Electrochimica Acta 245 (2017) 51–58

Contents lists available at ScienceDirect

Electrochimica Acta

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

Hierarchical Nickel Sulfide Coated Halloysite Nanotubes For Efficient Energy Storage

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ARTICLE INFO

Article history:
Received 8 February 2017
Received in revised form 11 May 2017
Accepted 21 May 2017
Available online 22 May 2017

Keywords:
Halloysite nanotube
nickel sulfide
sulfhydrylation
supercapacitor
energy storage

ABSTRACT

Cost-effective and robust energy storage systems have attracted great attention for portable electronic devices. Three-dimensional electrodes can effectively enhance the charge transfer, increase the mechanical stability and thus improve the electrochemical performance upon continuous charge-discharge. The earth abundant halloysite nanotubes (HNTs) have shown immense potential in constructing nanoarchitectural composites. Here, we first demonstrate the development of hybrid composite of nickel sulfide (Ni_3S_2) and HNTs with glucose as binders for efficient energy storage in supercapacitor. The surface sulfhydrylation of HNTs and glucose-assisted hydrothermal reaction are crucial for the preparation of well-structured composite. Due to the synergistic effect between components, the Ni_3S_2/HNTs@HS composite electrode delivers a capacity of 450.4C g^{-1} and high retention of 82.6% over 2000 cycles in three-electrode supercapacitors. Moreover, the Ni_3S_2/HNTs@HS// Whatman paper//Ni_3S_2/HNTs@HS two-electrode symmetric supercapacitor exhibits a maximum potential window of 1.3 V, with a capacity of 250C g^{-1} and performance loss of only 18.2% over 2000 cycling at 1 A g^{-1}. A maximum energy density of 79.6 Wh kg^{-1} is achieved at a power density of 1.03 kW kg^{-1}. Such excellent energy storage performance suggests the great potential of Ni_3S_2/HNTs@HS for high-efficiency energy storage systems.

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1. Introduction

Electrochemical capacitor (supercapacitor, SCs) has attracted tremendous interest for energy conversion/storage devices, thanks to its rapid power delivery, long cycling life (>100 times battery life), high power density and low maintenance cost when compared with traditional capacitors and batteries [1,2]. Varied in charge storage mechanism, supercapacitors can store energy via either ion adsorption (electrochemical double layer capacitors, EDLCs) or fast faradic charge transfer (pseudo-capacitors) [3,4]. Great progress has been made by strengthening the understanding of storage mechanisms and development of advanced nanostructured materials for the electrodes [5–7]. Featuring high specific surface area, carbon-based EDLCs boast large gravimetric capacitance [8–10]. But the charge is confined to the surface which leads to rather lower energy density than that of batteries. As candidates to carbon-based EDLCs, pseudocapacitive materials (RuO_2, MnO_2, to name a few) could supplement the electrochemical performance in terms of energy density without sacrificing the power density and cycle life. In this regards, a library of metal oxides [11–14] and their chalcogenide analogues [15,16] actuating the electrochemical process via reversible faradaic redox reactions have been established for high power density and energy density than the EDLCs despite of their apparent battery-like energy storage behaviors.

The properties and the nanostructures of electrode materials are crucial for the performance of supercapacitors. It has been well established that electrodes with well-defined nanostructured materials can not only enhance the power density but the cycling stability of devices. And the electrode kinetics and mass transport can be promoted by reducing charge transport length and ion diffusion distance [7]. To reduce electron transport length, high-performance supercapacitors are commonly fabricated using nanostructured electrodes, where thin layers of redox-active materials with certain porosity are employed. Such electrodes are advantageous to afford enhanced ion and electron transport, increased material loading per unit substrate area, and improved mechanical stability upon repeated charge–discharge [7]. Therefore, the current big challenge for high-efficiency supercapacitors

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http://dx.doi.org/10.1016/j.electacta.2017.05.140
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remains to cost-effectively prepare structurally-defined nanomaterials with facile preparation, excellent electrochemical activity and high operation stability. Rich in valence state and nanostructure, battery-type nickel sulfides with various structural architecture have been widely investigated as electrode materials for promising applications in lithium-ion batteries (e.g. Ni_3S_4 nanoparticles, Ni_3S_2 nanowire and nanoflakes) [17–19], oxygen reduction reaction (e.g. Ni_3S_2 nanorods) [20] and electrochemical

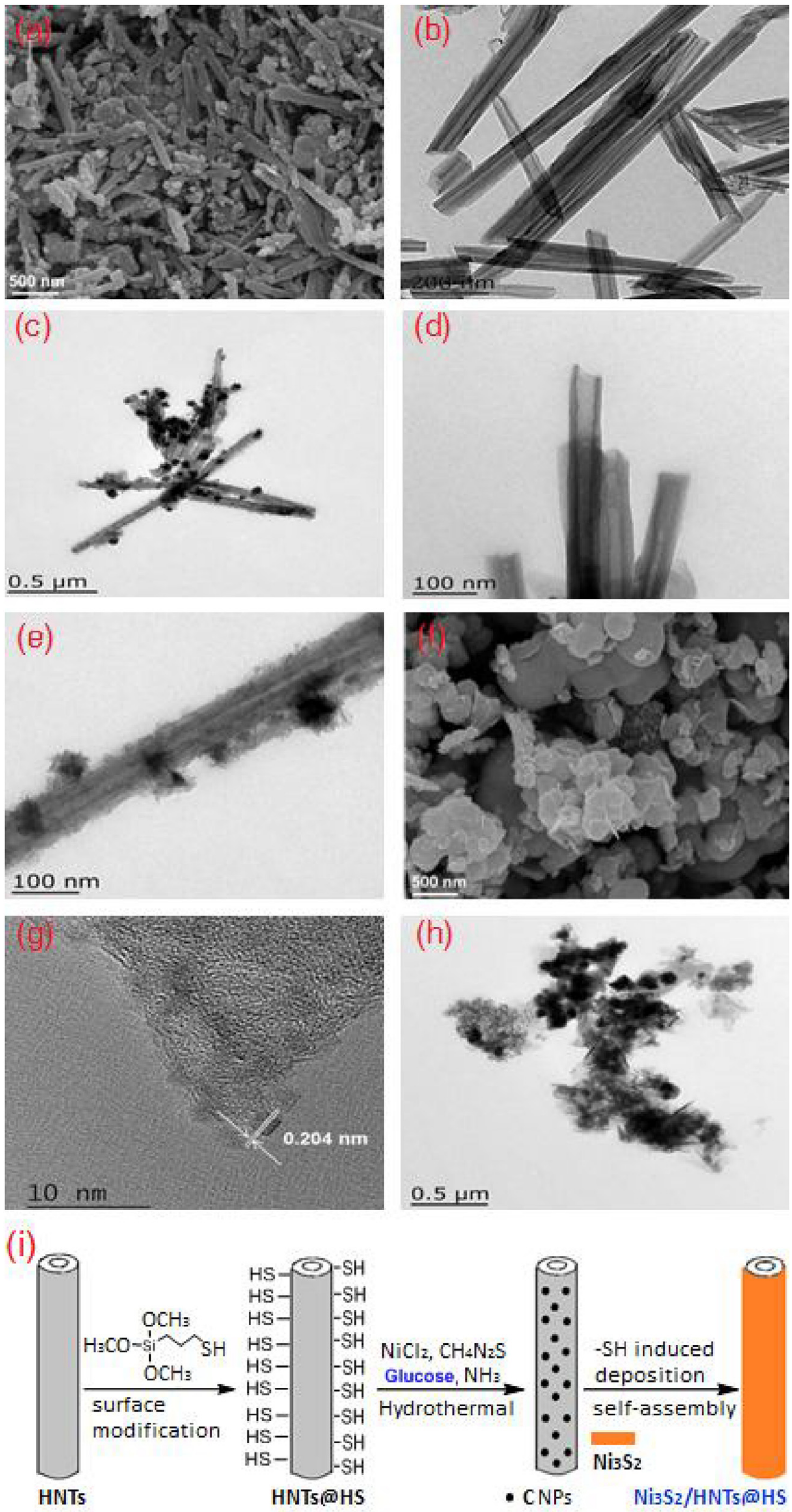

Fig. 1. (a) SEM image and (c) TEM image of Ni_3S_2/HNTs@HS; (b) TEM images of HNTs and (d) HNTs@HS; (e) TEM image and (g) HRTEM image of single Ni_3S_2/HNTs@HS nanotube; (f) SEM image and (h) TEM image of pristine Ni_3S_2; (i) Schematic illustration of glucose-assisted preparation of Ni_3S_2/HNTs@HS composites.

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