Electrochimica Acta 115 (2014) 566–572

Contents lists available at ScienceDirect

Electrochimica Acta

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

Sugar-derived carbon/graphene composite materials as electrodes for supercapacitors

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ARTICLE INFO

Article history:
Received 8 July 2013
Received in revised form
19 September 2013
Accepted 4 November 2013
Available online 17 November 2013

Keywords:
Graphene
Sugar-derived carbon
Composite materials
Supercapacitors

ABSTRACT

Sugar-derived carbon/graphene composite materials have been prepared by mixing glucose and graphene oxide with the assistance of ultrasonication and calcination. Microstructure measurements show that sugar-derived carbon nanoparticles are anchored to the graphene planes and used as spacers to inhibit the restacking of graphene sheets during calcination. The composite is a three-dimensional material with a layered and porous structure. Benefiting from such a unique structure, the sugar-derived carbon/graphene composite materials as electrodes for supercapacitors exhibit a high specific capacitance (273 $F{\cdot}g^{-1}$ at a current density of 0.5 $A{\cdot}g^{-1}$) as well as excellent electrochemical stability. Therefore, this remarkable performance suggests its promising application as an efficient electrode material for electrochemical capacitors.

1. Introduction

Graphene, a two-dimensional monolayer of sp^2-bonded carbon atoms, has attracted tremendous interest for applications in supercapacitors and Li-ion batteries in recent years, due to its high electrical and thermal conductivities, excellent mechanical properties and extremely large specific surface area [1]. In the current graphene-based supercapacitors, reduced graphene oxide (rGO) is mostly used as the alternative to pristine graphene, because rGO can be synthesized in large scale with low cost [2]. However, a critical issue encountered in this process is that rGO usually suffers from serious agglomeration and restacking during utilization as an electrode material due to the Van der Waals interactions between neighboring sheets, which leads to huge loss of effective surface area, thus a lower capacitance than expected [3]. Recently, it is reported that the specific capacitance of graphene materials as electrodes for electrochemical double-layer capacitors (EDLCs) is 135 $F{\cdot}g^{-1}$ in KOH solution [4] and 117 $F{\cdot}g^{-1}$ in H_2SO_4 solution [5]. However, this specific capacitance is far below the theoretical value of 550 $F{\cdot}g^{-1}$ calculated for single-layer graphene [6]. Consequently, to address these disadvantages, integration of graphene sheets (GNS) into macroscopic structures such as porous, films, scaffolds and networks will pave a way towards high-performance graphene-based materials for practical applications [7–10]. So far, three main kinds of materials: carbon materials, conducting polymers and metal oxides have been independently or collaboratively applied in carbon-based EDLCs [11–13], polymer-, metal oxide-based pseudo capacitors [14–16], and hybrid supercapacitors [17–20]. Among these materials, porous carbon materials with high surface area and good mechanical properties are widely used in supercapacitors. Yan et al. [21] prepared GNS/carbon black composites by the ultrasonication and in situ reduction methods whose capacitance was 175.0 $F{\cdot}g^{-1}$ at 10 $mV{\cdot}s^{-1}$ in 6 M KOH solution. Wang et al. [22] synthesized a high-surface-area carbon nanoparticle/graphene composite materials with a high specific capacitance of 324.6 $F{\cdot}g^{-1}$ at the current density of 0.3 $A{\cdot}g^{-1}$ in 1 M H_2SO_4 solution. So inserting carbon particles in-between the GNS is an effective way to improve energy storage. Therefore, it is essential to design carbon-based nanostructures for electrochemical energy storage.

In this work, a novel method to produce sugar-derived carbon/graphene (SCG) composite materials as electrodes for EDLCs has been presented with environmentally friendly materials and low fabrication cost. The incorporation of sugar-derived carbon into graphene layers can not only prevent the agglomeration of GNS, but also improve electrolyte–electrode accessibility as well as electrode conductivity. As a result, SCG exhibits a high specific surface area and excellent capacitance at room temperature.

2. Experimental

2.1. Synthesis of graphite oxide (GO)

All of the chemical reagents were analytical grade and used without further purification. GO was synthesized from

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0013-4686/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.electacta.2013.11.028

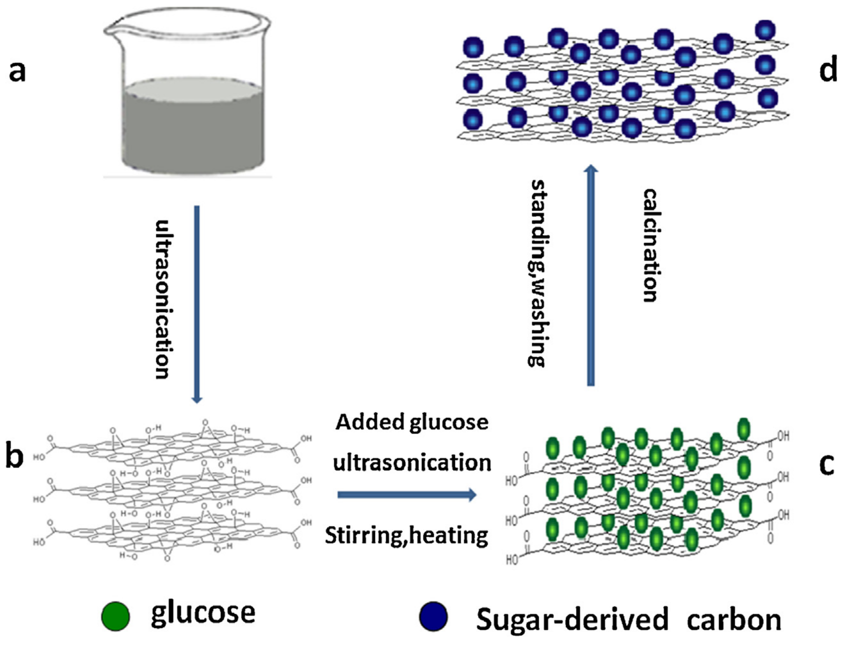

Fig. 1. Illustration of the synthesis route, (a) the dispersing of GO suspension; (b) the exfoliation of GO by ultrasonicating; (c) the mixing of GO and glucose in the solution; (d) the composite with sugar-derived carbon between the GNS layers.

natural graphite powder based on a modified Hummers's method [23].

2.2. *Synthesis of SCG*

The SCG were synthesized in three steps as shown in Fig. 1. Firstly, GO suspension was obtained by dispersing purified GO (0.4 g) in 400 ml distilled water with the aid of intensive 0.5 hour's ultrasonication (Fig. 1. b, the exfoliation of the GO). Secondly, 0.4 g glucose was added into a homogeneous GO suspension (1 mg·mL^{-1}) with the assistance of 2 hours' ultrasonication. Then, the suspension was transferred to a three-neck flask. And the mixture was heated at 95 °C in an oil bath for 24 h and cooled down to room temperature (Fig. 1. c, the mixing of the GO and glucose in the solution). Finally, the resulting stable black suspension was washed with distilled water for three times and dried at 50 °C overnight. Then, the SCG was obtained by calcined (Fig. 1. d, calcination) in tube furnace with a nitrogen gas atmosphere at 400 °C for 2 hours.

For comparison, the sugar-derived carbon was also prepared by calcining glucose through the above-mentioned process. And GNS was prepared by thermal chemically exfoliated GO in tube furnace with a nitrogen gas atmosphere at 400 °C.

2.3. *Characterization methods*

X-ray diffraction (XRD) was performed on Rigaku D/max 2500 v/pc diffractometer with Cu Kα radiation ($\lambda \approx 1.54$ Å). Raman spectra were obtained from a reflex Raman microscope (RENISHAW). Brunauer–Emmet–Teller (BET) specific surface area was determined from N_2 adsorption by using a NOVA2200e (USA) analyzer at liquid nitrogen temperature. The morphology of as-obtained products was characterized by a transmission electron microscope (TEM, PHILPS, TECNAI G2 F20) equipped with the selected area electron diffractions (SAED) and a scanning electron microscope (SEM, HITACHI S-4800 Japan).

2.4. *Preparation of electrodes and electrochemical measurements*

The electrochemical properties of as-obtained products were investigated under a three-electrode cell at room temperature. The working electrodes were prepared by mixing active material with acetylene black and polytetrafluoroethylene (PTFE) binder at weight ratio of 80:10:10 in alcohol to form a homogeneous slurry. The resultant slurry was uniformly pressed onto nickel foam current collectors (1.0 cm^2). The mass of active material contained in each working electrode was between 1 and 3 mg. Electrochemical measurements were carried out with 6 M KOH aqueous solution as the electrolyte. The sintered Ni electrode and Hg/HgO electrode were used as the counter and reference electrode, respectively.

Cyclic voltammogram (CV) and electrochemical impedance spectroscopy (EIS) measurements were conducted on Zennium electrochemical workstation. The galvanostatic charge-discharge measurement was performed on a Land Battery workstation (Wuhan Land Instrument Company, China).The specific capacitance of the electrode was calculated according to the equation: $C = I\ \Delta t/m\ \Delta V$, where I is the discharge current (A), Δt is the total discharge time (s), m is the mass of active material in the electrode (g) and ΔV is the potential range in the discharge process (V)

3. Results and Discussion

3.1. *Microstructure characterizations*

Fig. 2 shows the XRD patterns of GNS, sugar-derived carbon and SCG. For GNS (Fig. 2a), the intense and sharp diffraction peak is located at 2θ =24.8°, corresponding to the characteristic diffraction (002) of GNS, which indicates that the GO has been successfully reduced. For pure sugar-derived carbon (Fig. 2b), the diffraction visible peak appears at 2θ =18.9°. Whereas, the obtained SCG only shows a broad peak at 2θ =23.8° (Fig. 2c), which is different from those of GNS, pure sugar-derived carbon, mainly due to the strong interaction between these two components. The sugar-derived carbon nanomaterials on GNS can shorten the diffusion path of mass transfer and thus nanoelectro-active of SCG electrode materials can facilitate the mass transfer.

Fig. 3 shows the Raman spectra of GNS, sugar-derived carbon and SCG. It can be seen three main Raman peaks associated with different characteristics of carbon materials. In the Raman spectrum of GNS (Fig. 3a), the G band (1590 cm^{-1}) represents the in-plane