



Full Length Article

Achieving copper sulfide leaf like nanostructure electrode for high performance supercapacitor and quantum-dot sensitized solar cells

Ikkurthi Kanaka Durga, S. Srinivasa Rao, Araveeti Eswar Reddy, Chandu V.V.M. Gopi, Hee-Je Kim*

School of Electrical Engineering, Pusan National University, Busandaehak-ro 63beon-gil, Geumjeong-gu, Busan, 46241, Republic of Korea



ARTICLE INFO

Article history:

Received 10 August 2017

Received in revised form

17 November 2017

Accepted 20 November 2017

Available online 22 November 2017

Keywords:

Supercapacitors

Quantum-dot sensitized solar cells

Counter electrode

Nickel foam

Excellent specific capacitance

ABSTRACT

Copper sulfide is an important multifunctional semiconductor that has attracted considerable attention owing to its outstanding properties and multiple applications, such as energy storage and electrochemical energy conversion. This paper describes a cost-effective and simple low-temperature solution approach to the preparation of copper sulfide for supercapacitors (SCs) and quantum-dot sensitized solar cells (QDSSCs). X-ray diffraction, X-ray photoelectron spectroscopy, and transmission electron microscopy confirmed that the nickel foam with a coriander leaf like nanostructure had been coated successfully with copper sulfide. As an electrode material for SCs, the CC-3 h showed excellent specific capacitance (5029.28 at 4 A g^{-1}), energy density ($169.73 \text{ Wh kg}^{-1}$), and superior cycling durability with 107% retention after 2000 cycles. Interestingly, the QDSSCs equipped with CC-2 h and CC-3 h counter electrodes (CEs) exhibited a maximum power conversion efficiency of 2.52% and 3.48%, respectively. The improved performance of the CC-3 h electrode was attributed mainly to the large surface area (which could contribute sufficient electroactive species), good conductivity, and high electrocatalytic activity. Overall, this work delivers novel insights into the use of copper sulfide and offers an important guidelines for the fabrication of next level energy storage and conversion devices.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

The worsening energy crisis and global warming issues call for the development of renewable energy conversion systems. As one type of power source, supercapacitors can deliver high power density, superior safety, long cycle life, rapid charge/discharge rates compared to batteries, and higher energy density than conventional capacitors [1–3]. The electrode material is the most significant component of energy storage and conversion technologies, and supercapacitors (SCs) and quantum-dot sensitized solar cells (QDSSCs) have attracted consideration interest [4]. Three major types of electrode material have been investigated for supercapacitors: carbon materials, metal oxides/hydroxides, and electronically conducting polymers [5–7]. In addition to these widely-used electrode materials, transition metal oxides (TMOs) have been investigated widely and RuO_2 is recognized as the best electrode material owing to its high specific capacitance. On the other hand, the electrical conductivity of many TMOs is very low

(e.g., 10^{-5} – $10^{-6} \text{ S cm}^{-1}$ for MnO_2), leading to a deviation of the specific capacitance from the theoretical values [8,9]. The synthesis of transition metal nitrides is a difficult and time consuming process due to the formation of $\text{N}\equiv\text{N}$ bonds. In addition, these materials are sensitive to humid atmospheres and are unstable in air [10].

Recently, transition metal chalcogenides (TMCs) have attracted considerable attention in the supercapacitor field because of their high theoretical capacities, natural abundance, and low-cost due to the existence of minerals in nature [11]. Chalcogenides, such as ZnS , NiS and CoS nanoparticles, have been assessed as new type of energy storage material in supercapacitors, whereas SnS_2 and Bi_2S_3 are used in lithium-ion batteries [12–16]. As a typical example of TMCs, copper sulfide is a p-type semiconductor that is used widely in solar cells, photocatalysts, and as a cathode material in lithium ion batteries with charge/discharge stability for up to 1000 cycles owing to its metal like electronic conductivity of $10^{-3} \text{ S cm}^{-1}$, high theoretical capacity of 561 mA hg^{-1} , valence states, and complex structures [17]. Moreover, copper sulfide is an important multifunctional semiconductor with low toxicity that can be used in biosensors, gas sensors, superionic materials, catalysts, and as a counter electrode in photoelectrochemical cells

* Corresponding author.

E-mail address: heeje@pusan.ac.kr (H.-J. Kim).

owing to its promising redox reactions with the polysulfide electrolyte [18].

Chen et al. prepared Li/Copper sulfide coin cells using an electrodeposition method and as an electrode in supercapacitors and observed 350 mA h g^{-1} with capacity retention of 54.4% after 20 cycles [19]. Ting Zhu et al. used an efficient template-engaged chemical conversion route to prepare CNT@Copper sulfide as an electrode, which had a specific capacitance of 122 F g^{-1} in a KOH electrolyte with excellent cycling stability [20]. Jing et al. prepared copper sulfide microspheres from a Cu-based ionic liquid precursors and observed 237 F g^{-1} at 0.5 A g^{-1} with good rate capability [11]. These reports showed low capacitance using copper sulfide systems owing to their poor interfacial kinetics for charge-transfer at the interface and low surface area. Therefore, the development of new approaches to forming copper sulfide-based supercapacitors with higher areal capacitances, high rate capabilities with large surface areas, high energy density, and efficient interfacial kinetics is desirable.

Extensive studies have focused on the synthesis of copper sulfide materials with various architectures (hierarchical ball-flowers, shuttle-like bundles, nanorods, cubes, wires, wool-ball-like microflowers, nanoparticles, and nanoplates) using a range of synthesis routes (sputtering, thermal evaporation, chemical bath deposition (CBD), hydrothermal, electrodeposition, and spin coating) to improve their applications [11]. Many researchers concentrated on enhancing the specific capacitance of copper sulfide electrodes by 3D hierarchical architectures. On the other hand, these techniques require either extremely high temperatures or template-assisted pathways, which increase the reaction complexity with energy consumption.

Recently, room temperature ionic liquids (ILs), which are organic salts that are liquid below 100°C , have been considered as a new type of green alternative solvent owing to their unique chemical and physical properties [21]. As a form of supermolecular fluid, ILs are non-volatile, non-flammable, and recyclable. These ILs can have excellent capacity to self-assemble a range of nanostructures because of the presence of a huge number of non-covalent interactions, π - π stacking, and hydrogen bonding [21,22]. Owing to the numerous advantages of ILs, many studies have developed copper sulfide electrodes in supercapacitors using 1-butyl-3-methylimidazolium tetrafluoroborate ($[\text{B}_{\text{mim}}]\text{BF}_4$), and $[\text{C}_{8\text{mim}}]\text{BF}_4$. On the other hand, these methods used a toxic solvent, CHCl_3 , and the resulting materials were non-uniform with large quantities of copper sulfide microcrystallinities generated [23]. Many studies have assessed copper sulfide and their composites as electrode materials in both SCs and QDSSCs.

Considering all these issues combined, in this study, thin semiconductor films were deposited on substrates using a simple CBD method that is cost effective and convenient, and can be applied easily on an industrial scale. The effects of the deposition time and the temperature of copper sulfide electrodes and their electrochemical properties have been studied extensively by electrochemical impedance spectroscopy (EIS), cyclic voltammetry (CV), and galvanostatic charge-discharge tests in a 2 M KOH solution. As expected, the copper sulfide electrode exhibited a high specific capacitance of 5029.28 F g^{-1} at 4 A g^{-1} , energy density of $169.73 \text{ Wh kg}^{-1}$ at a power density of 1000 W kg^{-1} , approximately 107% capacity retention after 2000 cycles, signifying the prospective applications of copper sulfide as a superior and long-term performance electrode material for supercapacitor applications. For the power conversion efficiency measurements in QDSSCs, a sandwich structure with a photoanode and a CE were fabricated, and their values were measured using photocurrent-voltage (J-V) measurements.

2. Experimental section

2.1. Materials

All reagents were of analytical grade and used without further purification. Copper sulfate (CuSO_4), urea ($\text{CH}_4\text{N}_2\text{O}$), sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$), and potassium hydroxide (KOH) were purchased from Sigma-Aldrich.

2.2. Preparation of copper sulfide electrode

In a typical synthesis process, 0.1 M of CuSO_4 , 0.4 M $\text{CH}_4\text{N}_2\text{O}$, and 0.4 M $\text{Na}_2\text{S}_2\text{O}_3$ were dissolved in 50 mL of deionized (DI) water with vigorous stirring to form a clear white solution. After stirring for 30 min at room temperature, the ultrasonically well-cleaned (nickel foams for supercapacitors and fluorine-doped tin oxide (FTO) for quantum dot-sensitized solar cell applications) substrates were immersed vertically in the obtained solution and kept in a hot air oven maintained at 80°C for 2, 3, and 4 h. The resulting electrodes were washed several times with ethanol and DI water and dried at 60°C overnight in an inert atmosphere. The electrodes were called CC-2 h, CC-3 h, and CC-4 h for 2, 3, and 4 h, respectively, and were used for further characterization.

2.3. Characterization

The phase structures of the copper sulfide-based electrode was analyzed by X-ray diffraction (XRD, D/Max-2400, Rigaku) using a $\text{Cu K}\alpha$ source over the 2θ range of 20 – 80° and operated at 40 kV and 30 mA. X-ray photoelectron spectroscopy (XPS, KBSI, Busan) was performed to examine the chemical states of the elements using Al $\text{K}\alpha$ X-rays at 240 W. Field-emission scanning electron microscopy (FE-SEM) was carried out on a Hitachi, Model: Su-70 to identify their surface morphology with energy dispersive X-ray spectroscopy (EDS) for elemental analysis. The resulting CC-2, CC-3, and CC-4 h electrodes were also characterized further by transmission electron microscopy (TEM, Tecnai G2 F20).

2.4. Electrochemical measurements

All the electrochemical activities of the as-prepared bar leaf-like copper sulfide nanostructures were examined in a classified three-electrode set up in a KOH solution. Ag/AgCl, Pt, and copper sulfide electrodes were used as the reference, counter, and working electrodes, respectively. In this experiment, approximately 10 mg of copper sulfide active material was deposited on a piece of nickel foam ($1 \times 1 \text{ cm}^2$); the actual mass was calculated by weighing. A SP-150 Biologic science instrument was used for CV analyses at various scan rates (5, 15, 25, 35 and 45 mV s^{-1}) between 0.4 to -0.1 V vs. Ag/AgCl. The GCD test was conducted in a stable potential window with different current densities to evaluate the specific capacitance. EIS was conducted using a Biologic potentiostat/galvanostat/EIS analyzer at an AC voltage of 10 mV over the frequency range, 100 kHz–0.1 Hz. The specific capacitance (C_s), energy (E), and power densities (P) of the copper sulfide electrodes were estimated from the GCD curves using the following equations (Eqs. (1)–(3)).

$$C_s = \frac{i \Delta t}{m \Delta V} \quad (1)$$

$$E = \frac{1}{2C_s(\Delta V)^2} \times \frac{1000}{3600} \quad (2)$$

$$P = \frac{E}{t} = \frac{i \Delta V}{2m} \times 1000 \quad (3)$$

Where C_s is the specific capacitance in F g^{-1} ; I is the discharge current in mA or A; Δt is the discharge time difference in seconds;

Download English Version:

<https://daneshyari.com/en/article/7836089>

Download Persian Version:

<https://daneshyari.com/article/7836089>

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