Electrochimica Acta 164 (2015) 154–162

Contents lists available at ScienceDirect

Electrochimica Acta

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

Hydrothermal Self-assembly of Manganese Dioxide/Manganese Carbonate/Reduced Graphene Oxide Aerogel for Asymmetric Supercapacitors

Yongchuan Liu [a,*], Dawei He [b], Honglu Wu [b], Jiahua Duan [b], Yining Zhang [a]

[a] *Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, PR China*
[b] *Key Laboratory of Luminescence and Optical Information, Ministry of Education, Institute of Optoelectronic Technology, Beijing Jiaotong University, Beijing 100044, PR China*

ARTICLE INFO

Article history:
Received 14 January 2015
Accepted 29 January 2015
Available online 12 February 2015

Keywords:
manganese oxide
graphene
manganese carbonate
three-dimensional
asymmetric supercapacitor

ABSTRACT

A facile strategy has been used to prepare $MnO_2/MnCO_3$/rGO aerogels (MGA) with good electrical conductivity and high mechanical strength. Shape-controlled rod-like MnO_2 and particle-shaped $MnCO_3$ hybrid nanostructures is incorporated with reduced graphene oxide (rGO). The 3D aerogels were tailored and directly used as the electrode of supercapacitor without adding polymer binder or conductive additives. Asymmetric supercapacitors were fabricated using MGA as the positive electrode and rGO aerogel (GA) as the negative electrode in a neutral aqueous Na_2SO_4 electrolyte. The asymmetric supercapacitor exhibits an energy density of 17.8 W h kg^{-1} with a power density of 400 W kg^{-1} in a stable potential window of 0–1.6 V. In this study, we first provide a new pathway to fabricate $MnO_2/MnCO_3$/rGO ternary composite for aerogel-based asymmetric supercapacitors.

1. Introduction

Supercapacitors, also known as electrochemical capacitors, are kind of promising energy storage devices because of their high power density, long life and high rate capability [1–3]. However, their commercial applications have been limited due to lower energy density and higher cost [4,5]. According to the following Eq. (1):

$$E = 0.5 \times CV^2 \tag{1}$$

It is obvious that energy density can be increased by maximizing the specific capacitance(C) and/or the cell voltage (V).

Nowadays, one promising strategy to enhance the specific capacitance is to combine carbon materials (such as active carbon, CNTs and graphene) with transition metal oxides (such as RuO_2, NiO, Co_3O_4, and MnO_2) [6–11]. Graphene, as an individual two dimensional carbon material, has become one of the hottest materials for supercapacitor applications in the past few years, owing to its high electrical conductivity, large surface area and good chemical stability [12,13]. Among these transition metal oxides, manganese dioxide (MnO_2) is considered to be one of the most promising materials for supercapacitors owing to its high specific capacitance, environmental compatibility and lower cost [14–16]. However, the electrochemical performance of MnO_2 has still been severely stymied by its low specific surface area, dissolution problem and poor electronic conductivity (10^{-5}–10^{-6} S/cm) [3]. As a result, the combination of nano-MnO_2 with graphene has been investigated extensively [15,17–19].

The operating voltage is mainly determined by the electrolyte's stability window. Although the organic electrolytes can provide a wider potential window, they are limited by their poor conductivity, flammability and toxicity compared to aqueous electrolytes [20,21]. A promising way to extend the cell potential window of aqueous electrolytes (no more than 1.2 V) is to fabricate asymmetric supercapacitors [17,22]. An asymmetric supercapacitor includes two different electrode materials. One electrode is a capacitive electrode (like carbon materials), and the other one is a battery-like Faradic electrode (like transition metal oxides, conducting polymers or their composites) [23–26].

In the present work, we report a unique method to fabricate 3D $MnO_2/MnCO_3$/rGO aerogels (MGA). $MnO_2/MnCO_3$/rGO aerogels

---

[*] Corresponding author. Present Address: Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002. PR China. Tel.: +86 591 83708429; fax: +86 591 83708429.

E-mail address: ycliu@fjirsm.ac.cn (Y. Liu).

http://dx.doi.org/10.1016/j.electacta.2015.01.223
0013-4686/© 2015 Elsevier Ltd. All rights reserved.

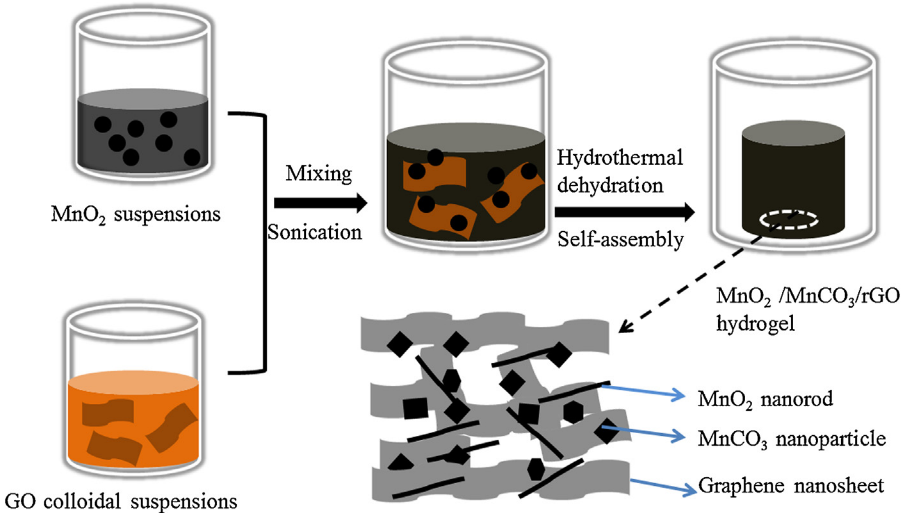

Fig. 1. Illustration of the fabrication process ofMnO_2/$MnCO_3$/rGO hydrogels.

with high mechanical strength have been prepared via soaking MGH in ammonia solution [16,20]. The MGA with 3D interconnected networks exhibit unique microstructure and enhanced electrochemical performance. An asymmetric supercapacitor was fabricated by using MGA as the positive electrode and a pure rGO aerogel (GA) as the negative electrode. The asymmetric supercapacitor exhibits an energy density of 17.8 W h kg^{-1} with a power density of 400 W kg^{-1} in a wide potential window of 0–1.6 V. The asymmetric supercapacitor shows satisfactory cycling stability, high energy density and power density.

2. Experimental

2.1. Material synthesis

2.1.1. Preparation of amorphous MnO_2

All reagents used in this experiment were of analytical grade. Amorphous MnO_2 was prepared by a simple precipitation reaction, in which the potassium permanganate ($KMnO_4$) solution was dropwise added into abundant sodium sulfite (Na_2SO_3) solution at room temperature.

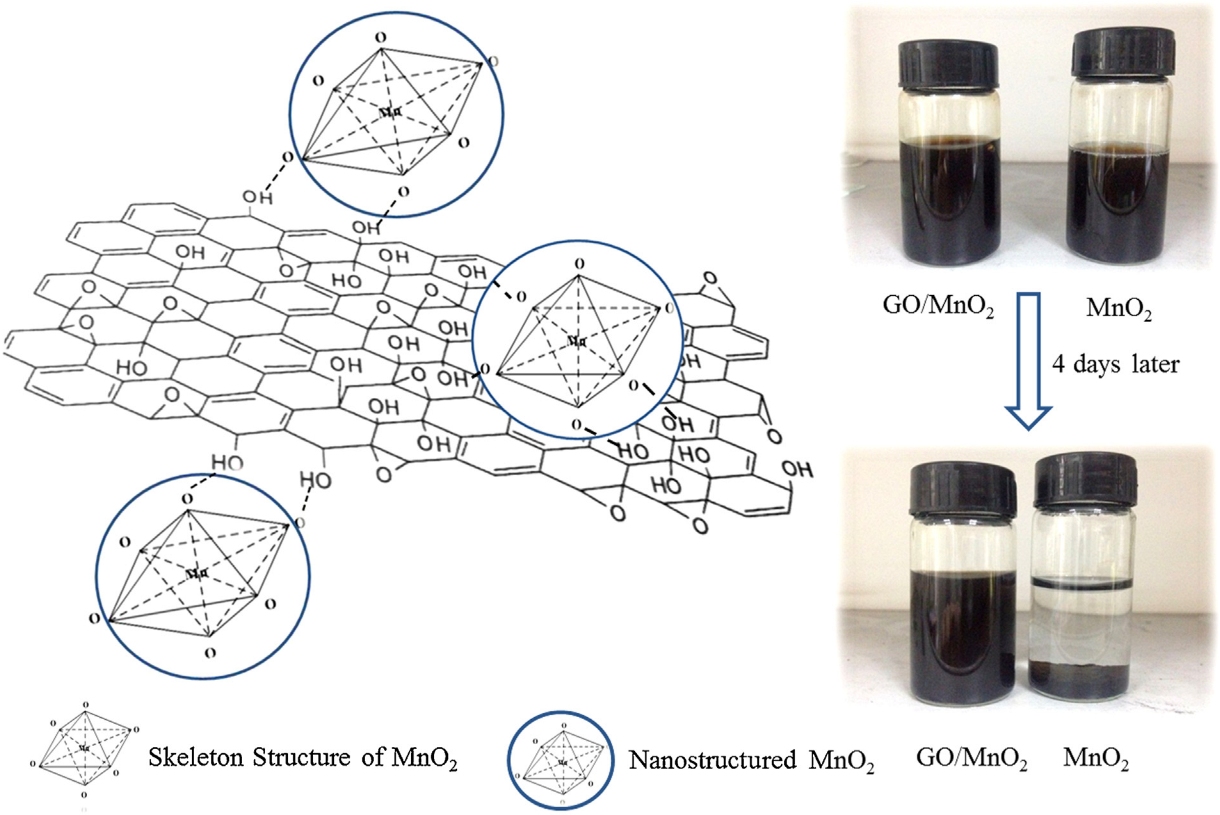

Fig. 2. Schematic mechanism for the formation of GO/MnO_2 complexes. MnO_2 has been dispersed uniformly in GO colloidal suspensions.