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Full Length Article

Rational design of unique graphene modified cobalt manganite hollow microcubes for supercapacitors

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ABSTRACT

A novel reduced graphene oxide (rGO) modified ternary metal oxide electrode material with rational microstructure was successfully developed by the hydrothermal approach following the heat treatment, in which gauze-like rGO sheets were homogeneously decorated on the surfaces of uniform $CoMn_2O_4$ hollow microcubes. Benefitting from this special hybrid morphology possessing large specific surface area and good conductivity, the $CoMn_2O_4$@rGO composite gave rise to a greater specific capacitance of 1194.7 F g^{-1} at a low current density of 2 mA cm^{-2}, longer cycle life (88.6% capacitance retention after 5000 cycles), and more excellent rate performance when fabricated into a promising electrode for electrochemical supercapacitors.

1. Introduction

With energy-saving and environmentally friendly new energy products such as electric buses, hybrid electric vehicles, and portable electronics gradually entering people's lives, the energy demand for high-power applications is fast growing [1–3]. As a significant new generation of high-efficiency energy storage/conversion device, supercapacitors, have attracted great research attention recently due to their satisfactory power density, controllable service voltage, long cycle life and relative safety performance [4,5]. With the continuous deepening of study on supercapacitors, a constant problem that needs to be solved by researchers all over the world is the shortages of their quite low energy density and performance degradation, which seriously affects the practical performance of supercapacitors. Fortunately, rational design and preparation of novel electrode materials, to a large extent, is the most direct and effective approach [6–8].

Generally, for an ideal supercapacitor electrode material, it should possess high conductivity, stable structure with large specific surface area, excellent ionic conductive rate, ecofriendly nature as well as abundant resources. After the deep study on many common used binary metal oxides (NiO, Cu_2O, and so on [9,10]), researchers also found that ternary transition metal oxides such as $NiCo_2O_4$, $ZnCo_2O_4$, $FeCo_2O_4$, and $CoMn_2O_4$ which have satisfactory conductivity and high theoretical capacitance could to be promising electrode materials [11–14]. Among them, cobalt manganite ($CoMn_2O_4$) has attracted great interest in the fields of catalyst [15,16], lithium ion battery [17,18], and electrochemical supercapacitor [19–22] due to its multiple oxidation states especially the manganese in chemical formula providing a large number of transport electrons during the redox reaction. In addition, in order to realize the superior improvement of functional properties of $CoMn_2O_4$ material especially its electrochemical performance, an effective way is to design and build a hybrid three-dimensional (3D) structure with multi-component system [23]. On one hand, the synergistic effect of all individual constituents can be adequately developed by this kind of 3D hybrid electrode. On the other hand, the hybrid structure possessing larger reaction region and higher conductivity can offer more efficient and rapid pathways for electron transport during the charging and discharging to improve the overall electrochemical performance [24]. Fortunately, graphene materials have been widely studied and considered as alternative supercapacitor support to enhance the electrochemical properties, owing to their large specific surface area, unique network structure, being light-weight, enhanced electron and ion transport, and outstanding electrical properties [25].

In this work, we reported a facile synthesis of rGO modified $CoMn_2O_4$ hollow microcubes as the supercapacitor electrode material via a hydrothermal method following the annealing treatment. A series of characterizations including XRD, XPS, SEM and TEM were conducted to confirm the perfect composition and stable hybrid microstructure before the assembling of the $CoMn_2O_4$@rGO electrode. When evaluated in a 3.0 M KOH solution, the electrochemical results of the $CoMn_2O_4$@

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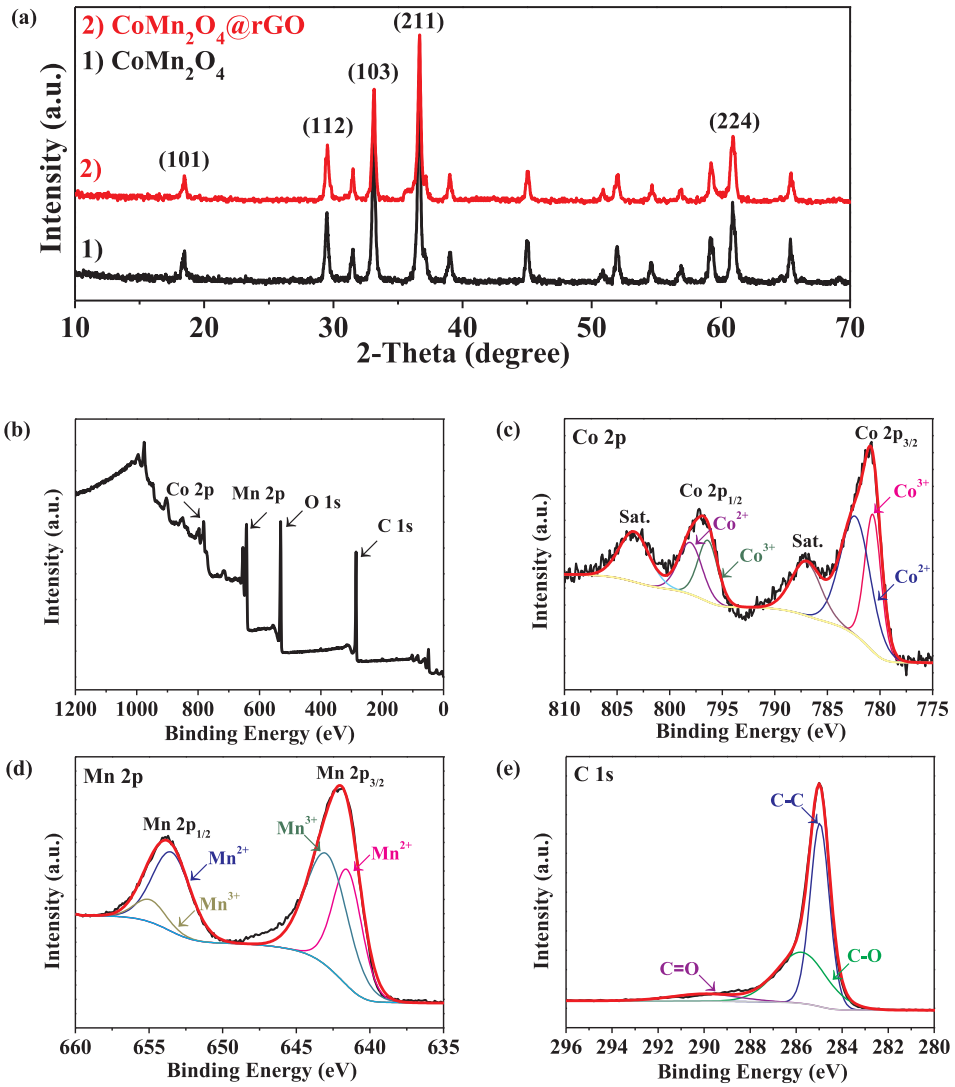

Fig. 1. (a) XRD patterns of $CoMn_2O_4$ and $CoMn_2O_4$@rGO electrode materials, XPS patterns of $CoMn_2O_4$@rGO powder, (b) survey, (c) Co 2p, (d) Mn 2p, (e) C 1s.

rGO electrode showed high specific capacitance and long cycle life at current densities of 2 and 10 mA cm^{-2}, respectively.

2. Experiment

2.1. Materials preparation

3 mol L^{-1} HCl solution was formulated and used to clean the surface of the pristine Ni foam removing the possible nickel oxide layers. These treated Ni foam were rinsed thoroughly with deionized (DI) water and ethanol, and then placed in a vacuum box. GO materials were prepared by the popularly used Hummers method [26] using graphite powder as the raw material.

A typical modified preparation of $CoMn_2O_4$ hollow microcubes based on a previous synthetic method [27]: 1.46 g of cobalt nitrate hexahydrate, 1.69 g of manganese sulfate monohydrate, and 20 g of ammonium sulfate were dissolved in 1 L of mixed solution (the ratio of DI water to ethanol is 10:1) to form solution I (in 5 L of beaker). 12 g of ammonium bicarbonate was dissolved in 1 L of DI water to form solution II. The solution II was transferred to the five liters of beaker slowly mixing with the solution I with vigorous stirring. About 10 min later, the mixed solution in the beaker was placed in a magnetic stirring thermostatic water bath at 50 °C for 9 h. After the reaction ended, the white precursor could be collected, then washed thoroughly with DI water and dried at 60 °C. At last, $CoMn_2O_4$ hollow microcubes could be obtained by heating the precursor to 600 °C and kept at 600 °C for 5 h in air.

Preparation of $CoMn_2O_4$@rGO composite: 20 mg of as-obtained $CoMn_2O_4$ powders and 600 μl of GO dispersion (10 mg/ml) were mixed into 15 ml of DI water. The suspension was ultrasonicated for about 30 min until it was well mixed. Subsequently, it was transferred in a 45 ml Teflon-lined stainless autoclave and heated to 180 °C for 9 h. After cooling down to the room temperature, the black precipitate was washed with DI water for 3 times and dried at 60 °C for 6 h. At last, the dried product was heated to 500 °C and maintained for 6 h in tube furnace with continuous nitrogen gas, further facilitating the reduction of GO.

2.2. Materials characterization

A JSM-7800F (JEOL) FE-SEM and a Tecnai G2 F20 S-TWIN (200 kV, FEI) TEM were used to characterize the morphologies and microstructures of both $CoMn_2O_4$ hollow microcubes and $CoMn_2O_4$@rGO composite. All X-ray diffraction (XRD) patterns of the powder samples were tested by PANalytical X'Pert Powder (Spectris Pte. Ltd.) with the Cu Kα radiation. The X-ray photoelectron spectrums (XPS) were collected using an ESCALAB250Xi (Thermo Fisher Scientific, USA). All binding energies were referenced to the C 1s core at 284.6 eV.