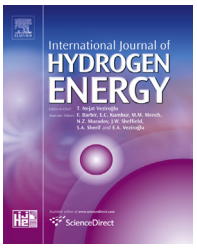
INTERNATIONAL JOURNAL OF HYDROGEN ENERGY XXX (2015) 1–10

Available online at www.sciencedirect.com

ScienceDirect

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



Synthesis of reduced graphene oxide wrapped-copper sulfide hollow spheres as electrode material for supercapacitor

Ke-Jing Huang[*], *Ji-Zong Zhang*, *Yang Liu*, *Yan-Ming Liu*

College of Chemistry and Chemical Engineering, Xinyang Normal University, Xinyang 464000, China

ARTICLE INFO

Article history:
Received 3 April 2015
Received in revised form
21 May 2015
Accepted 22 May 2015
Available online xxx

Keywords:
Copper sulfide hollow sphere
Reduced graphene oxide
Electrode materials
Supercapacitor
Enhanced electrochemical performance

ABSTRACT

Copper sulfide (CuS) is a promising candidate for the electrode material in supercapacitor due to its metal-like electronic conductivity and high theoretical capacity. However, volume change during cycling causes poor cycling stability and improving cycle life is a major research challenge. Herein, we present a strategy by fabricating reduced graphene oxide (rGO)-wrapped CuS hollow spheres using a simple solvothermal route assisted by ethylene glycol to improve the electrochemical performance of CuS in supercapacitors. The as-prepared samples are well characterized by utilizing Scan electron microscope, Transmission electron microscope, powder X-ray diffraction, X-ray photoelectron spectrum and Raman spectra techniques. It is demonstrated that the obtained CuS/rGO composite shows excellent electrochemical performance as electrode material for supercapacitors. The CuS/rGO electrode displays a significantly enhanced specific capacitance of 2317.8 F g^{-1} and an excellent cycling stability of 96.2% retention after 1200 cycles at a current density of 1.0 A g^{-1}. The likely cause is the synergetic effects between the hollow spherical structure and the high conductivity of rGO. More importantly, the present synthesis strategy may be readily extended to the preparation of other composites based on CuS with tailored morphologies and surface textures for potential applications in energy storage and conversion devices.

Copyright © 2015, Hydrogen Energy Publications, LLC. Published by Elsevier Ltd. All rights reserved.

Introduction

Recently, energy problems have undoubtedly become the greatest problems and attracted worldwide attention in the modern society [1]. Electrochemical supercapacitors have been recognized as one type of promising energy storage device owing to their high energy density, extremely long cycle life and fast charging-discharging rates, and have been extensively applied in areas of portable electrons, digital communication, hybrid electronic vehicles and renewable energy systems [2,3]. Generally, supercapacitors have two energy storage mechanisms: fast surface redox reaction (pseudocapacitors) and ion adsorption at the electrode/electrolyte interface (electrochemical double layer capacitors, EDLCs) [4,5]. Thereinto, pseudocapacitors have attracted more attention due to their higher power densities and capacitance [6].

* *Corresponding author*. Tel.: +86 376 6390611.
E-mail address: kejinghuang@163.com (K.-J. Huang).

http://dx.doi.org/10.1016/j.ijhydene.2015.05.152

0360-3199/Copyright © 2015, Hydrogen Energy Publications, LLC. Published by Elsevier Ltd. All rights reserved.

Please cite this article in press as: Huang K-J, et al., Synthesis of reduced graphene oxide wrapped-copper sulfide hollow spheres as electrode material for supercapacitor, International Journal of Hydrogen Energy (2015), http://dx.doi.org/10.1016/j.ijhydene.2015.05.152

RuO_2 and other transition metal oxides have been widely used as electrode material in pseudocapacitors due to their high specific capacitance [7]. However, some defects such as expensive nature of RuO_2 and poor electrical conductivity (10^{-5} to 10^{-6} S cm^{-1}) of MnO_2 have limited their widely application in energy-related fields [8]. Compared with these materials, metal sulfides are abundant and cheap due to the existence of minerals in nature, and most of them are good metallic conductors [9]. Recently, some metal sulfides, such as MoS_2 and CoS, have been investigated as electrode materials for supercapacitors in view of their special structural properties and high theoretical capacities [10,11]. CuS is an important transition metal chalcogenide [12–14]. It has been widely applied as chemical sensors, Li-ion batteries, catalyst, solar cells and so on [15–21]. Several attempts have been made to explore CuS as an electrode material for supercapacitors due to its metal-like electronic conductivity (10^{-3} S cm^{-1}) and high theoretical capacity (561 mAh g^{-1}) [22,23]. However, it is not favorable for applications in supercapacitor because pure CuS is a semiconductor and has relatively low conductivity when compares to carbon nanomaterials and its volume change during cycling causes poor cycling stability. Thus, it is highly desirable to geometrically control over the preparation CuS composites and combine with electronically conductive substance to greatly enhance supercapacitor performance.

In the past decade, carbon materials and their composites are always the fascinating candidates in energy-related fields, such as carbon nanotubes, acetylene black, carbon aerogel and reduced graphene oxide (rGO) [24–26], which is a two-dimensional single-layer sheet of sp^2-hybridized conjugated carbon atoms. Compared with other carbon materials, rGO has more prominent intrinsic physical and chemical properties, including room-temperature electron mobility (2.0×10^5 cm^2 V^{-1} s^{-1}), theoretical specific surface area (2630 m^2 g^{-1}), and high chemical stability [27]. More significantly, the intrinsic capacitance of rGO is recently found to be 21 mF cm^{-2}, which sets the upper limit of EDLCs capacitance for all carbon-based materials and asserts that rGO is an ideal carbon electrode material for EDLCs supercapacitors [28]. However, pure rGO-based electrodes can only reach an EDLCs capacitance of less than 200 F g^{-1} as a result of the strong stacking of rGO sheets [29]. An efficient way to functionalize and tune the properties of assembled rGO is by the combining of the planar rGO structures with other materials [30,31]. Usually, there are two types among the rGO-based composites according to the architectures of the second components, including rGO supported nanocomposites and rGO-wrapped composites.

Hollow micro-/nano-structured materials have been recognized as one type of promising material with numerous applications in energy-related fields [32]. This unique nanostructure provide particular advantages to supercapacitors due to the enhanced surface-to-volume ratio and reduced transport lengths for both mass and charge transport [33,34]. CuS hollow spheres, formed by accumulation of CuS nanosheets, combine the merit of a nanoporous structure with the high surface area of nanosheets, yet their capacitive properties have not been extensively studied. Therefore, combining rGO and CuS hollow spheres into an rGO wrapped hollow structure could be considered as an effective and competitive route to obtain novel composites with outstanding electrochemical performance.

Herein, we synthesize the rGO wrapped hollow CuS sphere composite by *in situ* formation of hollow CuS sphere on the surface of rGO nanosheet under simple one-step solvothermal route assisted by ethylene glycol. The synthesis of rGO-wrapped hollow CuS sphere is a newly-developed method, which is more facile to design microstructure materials without sacrificing the contact between rGO and the CuS sphere. The idea of creating such a structure not only cushions the internal stress induced during the volume change, but also makes the composite more conductive. The structure, morphology and chemical composition of CuS-rGO are investigated. Moreover, the electrochemical tests indicate that the composite shows a positive synergistic effect between rGO and hollow CuS sphere, resulting in good pseudocapacitive behavior in terms of high specific capacitance, excellent rate capability and good cycle stability. The advantages combining easy process and excellent electrochemical property suggest great potential application of CuS-rGO in supercapacitors.

Experimental

Synthesis of CuS-rGO composites

Graphene oxide (GO) was prepared by oxidizing natural graphite powder based on a modified Hummers method [35]. In a typical process, 5 g graphite was slowly added into a mixture of concentrated H_2SO_4 (87.5 mL) and fuming HNO_3 (45 mL) (warning: concentrated H_2SO_4 and fuming HNO_3 are strongly oxidizing and should be handled with care!). 55 g $KClO_3$ was then added in above mixture, and was kept stirring for 96 h. Then the slurry was poured into water and filtered to obtain graphite oxide. After dried at 80 °C, 0.5 g graphite oxide was exfoliated in 500 mL water with ultrasonic treatment to form a colloidal GO suspension (1 mg mL^{-1}). To get rGO, chemical reduction of the suspension of GO was carried out with hydrazine monohydrate for 24 h at 80 °C. The final product was isolated by filtration, and rinsed thoroughly with pure water and ethanol. Then the product was dried in vacuum and rGO was obtained.

The rGO wrapped CuS hollow spheres were synthesized by a one-step solvothermal reaction using $Cu(NO_3)\cdot 3H_2O$, thiourea, and rGO as starting materials. In a typical synthesis, 0.243 g of $Cu(NO_3)\cdot 3H_2O$ was first dissolved in 30 mL ethylene glycol with continue stirring until the formation of uniform solution. Subsequently, 0.152 g thiourea was added to above solution and stirred for 30 min. 9.6 mg rGO was then added and mixed under stirring for 60 min. The obtained mixture was transferred into a 100 mL Teflon-lined stainless steel autoclave and sealed tightly, heated at 180 °C for 24 h and then cooled to room temperature naturally. The black precipitate was collected by centrifugation, washed thoroughly with deionized water, ethanol for several times, and dried at 60 °C in a vacuum oven for 24 h. For comparison, CuS hollow spheres were synthesized without rGO via the same route. The procedure for CuS-rGO composites preparation is illustrated in Fig. 1.

Please cite this article in press as: Huang K-J, et al., Synthesis of reduced graphene oxide wrapped-copper sulfide hollow spheres as electrode material for supercapacitor, International Journal of Hydrogen Energy (2015), http://dx.doi.org/10.1016/j.ijhydene.2015.05.152

Download English Version:

https://daneshyari.com/en/article/7714819

Download Persian Version:

https://daneshyari.com/article/7714819

Daneshyari.com