Journal of Physics and Chemistry of Solids 115 (2018) 317–321

Contents lists available at ScienceDirect

Journal of Physics and Chemistry of Solids

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

$CoFe_2O_4$ derived-from bi-metal organic frameworks wrapped with graphene nanosheets as advanced anode for high-performance lithium ion batteries

Hongxun Yang [a,b,*], Kaixuan Zhang [a,b], Yang Wang [a], Chao Yan [c], Shengling Lin [a,**]

[a] School of Environmental & Chemical Engineering, Jiangsu University of Science and Technology, Zhenjiang, 212003 Jiangsu, China
[b] Marine Equipment and Technology Institute, Jiangsu University of Science and Technology, Zhenjiang, 212003, Jiangsu China
[c] School of Material Science and Engineering, Jiangsu University of Science and Technology, Zhenjiang, 212003, China

ARTICLE INFO

Keywords:
$CoFe_2O_4$
Graphene nanosheets
Lithium ion batteries
Anode

ABSTRACT

$CoFe_2O_4$/graphene nanosheets (GNS) nanocomposites derived from bi-metal organic frameworks and graphene oxides were firstly synthesized via a facile one-pot chemical precipitation with subsequent thermal decomposition method. The as-prepared $CoFe_2O_4$/GNS were characterized by XRD, Raman, SEM, TEM and BET adsorption-desorption. As an anode for lithium ion batteries, the $CoFe_2O_4$/GNS nanocomposites exhibited an obvious enhancement electrochemical property in terms of a higher discharge capacity of 1061.7 mAh g^{-1} after 100 cycles at 100 mA g^{-1} with 75.1% capacity retention and the excellent reversible capacity of 956.2 mAh g^{-1} when the charge-discharge rate returned from 2 A g^{-1} to 0.1 A g^{-1} after 60 cycles. This enhancement could be attributed to the synergistic effects between Co and Fe oxides, and the graphene nanosheets which could not only accommodate the volume variations of $CoFe_2O_4$ nanoparticles during cycling, but also improve the contact area between electrolyte and electrodes.

1. Introduction

Lithium ion batteries (LIBs), as one of the most popular energy storage devices, have been extensively used in the field of upcoming electric vehicles and popular portable devices [1–5]. However, the current graphite anode material has become one of important issues that limit the development of high-power LIBs due to its low theoretical capacity (372 mAh g^{-1}) [6–9]. Thus, the seeking for alternative anode with high energy density and long cycle life has become an urgent task for constructing next generation high-power LIBs. Single metal oxides as advanced anodes for next generation LIBs have been attracted much attentions because of their much higher energy density and excellent electrochemical properties compared to graphite [10–26]. In addition, metal oxides derived from metal-organic frameworks (MOFs) as sacrificial templates behave porous nanostructures, such as hollow microfibers, nanotube, microflower-like [27,28]. These specific microstructures help to enhance the surface area between electrolyte and active materials, accommodate the volume changes of electrode during cycling, shorten Li^+ transport path [29–33]. When these porous metal oxides were applied as anode materials for LIBs, porous nanostructures could not only improve the contact area between electrode and electrolyte, but also accommodate the volume variations and shorten Li^+ ion diffusion lengths during charge-discharge processes resulting in the improvement capacity retentions and rate capabilities [34,35]. Recently, our group has reported porous Fe_2O_3 nanotubes and Co_3O_4 microfibers derived-from MIL-88A and Co-based MOF using different organic agent, respectively, delivering obvious the enhancement capacity retentions as anodes for LIBs [36,37]. Otherwise, binary metal oxide combining different transition metal together could gain better electrochemical properties because of the synergistic effect between the different constituents. Iron-based spinel oxides with formula AFe_2O_4 (A=Ni, Co, Zn, Mn) with higher capacity and low cost have been used as anodes for LIBs. Especially for cobalt ferrite ($CoFe_2O_4$) with high theoretical capacity of 916 mAh g^{-1} have been reported as anode for LIBs [38,39]. However, the electrode pulverization caused by the large volume variations during cycling and the poor electrical conductivity seriously limited its applications [16,17].

On the other hand, graphene nanosheets (GNS) have been widely studied as a famous conductive buffer and a promising support to fabricate composites for LIBs electrode materials because of its larger BET surface area, high electronic conductivity, and excellent structural flexibility [40–45]. The synergistic effects between GNS and metallic compounds play a key role in improving the capacity retention and rate

* Corresponding author. School of Environmental & Chemical Engineering, Jiangsu University of Science and Technology, Zhenjiang 212003, Jiangsu, China.
** Corresponding author.
E-mail addresses: yhongxun@126.com (H. Yang), linshl5757@sina.com (S. Lin).

https://doi.org/10.1016/j.jpcs.2017.12.042
Received 17 August 2017; Received in revised form 9 November 2017; Accepted 21 December 2017
Available online 24 December 2017

capability of electrodes due to the improved interaction [40,41]. Some synthetic methods have been also reported to prepare $CoFe_2O_4$/GNS nanocomposites as anodes for LIBs. For example, Xiao et al. reported $CoFe_2O_4$/GNS synthesized via an ultrasonic method combined with calcination, showing improvement rate capability [25]. Zhao and his co-workers successfully synthesized a $CoFe_2O_4$/GNS sandwich via heating the solution followed by the hydrothermal method [24]. Although the reported nanostructured $CoFe_2O_4$/GNS composite exhibited enhanced capacities, to explore a simple method for preparing $CoFe_2O_4$/GNS nanocomposites with satisfied electrochemical properties is still required for its practical application in LIBs. To our knowledge, $CoFe_2O_4$/GNS nanocomposites derived from dimetal organic frameworks and graphene oxides synthesized via a simple one-pot chemical precipitation method has not been reported.

Herein, we report a binary metal oxide $CoFe_2O_4$ derived from bimetal organic framework wrapped with GNS. Benefiting from the synergistic effect of Co and Fe oxide and GNS, as anode for LIBs, the $CoFe_2O_4$/GNS nanocomposites could be expected to deliver obviously enhanced reversible capacity, capacity retentions, and rate capabilities.

2. Experimental section

2.1. Synthesis of the $CoFe_2O_4$/GNS nanocomposites

Graphene oxide (GO) was prepared from natural graphite powder by a modified Hummers method [21]. 40 mg graphene oxide was dispersed into 40 ml ethanol by ultrasonic cleaner for 1 h at room temperature, then 0.138 g 1, 3, 5-benzenetricarboxylic acid (BTC) was added under continuous stirring as solution A. 0.498 g cobalt acetate, 0.146 g L-glutamic acid and 0.27 g ferric chloride were dissolved in 40 ml deionized water and stirred at room temperature for 30 min as solution B. Then solution B was poured into solution A with continuous stirring. After being stirred for 24 h, the precipitation was washed with ethanol and distilled water for three times and then was dried in vacuum at 60 °C to obtain bimetal CoFe-based MOFs/GO product. The porous $CoFe_2O_4$/GNS nanocomposites were obtained by the calcination of the as-synthesized precursor at 550 °C for 2 h with a ramp rate of 2 °C min^{-1} under N_2 atmosphere. For comparison, pure $CoFe_2O_4$ was prepared under the same conditions without the presence of GO.

2.2. Material characterizations

The microstructures and morphologies of the as-synthesized product were characterized with a X-ray diffraction analyzer (Shimadzu XRD-6000 diffractometer using Cu-Kα radiation (0.15406 nm), scanning electron microscope (SEM, JEOL, JSM-6700 F, 5 kV), and transmission electron microscope (TEM, JEOL JEM-1400). An ASAP 2020 surface analyzer was used to measure the BET surface area and pore size distribution of $CoFe_2O_4$/GNS nanocomposites using nitrogen adsorption-desorption isotherms determined at 77 K using.

2.3. Electrochemical measurements

The working electrodes were prepared by mixing 80 wt% $CoFe_2O_4$/GNS, 10 wt% Super P, and 10 wt% polyvinylidene fluoride binder dissolved in N-methyl-2-pyrrolidinone. Coin-type half cells (2032) were fabricated in an argon-filled glove box to evaluate the electrochemical properties using a battery cycle tester (CT2001A, Wuhan LAND electronics Co., China). Cyclic voltammetry (CV) measurements were carried out on an electrochemical workstation (Autolab302N) at 0.2 m V s^{-1} rate between 0.01 and 3 vs. (Li/Li^+)/V. Electrochemical impedance spectroscopy (EIS) tests were also measured on the same electrochemical workstation in the frequency range of 0.1 Hz–10^6 Hz with *ac* amplitude of 10 mV.

3. Results and discussion

3.1. Characterizations of $CoFe_2O_4$/GNS nanocomposites

Fig. 1 exhibits the SEM and TEM images of the $CoFe_2O_4$/GNS nanocomposites. As shown in Fig. 1a and b, the as-prepared product consists of graphene nanosheets and nanoparticles with diameter of 90 nm. These nanoparticles appear to be wrapped between the graphene nanosheets. Fig. 1c shows the TEM images of the $CoFe_2O_4$/GNS nanocomposites. It can be seen that the as-prepared product consists of graphene nanosheets and $CoFe_2O_4$ nanoparticles, which are consist with the results of SEM

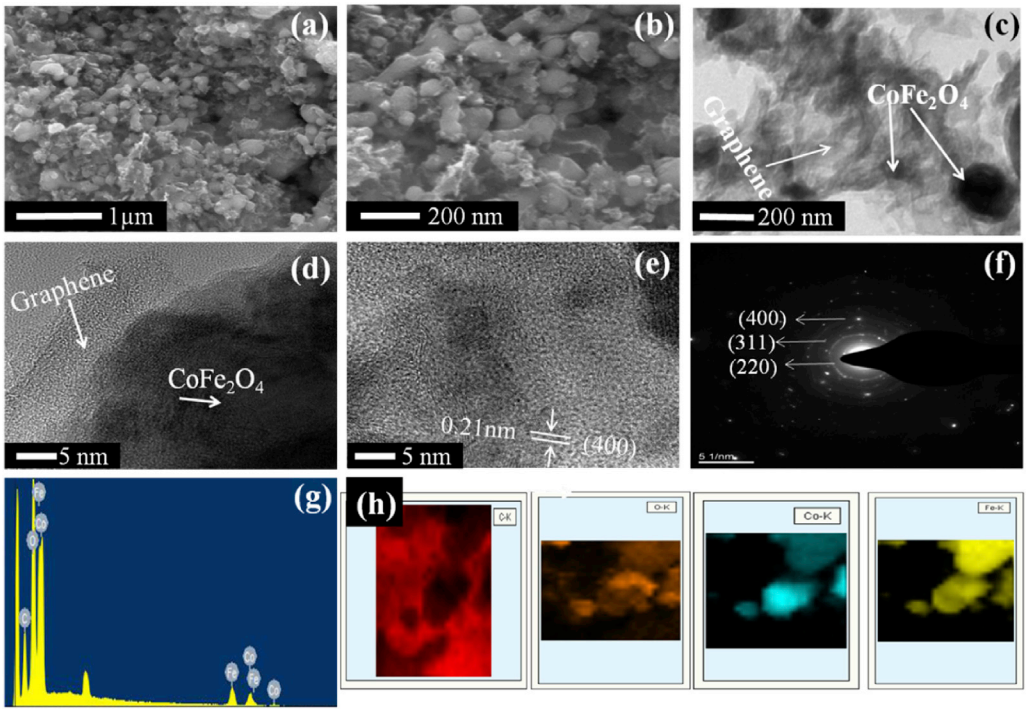

Fig. 1. SEM images of $CoFe_2O_4$/GNS nanocomposites of (a) low and (b) high magnification. (c) TEM images of $CoFe_2O_4$/GNS nanocomposites. (d-e) High-resolution transmission electron microscopy (HRTEM) images of $CoFe_2O_4$/GNS nanocomposites. (f) SAED pattern of $CoFe_2O_4$/GNS nanocomposites. (g) EDS spectrometry of $CoFe_2O_4$/GNS nanocomposites. (h) EDS mapping of $CoFe_2O_4$/GNS nanocomposites.