



Contents lists available at ScienceDirect

Thin Solid Films

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

Surface modified catalytically grown carbon nanofibers/MnO₂ composites for use in supercapacitor

Fitri Nur Indah Sari, Hsuan-Min Lin, Jyh-Ming Ting*

Department of Materials Science and Engineering, National Cheng Kung University, Tainan, Taiwan

ARTICLE INFO

Article history:

Received 14 May 2016

Received in revised form 19 July 2016

Accepted 27 July 2016

Available online xxx

Keywords:

Carbon nanofiber

MnO₂

Supercapacitor

Acid treatment

Microwave-assisted hydrothermal

ABSTRACT

We have reported a fast and eco-friendly method to synthesize the MnO₂ on catalytically grown carbon nanofiber (CGCNF). The CGCNF was functionalized by acid treatment under various H₂SO₄/HNO₃ ratios. A microwave-assisted hydrothermal method was then used to synthesize MnO₂/CGCNF composites at a very short time of 5 min. We demonstrated that the surface modification has significant effect on the MnO₂ deposition and the electrochemical performance of the resulting MnO₂/CGCNF composites. Electrical impedance spectroscopy analysis and cyclic voltammetry showed that O-functional group controls the electrical conductivity and the electrochemical performance of both CGCNF and CGCNF/MnO₂ composites, respectively. It was found that C=O bond assists the MnO₂ deposition. CGCNF/MnO₂ composite showing specific capacitance (C_{sp}) of 257 F/g at a scan rate of 5 mV/s and electrical resistance of 19 Ω was demonstrated.

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1. Introduction

Energy storage devices have attracted more and more attentions [1–3] for use in, for example, mobile phone and electric automobile. One of such energy storage devices is supercapacitor. Supercapacitor provides high energy density, long cyclic stability, and excellent charge/discharge characteristics [1,2,4]. Based on the energy storage mechanism, supercapacitor can be an electrical double-layer capacitor (EDLC) where porous carbon materials dominate the electrodes [5,6] and pseudo-capacitors where redox-active materials serve as the electrodes [7,8]. In general, pseudo-capacitors based on transition metal oxides/hydroxides and conducting polymers have higher specific capacitance (C_{sp}) than the EDLCs based on carbonaceous materials [9,10]. Some of the common redox-active materials include RuO₂, Co₃O₄, NiO, NiOH, and MnO₂ [11–14].

Among these redox-active materials, RuO₂ exhibits superior C_{sp} but suffers from its high cost and toxicity [15,16]. Low cost, environmental friendly oxides are thus called for. One of such materials is MnO₂, which can be operated in a neutral aqueous electrolyte [17–19]. However, it is also known that MnO₂ has apparent drawbacks, for example, low electronic conductivity (10⁻⁵–10⁻⁶ S cm⁻¹). Therefore, the addition of a conductive material such as activated carbon, carbon fiber, carbon nanotube, and graphene into MnO₂ has been investigated [20,21]. These carbon materials are known to provide advantages of

high chemical and mechanical stability, low electrical resistance, and long aspect ratio. They are popular carbonaceous backbones in metal oxide/carbon material composites. However, the hydrophobicity of carbon can influence the growth of MnO₂ on the surface [22]. To decrease the hydrophobicity, surface modification through high temperature atmospheric oxidation [21,23], plasma treatment [24–26], electrochemical treatment [27], surface functional group grafting [28], or chemical oxidation [25,29–32] are used. In the context of MnO₂/carbon nanofiber (CNF) composite synthesis, surface treatment of the CNFs is often required. Various agents have been used for the surface treatments. MnO₂ was grown on HNO₃ treated plasma enhanced chemical vapor deposited vertically aligned CNFs using an electrochemical deposition method [31], and HCl treated electrospun CNFs [32], as-made electrospun CNFs [33], and H₂SO₄ treated electrospun CNF/CNT using wet chemistry methods [34]. Furthermore, none of the CNFs used exhibits better electrical conductivity than the catalytically grown CNF (CGCNF) [35] used in this study.

In the present study, CGCNF is used as the backbone for the growth of MnO₂, leading to the formation of MnO₂/CGCNF composites. The CGCNFs were treated with HNO₃/H₂SO₄ solutions having different compositions. This type of CNFs is highly graphitic, giving low electrical resistance. The growth of MnO₂ on the CGCNFs was performed using a simple, fast, and nonpolluting process, which is a microwave-assisted hydrothermal (MHT) method. We demonstrate that MnO₂ can be deposited on the CGCNF at a very short time of 5 min by the MHT, and the capacitance of the resulting MnO₂/CGCNF composite is as high as 257 F/g at a scan rate of 5 mV/s and the electrical resistance is as low as 19 Ω.

* Corresponding author.

E-mail address: jting@mail.ncku.edu.tw (J.-M. Ting).

Table 1
Experimental matrix.

Fiber ID	Acid-treatment solution composition	Composite ID	MHT solution composition ^a
CGCNF	–		
AT	100% HNO ₃	1-20AT	0.0025 g AT fiber + 0.05 g KMnO ₄
SN19	10% H ₂ SO ₄ + 90% HNO ₃	1-20SN19	0.0025 g SN19 fiber + 0.05 g KMnO ₄
SN28	20% H ₂ SO ₄ + 80% HNO ₃	1-20SN28	0.0025 g SN28 fiber + 0.05 g KMnO ₄
SN37	30% H ₂ SO ₄ + 70% HNO ₃	1-20SN37	0.0025 g SN37 fiber + 0.05 g KMnO ₄
SN46	40% H ₂ SO ₄ + 60% HNO ₃	1-20SN46	0.0025 g SN46 fiber + 0.05 g KMnO ₄
SN55	50% H ₂ SO ₄ + 50% HNO ₃	1-20SN55	0.0025 g SN55 fiber + 0.05 g KMnO ₄
SN64	60% H ₂ SO ₄ + 40% HNO ₃	1-20SN64	0.0025 g SN64 fiber + 0.05 g KMnO ₄
SN73	70% H ₂ SO ₄ + 30% HNO ₃	1-20SN73	0.0025 g SN73 fiber + 0.05 g KMnO ₄
SN82	80% H ₂ SO ₄ + 20% HNO ₃	1-20SN82	0.0025 g SN82 fiber + 0.05 g KMnO ₄
SN91	90% H ₂ SO ₄ + 10% HNO ₃	1-20SN91	0.0025 g SN91 fiber + 0.05 g KMnO ₄

^a All contain 0.2 ml 37% HCl.

2. Experimental

2.1. Surface treatment of CGCNFs

The CGCNFs were provided by Pyrograf Products, Inc. of USA. In the beginning, as-received CGCNFs were immersed in acetone under magnetic stirring at room temperature for a few hours in order to remove the organic residues on the fiber surface. The CGCNFs were then surface treated in an acid solution at 90 °C for various durations. 6 h when HNO₃ concentration \geq H₂SO₄ concentration and 1 h when H₂SO₄ concentration > HNO₃ concentration to prevent the dissolution or over etching of the CGCNFs. The conditions are summarized in

Table 1. After the acid treatment, the resulting suspension fluid was washed with de-ionized (DI) water for several times and filtered using a 0.2 μ m nylon filter paper. At the end, the fibers were dried at 100 °C overnight.

2.2. Synthesis of MnO₂/CGCNFs composites

MnO₂/CGCNF composites were fabricated using a MHT method. CGCNFs were mixed with KMnO₄ (J.T. Baker) at a desired ratio in a 37% HCl aqueous solution and then sonicated for 15 min. The CGCNF types and the CGCNF to MnO₂ ratios used in the solutions are also summarized in **Table 1**. The solution was then subjected to MHT

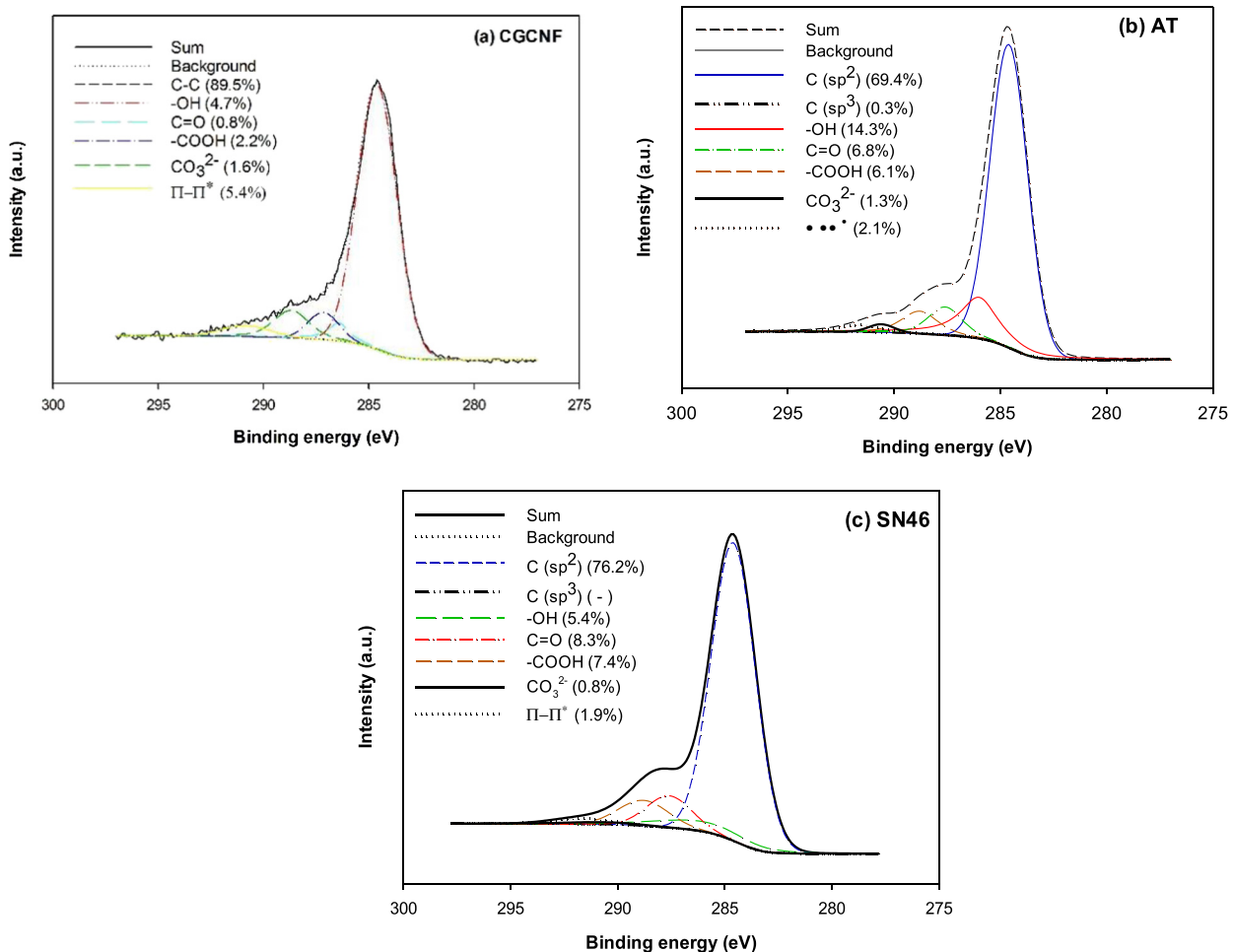


Fig. 1. XPS C1s spectra for Samples (a) CGCNF, (b) AT, and (c) SN46.

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