



Synthesis of copper sulfide nanowire arrays for high-performance supercapacitors



Yu-Kuei Hsu^{a,*}, Ying-Chu Chen^b, Yan-Gu Lin^{c,*}

^a Department of Opto-Electronic Engineering, National Dong Hwa University, Hualien, 97401, Taiwan

^b Karlsruhe Institute of Technology (KIT), Institut für Anorganische Chemie, Engesserstraße 15, D-76131 Karlsruhe, Germany

^c National Synchrotron Radiation Research Center, Hsinchu 30076, Taiwan

ARTICLE INFO

Article history:

Received 23 April 2014

Received in revised form 7 June 2014

Accepted 21 June 2014

Available online 11 July 2014

Keywords:

Copper sulfide

Nanowires

Chemical synthesis

Electrochemical

Supercapacitor

ABSTRACT

A copper sulfide (CuS) nanowire (NW) array with a hierarchical nanoarchitecture is directly fabricated on copper foil using a simple and cost-effective liquid-solid reaction. The morphology and microstructure of CuS NW arrays are systematically investigated by scanning electron microscopy, X-ray diffraction spectroscopy, Raman spectroscopy, and X-ray photoelectron spectroscopy. Electrochemical results obtained at various polarization cut-offs and scan rates reveal that the CuS NW array shows highly reversible features and favorable rate abilities. Most importantly, the excellent specific capacitance that is achieved in CuS NW nanoelectrodes is as high as 305 F g^{-1} , which is one of the high value reported CuS-based pseudocapacitors. An energy density of 70.8 Wh kg^{-1} is obtained at a current density of 2 mA cm^{-2} . The CuS NW nanoelectrode has superior cycling stability with 87% retention of initial specific capacitance after 5000 cycles.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

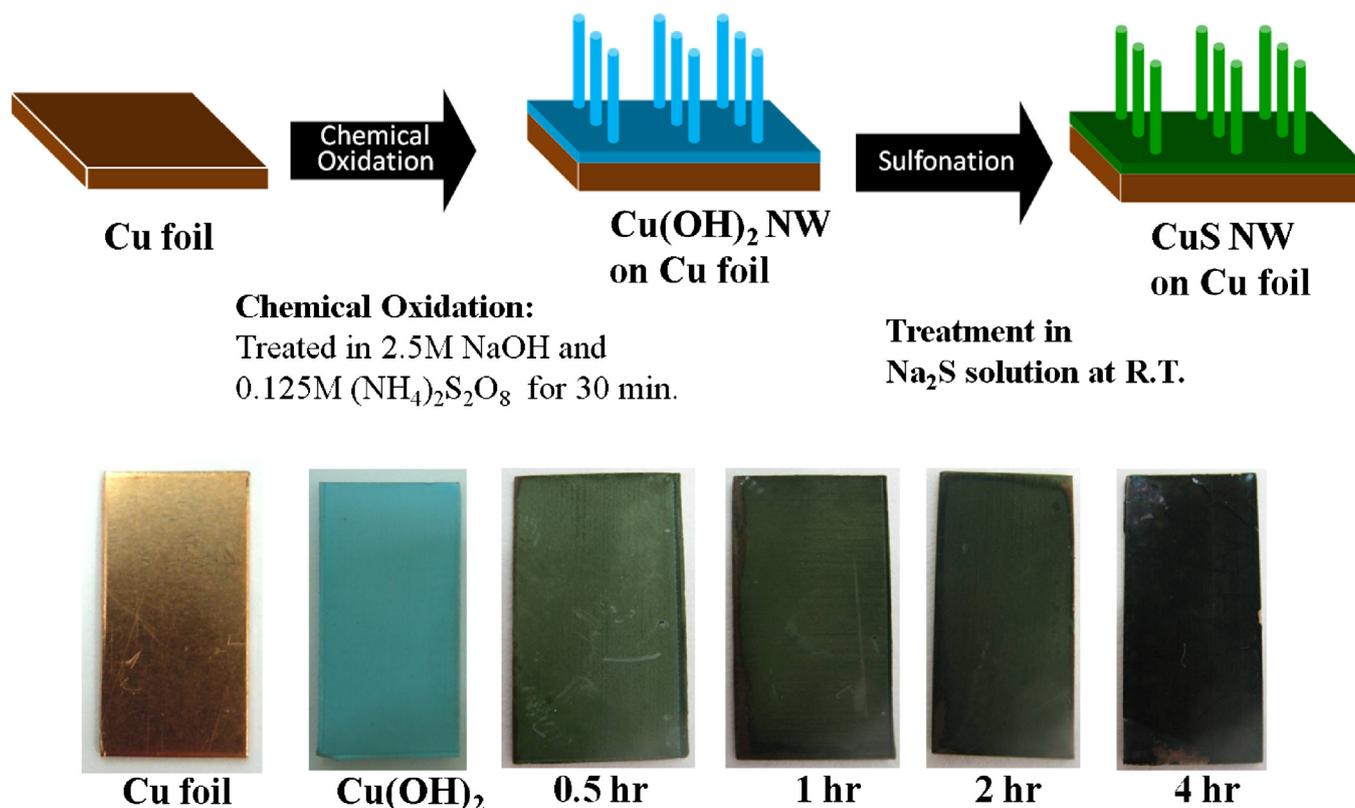
To satisfy the urgent need for sustainable and renewable power sources in the modern electronics industry, substantial efforts has been made to develop advanced energy storage devices. Electrochemical capacitors (ECs), also called supercapacitors, are attracting particular attention owing to their high power density, rapid charging/discharging rate, and long cycle life. ECs are divided into two types, depending on their underlying energy storage mechanism- electrical double-layer capacitors (EDLCs) and pseudocapacitors [1–3]. Whereas EDLCs store electrical energy by the electrostatic accumulation of charges in an electric double-layer close electrode/electrolyte interfaces, pseudocapacitors exploit reversible Faradaic reactions that occur at the electrode surface, and so have a much higher specific capacitance. Transition metal oxides and their hydroxides are being extensively explored for use in high-performance pseudocapacitors because of their low cost, low toxicity, and great flexibility of structure and morphology. Recent research results have also established that some metal sulfides can be used as potentially active materials for pseudocapacitor applications [4–9]. The existence of two or more valance states of

metal constituents in sulfides and the high theoretical capacity of sulfur and sulfur compounds improve capacitive behavior.

Among metal sulfide compounds, CuS is an important multifunctional semiconductor material with great potential applications in gas sensors, lithium ion batteries, and solar energy devices [10–12]. For instance, various attempts have been made to study the use of CuS as a cathode material in rechargeable batteries, which yields comparable rechargeability for up to 1000 cycles [13,14]. CuS has been used as a counter electrode in photoelectrochemical cells owing to its promising redox reaction with polysulfide electrolyte [15,16]. However, to the best of our knowledge, investigations of the application of CuS in ECs are few. Zhu *et al.* utilized the template-engaged chemical conversion route to prepare CuS nanoneedles on carbon nanotube as electrode, which exhibited a specific capacitance of 122 F g^{-1} in KOH electrolyte [9]. More recently, Raj *et al.* formed CuS nanoplatelets as an electrode with a specific capacitance of 73 F g^{-1} using chemical bath deposition [17]. To date, only relatively low capacitance has been observed in CuS systems, owing to the low surface area of the CuS electrode and the poor interfacial kinetics for charge-transfer at the liquid/solid interface. Hence, developing new approaches to forming CuS-based supercapacitors with particular characteristics, high surface area and efficient interfacial kinetics is very desirable. For CuS-based ECs to be used at a scale that is commensurate with the global energy demand, a method for fabricating nanostructured CuS simply and cost-effectively is required. This work

* Corresponding author.

E-mail addresses: ykhsu@mail.ndhu.edu.tw (Y.-K. Hsu), lin.yg@nsrrc.org.tw (Y.-G. Lin).



Scheme 1. Schematic diagram of synthesis of CuS NWs on copper foil.

demonstrates an easy and reliable procedure for synthesizing 1-D CuS nanowire (NW) arrays on copper foil at room temperature without using additives or binders. The electrochemical performance of directly grown CuS-NW arrays in ECs was systematically evaluated. Microstructural characterization, elemental analysis, and electrochemical impedance spectroscopy (EIS) of the CuS-NW electrodes were performed to elucidate the relationship between improved capacitive performance and the surface electrochemistry of the CuS NWs.

2. Experimental

CuS NW arrays on copper foil were synthesized using a simple wet-chemical process, shown as in [Scheme 1](#). The first step was the formation of $\text{Cu}(\text{OH})_2$ NWs via a liquid-solid reaction without any template [18,19]. A reaction solution was prepared in a 100 mL glass bottle; 2.5 mol L⁻¹ NaOH and 0.125 mol L⁻¹ $(\text{NH}_4)_2\text{S}_2\text{O}_8$ solutions with a total volume of 50 mL were mixed. A piece of copper foil ($10 \times 20 \times 2$ mm³), which had been ultrasonically cleaned in acetone and subsequently in DI water, was immersed in the solution. A few minutes later, a faint blue color appeared on the surface of the copper foil, and the initially colorless solution became increasingly blue. In 10 min, a light-blue film covered the copper foil surface. The copper foil was extracted from the solution, rinsed with water and ethanol, and dried in air. The subsequent step was sulfonation, which involved immersing the light-blue sample into aqueous 5 mM Na_2S solution for different reaction times. Following sulfonation, the sample was extracted from the solution, rinsed with water, and dried in air. The hierarchical electrode was prepared by bonding a copper wire onto the edge of approximately 1×1 cm². The bonding was carried out using silver paste, with curing for 20 min at 80 °C. The bonding pad was covered with epoxide to expose only the cupric oxide surface to the test solutions.

The morphologies of the hierarchical CuS NW arrays were investigated by scanning electron microscopy (SEM, JEM-4000EX), and the structure of the samples were analyzed using an X-ray diffractometer (XRD, Bruker D8 Advance diffractometer) with Cu K α radiation ($\lambda=0.1506$ nm). TEM images were analyzed using a JEOL JEM-2100 TEM system. X-ray absorption spectroscopy (XAS) analyses were performed on a beamline 16A in NSRRC. The chemical states of the elements were determined by X-ray photoelectron spectroscopy (XPS, Perkin-Elmer model PHI 1600). Raman spectra were measured using a LabRAM HR 550 system that was equipped with a HeNe laser (632.8 nm, 5 mW) and a 50 \times objective. To evaluate the electrochemical performance of CuS NW arrays, cyclic voltammetry (CV) and a galvanostatic charge/discharge method were employed with a CHI 627D potentiostat/galvanostat. All electrochemical measurements were made in 1 M NaOH electrolyte solution. A conventional three-electrode system that consisted of the hierarchical CuS NW array as the working electrode, a square platinum sheet as the auxiliary electrode, and an Ag/AgCl reference electrode in 3 M KCl solution was implemented. All potentials reported in this article were regarding Ag/AgCl (3 M KCl, 0.207 V vs. SHE). The amount of CuS NWs loaded on the copper foil electrode was determined using a microbalance with an accuracy of 10 μg (Sartorius BP 211D, Germany). The loading of the active materials was found to be around 0.3 mg.

3. Results and discussion

3.1. Structural and compositional characterizations

[Fig. 1a](#) shows the surface morphologies of $\text{Cu}(\text{OH})_2$ NW arrays that were synthesized with a reaction time of 10 min. The dense and straight NW structures uniformly and compactly cover a large area of the copper substrate; the NWs have a length of over 8 μm and a diameter of 70–120 nm. The as-grown $\text{Cu}(\text{OH})_2$ NW samples

Download English Version:

<https://daneshyari.com/en/article/185373>

Download Persian Version:

<https://daneshyari.com/article/185373>

[Daneshyari.com](https://daneshyari.com)