Ceramics International 42 (2016) 9858–9865

Contents lists available at ScienceDirect

Ceramics International

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

Enhanced rate capability of nanostructured three-dimensional graphene/Ni_3S_2 composite for supercapacitor electrode

Mingxing Wang [a], Yongzhen Wang [a], Huanglin Dou [a], Guoqiang Wei [b], Xiaomin Wang [a,*]

[a] Department of Materials Science and Engineering, Taiyuan University of Technology, 030024, PR China
[b] Laboratory of Green Energy Materials and Storage Systems, Taiyuan University of Technology, 030024, PR China

ARTICLE INFO

Article history:
Received 27 January 2016
Received in revised form
9 March 2016
Accepted 10 March 2016
Available online 11 March 2016

Keywords:
B. Microstructure
B. Nanocomposites
E. Capacitors
Three-dimensional graphene

ABSTRACT

Three-dimensional graphene/Ni_3S_2 (3DG/Ni_3S_2) composite electrodes were produced by a facile two-step synthesis route involving chemical vapor deposition (CVD) growth of graphene foam and in situ hydrothermal synthesis of Ni_3S_2. The porous structure of the prepared 3DG is ideal for use as a scaffold for fabricating monolithic composite electrodes. The relative content of Ni_3S_2 initially increased and then decreased with increasing hydrothermal reaction time. The basal surface of the electrode was completely covered after 6 h of hydrothermal reaction. The size of the Ni_3S_2 microspheres also increased with increasing hydrothermal reaction time. The composite electrodes exhibited good specific capacitance (11.529 F cm^{-2} at 2 mA cm^{-2}, i.e., 2611.9 F g^{-1} at 5 mV s^{-1}) and cyclability (retention of 88.97% capacitance after 1000 charge/discharge cycles at 20 mA cm^{-2}). These results are attributed to the fact that the uniform distribution of the Ni_3S_2 microspheres increased the specific surface area of the electrode and facilitated electron transfer and ion diffusion. The 3D multiplexed and highly conductive pathways provided by the defect-free graphene foam also ensured rapid charge transfer and conduction to improve the rate capability of the supercapacitors.

1. Introduction

Three-dimensional graphene (3DG) can easily overcome the strong π–π interactions and contact resistance between the graphene sheet, which exhibited high conductivity and specific surface area due to its three-dimensional structure without defects [1,2]. 3DG has recently gained increased attention as a new composite electrode material for supercapacitors. Dong et al. [3] prepared Co_3O_4 nanotube arrays supported on 3DG to achieve a high-performance supercapacitor composite electrode exhibiting a maximum specific capacitance of 1100 F g^{-1} at a current density of 10 A g^{-1} and good cyclability with a stable capacitance after 1000 charge/discharge cycles. These properties result from the excellent mechanical strength, electrical conductivity, and multiplex structure features of 3DG, all of which decrease the electrode quality and increase electron transfer rates. Wang et al. [4] synthesized a 3DG/NiO composite electrode after preparing 3DG by the CVD method; this electrode manifested interesting supercapacitive properties of 1225 F g^{-1} at 2 A g^{-1} and about 68% of its initial capacitance was maintained at 100 A g^{-1}. Such properties are attributed to the 3D open structure of the electrode and the good electrical conductivity of 3DG. Sulfide was grown on 3DG and a specific capacitance of 9.2 F cm^{-2} at 100 mA cm^{-2} was achieved by Nguyen et al. [5]. This performance can be explained by the high electrical conductivity and natural mesoporous structure of 3DG enhancing the electron transfer rate, ion transport speed, and structural stability of the composite electrode. 3DG is an ideal scaffold with excellent properties for fabricating monolithic composite electrodes, which have been widely investigated worldwide.

Among the multitudinous available pseudocapacitive materials, nanostructured metal sulfides(eg., NiSx, CuSx and CoSx) have been subject to intense research in recent years, due to their excellent intrinsic properties and good electrochemical performance [6–8]. Nickel sulfides constitute an important class of metal sulfides and form many different phases, such as NiS, Ni_3S_2, NiS_2, Ni_3S_4, Ni_7S_6, Ni_9S_8, these materials have been extensively investigated in recent decades because of their versatile applications in supercapacitors, hydrogenation catalysts, dye-sensitized solar cells, and lithium ion batteries [9,10]. Ni_3S_2, one of the most important phases of nickel sulfide, is of great interest as it offers various advantages, such as high theoretical capacity, excellent rate performance, and good conductivity [11,12]. These properties are expected to meet the increasing requirements of energy storage systems. Ni_3S_2 is abundant and inexpensive since it exists in nature as minerals such as hazelwoodite. Huo et al. [13] fabricated Ni_3S_2

* Corresponding author.
E-mail address: wangxiaomin@tyut.edu.cn (X. Wang).

http://dx.doi.org/10.1016/j.ceramint.2016.03.085
0272-8842/

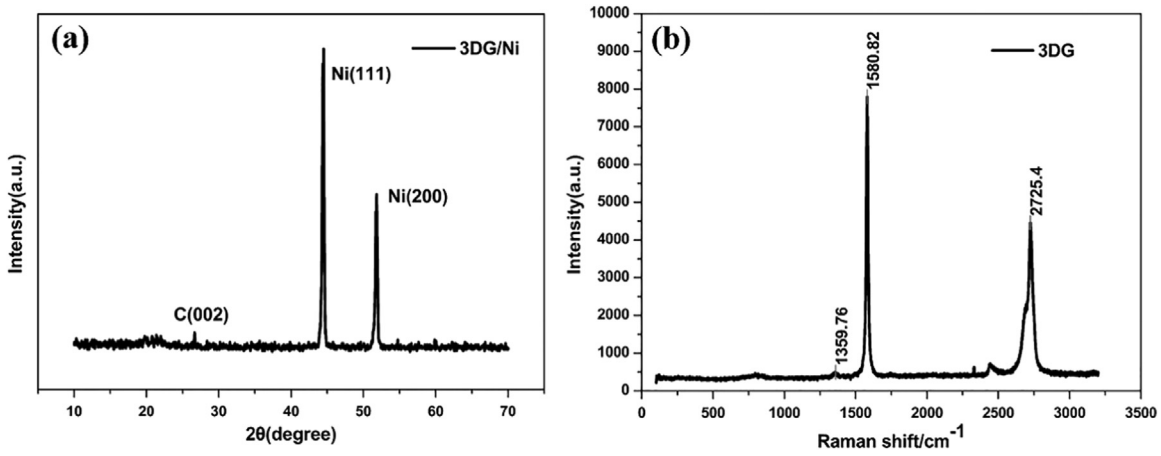

Fig. 1. (a) XRD patterns of the prepared 3DG/Ni. (b) Raman spectra of the prepared 3DG.

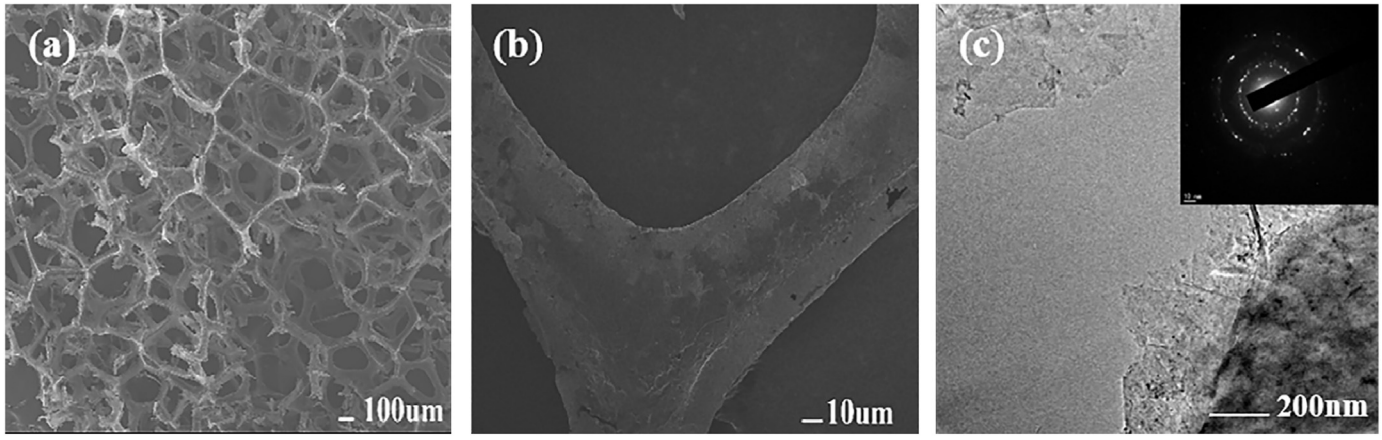

Fig. 2. (a, b) SEM images of 3DG; (c) HRTEM image of 3DG. Inset: SAED pattern.

nanoparticles on Ni foam and obtained products with a specific capacitance of 1370 F g^{-1} at a current density of 2 A g^{-1}; these products maintained 69.48% specific capacitance at 20 A g^{-1}. Dai et al. [14] formed Ni_3S_2 on multiwalled carbon nanotubes as an electrode with a specific capacitance of 1024 F g^{-1} at 0.8 A g^{-1}; however, this electrode maintained only 46.88% its original specific capacitance at 25.6 A/g. Zhang et al. [15] successfully synthesized porous Ni_3S_2-reduced graphene oxide composites directly supported on NF using *Bacillus subtilis* as spacers. This electrode showed a relatively high specific capacitance of 1424 F g^{-1} at 0.75 A g^{-1}, and maintained a specific capacitance of 67.5% when the current density was increased to 15 A g^{-1}. Lin et al. [16] successfully synthesized micro globular Ni_3S_2 on 3D redox graphene; the materials obtained maintained 74% specific capacitance after 1000 cycles and 49.17% specific capacitance after the charge/discharge current density was amplified 16 times. Zhou et al. [17] prepared Ni_3S_2/3DG grown on NF through a one-step hydrothermal reaction; the product of this reaction exhibited a high capacitance of 1037.5 F g^{-1} at 5.1 A g^{-1}. Unfortunately, only 38% of its original capacitance was retained as the current density increased from 5.1 A g^{-1} to 19.8 A g^{-1}. Overall, the specific capacitance of Ni_3S_2/3DG was unsatisfactory even at low mass loadings because the experimentally determined specific capacitance was much lower than the theoretical value of 2412 F g^{-1}, and the cycling performance of the material required further improvement. Therefore, studies to explore effect of crystal morphology on the capacitance performance of active materials with different shapes are highly necessary.

To prepare composite electrodes with high energy density, ratio capability, and long cycle performance and investigate the effect of the crystal morphology of active material on its capacitance, Ni_3S_2 microsphere arrays were grown on 3DG through a facile one-step hydrothermal approach and then directly applied as the electrode of a high-performance supercapacitor. The crystal structure, morphology, composition, and electrochemical performance of the 3DG and composite electrode were characterized. The effect of crystal morphology on the capacitance of the electrode were also evaluated.

2. Experimental

2.1. Preparation of 3DG/ni

3DG was prepared by the CVD method [1]. Ni foam (130 PPI, mass density of ~30 mg cm^{-2}) was placed in the middle of a quartz tube and heated to 1000 °C at a heating rate of 50 °C min^{-1} under H_2/Ar flow (H_2/Ar=500:200 sccm) and atmospheric pressure. The material was annealed at 1000 °C for 10 min to remove the remaining impurities and thin native oxide layer. The 3DG was synthesized on top of the Ni foam under flowing CH_4 gas (7 sccm) for 10 min and then quickly cooled down to room temperature under H_2/Ar flow.

2.2. Preparation of 3DG/Ni_3S_2 composite electrode

3DG/Ni_3S_2 heterostructures were prepared using a simple one-step hydrothermal process [17]. In a typical experiment, a piece of