aqueous solution [1]. Other studies have reported that GO solutions possess a phase change property [2–4].

Phase change materials (PCMs) are substances that obtain energy through a variation of properties or structures, and the phase-change types have solid–solid, solid–liquid and liquid–gas phases [5]. The PCMs could be applied to electricity or thermal storage; therefore, GOPs could be used as electrical or thermal storage materials.

In the past, the oxidation processes of graphite were conducted by used HNO_3 and KCl [6]. In 1958, Hummers et al. preparation of GO by $NaNO_3$, $KMnO_4$ and H_2SO_4 mixture, the process of GO more effectively, and they are discover 188 g of GO containing 23% H_2O and 2–3% ash [7]. And subsequently, the studied report used pyrenebutyrate by oxidation process can produced of single atomic layer for GO [8].

In some studies, researchers have used graphite powder in dry air (the water content < 2 ppm) as oxidants and conducted heating to produce GO [9]. However, this preparation of GO are used the graphite of high purity. But low cost natural graphite mineral products are principally distributed in China, Germany and Mexico. However high cost artificial graphite powder, produced through heat-treatment with temperatures above 2700 °C. Therefore, the cost of GO can not be reduced, in this study, we put forward a mass production of GOPs from any graphene sheets containing carbon materials (GSCCMs).

2. Experimental

2.1. Preparation of graphene sheet containing carbon materials (GSCCMs)

In this study, woody material was sampled from fibers of *Elaeis guineensis Jacq*. This was cut into dimensions of $(2 \times 0.05\text{–}0.2 \times 0.05\text{–}0.2)$ mm^3 (length, width and height). Then, two stepwise heat-treatment processes were used to render the woody materials into graphene sheets containing carbon materials. The first carbonization temperature was set at 350 °C, while the temperature for the secondary pyrolysis was set at 1500 °C under a vacuum, for samples with and without a MnO_2 catalyst (added amount of 1 g). The samples' IDs are denoted as GSCCM-A and GSCCM-B, respectively. And the graphene sheet content of GSCCM-A and GSCCM-B is 80.6% and 81.2%, respectively from our report the empirical formula of graphene sheet content [10].

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http://dx.doi.org/10.1016/j.mseb.2014.11.007
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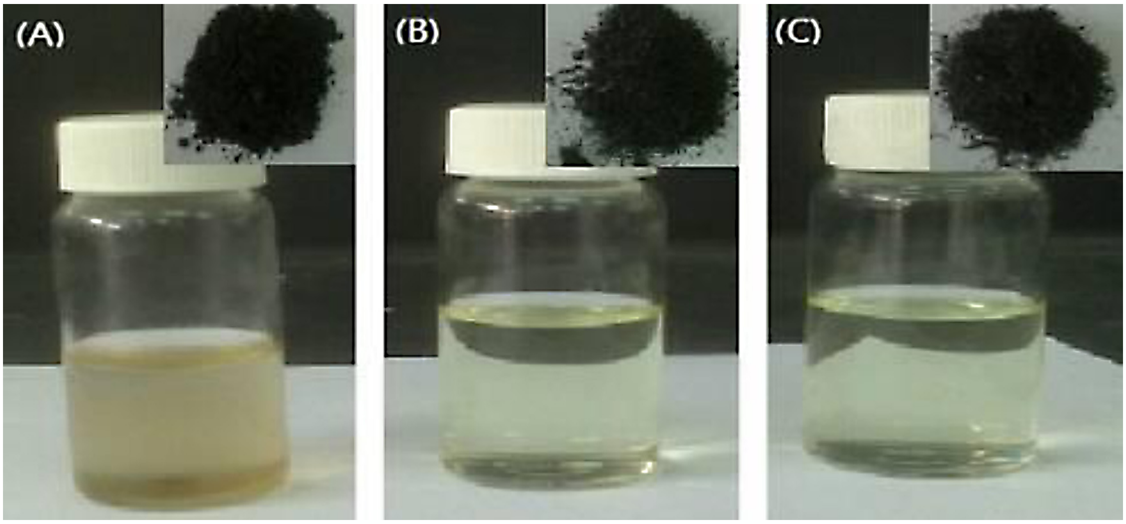

Fig. 1. Photograph of graphene oxide solution for (A) GOS-G, (B) GOS-A and (C) GOS-B.

2.2. Synthesis of graphite oxide solution (GOS) and graphene oxide paper (GOP)

A graphene oxide solution (GOS) as synthesized using oxidation commercial graphite and graphene sheet content carbon materials from woody material using a wet-type oxidation process, called Hummers' method. H_2SO_4 and H_3PO_4 in a ratio of 9:1 and then, 2.25 g of $KMnO_4$ were added into the above mixed acid solution. Next, we added 0.375 g of graphite powder to the oxidant and conducted heat-treatment at 50 °C for 24 h. After cooling, we added 3 mL of H_2O_2 and 200 mL of H_2O into the cooled solution. Then, the abovementioned solution underwent centrifuge at 3000 rpm and the sediment was collected. Next, we added the sediment to 200 mL of 30% HCl followed by centrifuge again. We kept repeating the steps until the sediment was dissolved and uniformly dispersed in the solvent. The sample IDs are denoted as GOS-G (from commercial graphite), GOS-A and GOS-B (from GSCCMs). The GOP was prepared simply by filtration of the GOS using a Whatman No.1 filter. The fresh GOP samples were annealed in a vacuum oven at 360 °C for 1 h. The sample IDs are denoted as GOP-G (from commercial graphite), GOP-A and GOP-B (from GSCCMs).

2.3. Property analysis of GOP samples

The field emission scanning electron microscope (FE-SEM) was used to analyze the surface morphology of different samples (JSM-7600F FESEM, JEOL Ltd., Japan). A Fourier transform infrared spectrometry (FT-IR) was used to analyze the functional groups of the samples (Vector22, Bruker, Germany). The parameters of this instrument were a scanning time of 128 times, with a wave number of 4000–400 cm^{-1}. An X-ray diffraction (XRD) was used to analyze the lattice structure (D8 Advance, Bruker, Germany). The scanning angles were 10°–80° (2θ degree). A differential scanning calorimeter (DSC) was used to analyze the thermology transitions of the samples (DSC-822, Mettle Toledo, Switzerland). The heating and cooling rates were 20 °C/min and the flow rate of N_2 was 50 mL/min.

3. Results and discussion

Fig. 1 shows a photograph of the GOS; the color of the GOS is a pale tawny caused from the effective dispensability of graphene oxide sheets in solution. Fig. 2 shows the FT-IR spectra of commerce graphite, GSCCMs and GOP samples. The peaks at 3850 and 3745 cm^{-1} corresponded to amide groups. The peak at 3500 cm^{-1} corresponded to a —OH stretching vibration motion, and the peak at 2950 cm^{-1} corresponded to —CH_2—. The region between 1700 and 1650 cm^{-1} corresponded to a C=O stretching vibration motion, and the region between 1200 and 1000 cm^{-1} corresponded to a C—O and C—OH stretching vibration motion. The peaks at 1397 cm^{-1} corresponded to a —CH_3 stretching vibration motion, and the region between 1600–1450, 878, 650 and 590 cm^{-1} corresponded to the aromatic groups. As the results show, there is an obvious decrease in the intensities of amide groups, aromatic groups, —CH_2— and —CH_3 stretching vibration peaks; in comparison, there is an obvious strengthening in the intensities of —OH, C=O, C—OH and C—O stretching vibration peaks in GOPs compared to those in graphite and GSCCMs.

The authors also have used Raman spectroscopy to analyze the pure graphite, graphene and graphene oxide papers. (See Supply Fig. S1 and S2). And we found that the graphene oxide papers has a Raman shift from 2200 to 3300 cm^{-1}.

Fig. 3 illustrates the XRD spectra of the samples. From the XRD analysis, the peaks around 2θ degree = 26° (d_{002}), 41° (d_{100}), 44° (d_{101}), 54° (d_{004}), and 78° (d_{110}) correspond to classical graphite crystals (JCPDS No. 75-1621). The GSCCM-A and GSCCM-B have peaks of cellulose at around 2θ degree = 22°. The sample peaks (d_{002}, d_{100} and d_{101}) show an obvious decrease in intensity due to

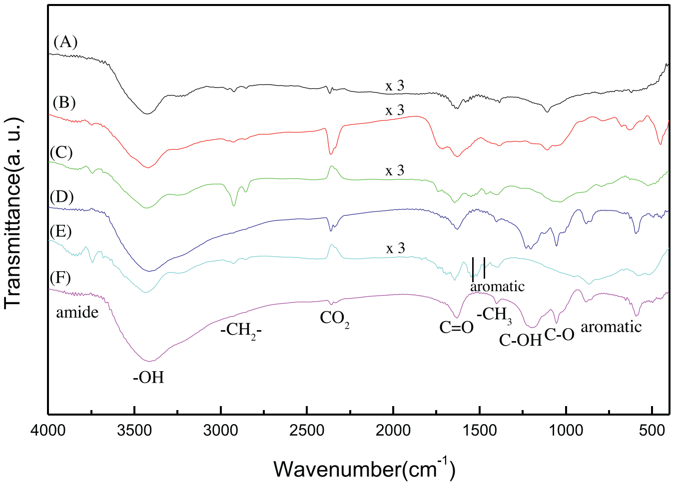

Fig. 2. FT-IR spectrums of (A) commerce graphite, (B) GOP-G, (C) GSCCM-A, (D) GOP-A, (E) GSCCM-B and (F) GOP-B.