Electrochimica Acta 188 (2016) 704–709

Contents lists available at ScienceDirect

Electrochimica Acta

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

Fabrication of hierarchical porous cobalt manganese spinel graphene hybrid nanoplates for electrochemical supercapacitors

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ARTICLE INFO

Article history:
Received 3 October 2015
Received in revised form 25 November 2015
Accepted 6 December 2015
Available online 8 December 2015

Keywords:
Cobalt manganese spinel
Nanoplate
Graphene
Supercapacitor

ABSTRACT

Facile synthesis of porous and high conductive materials is highly desirable for supercapacitor electrode application. In this work, hierarchical porous $CoMn(CoMn)_2O_4$ spinel coated on reduced graphene oxide (rGO) was synthesized successfully through mixed solvothermal process followed by calcination. By adjusting the solvent ratio of dimethyl formamide (DMF): deionized (DI) water used in the mixed solvothermal process, the surface morphology of $CoMn(CoMn)_2O_4$/rGO can be tuned from nanofiber to nanoplate. The nanoplates display the highest surface area of 133.1 $m^2 g^{-1}$ with the pore size of ~3 nm, whereas the corresponding electrode exhibits the highest capacitance of 571 $F g^{-1}$ at a current density of 1 $A g^{-1}$, with the working potential as high as 1 V. In addition, the electrode based on nanoplates can retain about 84% of the initial capacitance after 1500 cycles at a charge current density of 5 $A g^{-1}$. These results confirm that the mesoporous $CoMn(CoMn)_2O_4$ nanoplates supported on rGO, synthesized the facile method described here, is a promising candidate for supercapacitor applications.

1. Introduction

Highly efficient, environmentally friendly and low cost energy storage devices are required in various applications, such as electrical vehicles, portable electronics, and mechanical tools. The supercapacitor, also called an electrochemical capacitor, has attracted attention in recent years [1,2], due to being environmentally friendly, having excellent cycle stability, and a higher power density with stable performance over a wide temperature range. Depending on the energy storage mechanism, the supercapacitors can be classified as [i] electrical double-layer capacitors (EDLC) or [ii] pseudocapacitors [3,4]. EDLCs store energy by ion absorption and desorption on the surface of an electrode [5,6]. While a pseudocapacitor typically generate a higher capacitance by storing energy through a fast redox reaction between an electrode and the electrolyte [7,8].

Transition metal oxides such as Co_3O_4 [9], NiO [10], RuO_2 [11] are ideal electrode materials for pseudocapacitors because the metal ions have multiple valence states which enhance the capability of metal oxides to participate in redox reactions. Recently, many binary transition metal oxides with spinel structure have been prepared as pseudocapacitor electrode materials, for example $NiCo_2O_4$ [12], $CoMn_2O_4$ [13], $ZnCo_2O_4$ [14], and $FeCo_2O_4$ [15] synthesized by aqueous hydrothermal route. These spinel materials, when formed with a special morphology, and typically have an even better electrochemical performance by promoting the diffusion of the electrolyte. Among the spinels, Mn-Co oxide shows promise as a supercapacitor electrode due to the high capacitance and the multiple redox reactions compared to single Mn or Co oxides [13,16]. Although the above mentioned merits of spinel materials make them very promising, their low electronic conductivity limits their applications. Graphene and its derivatives, with single sp^2 hybridization carbon structure [17], have excellent electrical conductivity with low theoretical specific capacity. Graphene has been widely used as a conductivity media to enhance the conductivity of transition metal oxides or spinel, and improve the capacitance and energy density.

In this work, instead of hydrothermal synthesis in aqueous solution, we use mixed solvothermal route by using the mixture of DMF and DI water as reaction medium, which had been proved to

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http://dx.doi.org/10.1016/j.electacta.2015.12.052
0013-4686/

be effective in tuning the morphology [18,19]. Consequently, hierarchical structured porous $CoMn(CoMn)_2O_4$ nanoplates or nanofibers supported on rGO were synthesized, through a mixed solvothermal step followed by calcinations to enhance crystallinity. The effect of the solvent volume ratio (DMF: DI water) on the surface morphology has been examined and the composite materials, as a capacitor electrode, characterized by electrochemical methods.

2. Experimental

$Mn(OAc)_2{\cdot}4H_2O$ (AR 98%), $Co(OAc)_2{\cdot}4H_2O$ (AR 98%), dimethyl formamide (DMF) (GC 99.9%) and NaOH (AR 96%) were supplied by Shanghai Aladdin Chemical Reagent Co. Ltd. All chemicals were used as received without further purification.

2.1. Synthesis of $CoMn(CoMn)_2O_4$/rGO hybrid

Graphene oxide (GO) was first prepared according to the modified Hümmers method [20]. The hierarchical structured porous $CoMn(CoMn)_2O_4$ nanoplatelets supported on rGO were prepared through solvothermal method followed by calcinations. In a typical procedure 120 mg of previously prepared GO, 1.75 mmol $Co(OAc)_2{\cdot}4H_2O$ and 3.5 mmol $Mn(OAc)_2{\cdot}4H_2O$ were dispersed in 20 ml of a solvent solution made by DMF:DI equal to 5:1 (v/v) (50 ml:10 ml), respectively. Afterwards 2 ml NaOH solution (10 M) was added drop wise to the combined solutions before being transferred into 100 ml Teflon-lined stainless steel autoclave. The autoclave was kept at 200 °C for 6 h before cooling down to room temperature. The precursors were obtained by washing and centrifuging the precipitate with DI water several times. Finally the obtained precursors were treated by freeze-drying to remove excess of water entrapped in the porous structure. At last the $CoMn(CoMn)_2O_4$/rGO precursors were calcined at 300 °C in air for 1 h and the obtained composites were labeled as CMOG5 (i.e. 5 DMF:1 DI water). Similarly, CMOG1, CMGO2, CMOG3 were named by adjusting the volume ratio of DMF to DI water as 1:1 (30 ml:30 ml), 2:1 (40 ml:20 ml), 3:1, (45 ml:15 ml) respectively. For comparison, pristine $CoMn(CoMn)_2O_4$ without any rGO was synthesized by mixed solvothermal method as well.

2.2. Characterization

The crystalline structure and morphology of $CoMn(CoMn)_2O_4$/rGO hybrid materials were characterized by X-ray diffraction (XRD) in Rigaku D/max 2500PC system (Cu-Kα 40 kV, 200 mA) in the range between 10° and 80° 2θ using a scan rate of 8°/min. Surface

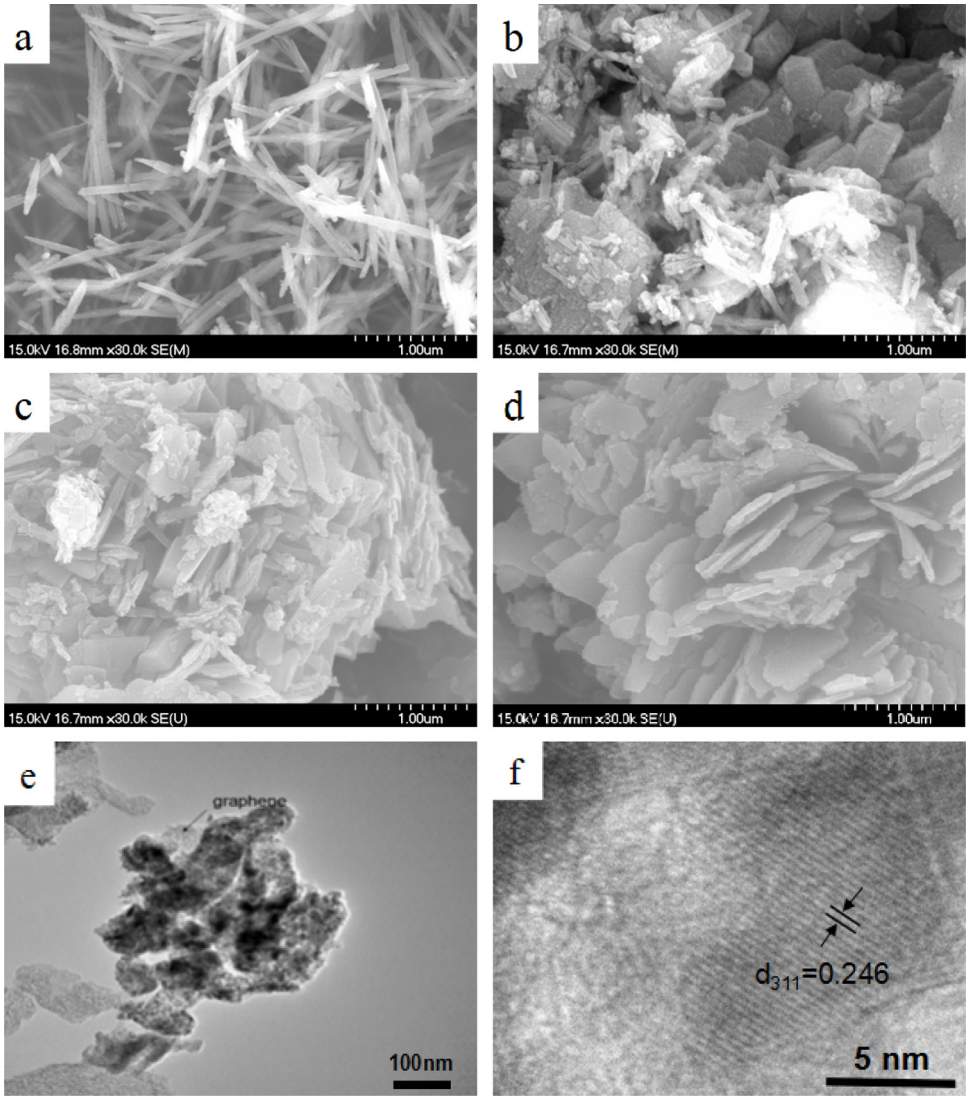

Fig. 1. The SEM images of metal oxide/rGO composites after 300 °C calcination CMOG1, b) CMOG2, c) CMOG3, d) CMOG5 (e) TEM, (f) HRTEM images of the CMOG5 composite.