



Carbon dot stabilized copper sulphide nanoparticles decorated graphene oxide hydrogel for high performance asymmetric supercapacitor



Bibekananda De ^a, Tapas Kuila ^b, Nam Hoon Kim ^{a, *}, Joong Hee Lee ^{a, c, *}

^a Advanced Materials Institute for BIN Convergence Technology (BK21 Plus Global), Department of BIN Convergence Technology, Chonbuk National University, Jeonju, Jeonbuk, 54896, Republic of Korea

^b Surface Engineering & Tribology Division, Council of Scientific and Industrial Research-Central Mechanical Engineering Research Institute, Durgapur, 713209, India

^c Carbon Composite Research Centre, Department of Polymer-Nano Science and Technology, Chonbuk National University, Jeonju, Jeonbuk, 54896, Republic of Korea

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ABSTRACT

A three-dimensional (3-D) porous structure was designed based on carbon dot (CD)-supported copper sulphide (CuS)-decorated graphene oxide (GO) hydrogel for using in a high-performance asymmetric supercapacitor device to improve the specific capacitance, cyclic stability and energy density of CuS as well as GO based supercapacitors. CD coated CuS (CuS@CD) decorated GO hydrogels (CuS@CD-GOH) were prepared by a simple hydrothermal reaction at 180 °C and optimized through different spectroscopic, diffraction, microscopic and electrochemical analyses. CD acted as a stabilizer for the CuS nanoparticles and help to bind strongly CuS nanoparticles with GO inside the 3-D hydrogel structure. The CuS@CD-GOH exhibited high specific capacitance of 920 F g⁻¹ at a current density of 1 A g⁻¹. The optimal CuS@CD-GOH was used as a positive electrode for the fabrication of asymmetric supercapacitor along with reduced GO as the negative electrode, which delivered the highest energy density up to 28 W h kg⁻¹ along with long cycling life and retains up to 90% specific capacitance after 5000 cycles. The results are excellent in comparison to the reported CuS and composite GO hydrogel based supercapacitors. Thus, this work will provide a new insight of CuS and GO based composite 3-D structures for supercapacitor applications.

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1. Introduction

Supercapacitor is one of the most promising devices to store electrical energy for the next-generation wearable electronics due to the transport of high power within a very short period. Carbon based electrical double layer capacitors (EDLCs) including graphene-based materials are the most widely investigated as electrodes of supercapacitors [1–4], which possess dramatic advantages of high power density and excellent cycling stability due to their large specific surface area, superior elasticity, high chemical stability and excellent electrical conductivity [5–9]. However,

graphene's propensity towards aggregation and restacking significantly affect the supercapacitor performance by reducing the ion-accessible surfaces and limiting ion and electron transport due to narrower channels. Therefore, a variety of graphene-based three-dimensional (3-D) porous materials, like hydrogel, aerogel, sponges, porous films, etc. have been extensively investigated to overcome these limitations through providing additional ion-accessible surface for charge storage and also facilitate the ion diffusion within the structure [10–14]. Several synthesis methods for 3D graphene have been reported to realize a wide range of pore morphologies from ultrafine (<100 nm) to macroscale (>1 μm) [15–18]. However, the specific capacitance values of these hydrogels are not up to the mark for advanced energy storage applications due to the finite electrical charge separation at the interface between the electrode materials and electrolyte.

On the other hand, pseudocapacitors based on red-ox-active

* Corresponding authors. Advanced Materials Institute for BIN Convergence Technology (BK21 Plus Global), Department of BIN Convergence Technology, Chonbuk National University, Jeonju, Jeonbuk, 54896, Republic of Korea.

E-mail addresses: nhk@chonbuk.ac.kr (N.H. Kim), jhl@chonbuk.ac.kr (J.H. Lee).

materials like transition metal oxides or sulphides exhibit high specific capacitance and energy density because they employ fast and reversible surface red-ox reactions for charge storage [19–22]. However, their drawbacks associated with poor electrical conductivity, rate capability and cyclic stability due to the volume change in electrolyte solution during electrochemical analyses. Moreover, the preparation and stabilization of the metal-based nanoparticles with desired shape and size is very difficult. Therefore, current research is mainly focusing on the hybrid supercapacitors based on carbon and transition metal based hybrid nanostructures [23–26]. Based on these concepts, preparation of these metal based nano-materials in presence of functionalized carbon based materials, as well as 3-D conversion of the hybrid system will enhance both the specific capacitance value and cyclic stability with desired shape and size of the nanoparticles. In this regards, carbon dot (CD), a highly functionalized quantum sized carbon nanomaterial is widely used as a surface stabilizer for metal nanoparticles [27,28]. Recently, composites of CD with transition metal nanoparticles and CD based hydrogels are also used in energy storage applications, as its surface functional groups facilitate the redox reaction with electrolyte and rise to an additional pseudo-capacitance contribution [26,27,29–34]. Due to the presence of CD in these composites, they also possess better conductivity because of improved crystallinity, which enhances the transport of electrons during particles, leading to improved rate capability [34]. Further, metal sulphides including copper sulphide (CuS) are cheap and environment friendly important semiconductor materials due to its abundance and low toxicity. Thus, they have recently emerged as promising electrode materials in energy storage applications [35]. Currently, CuS has been utilized as a potential material for supercapacitor applications [36–40]. However, low specific capacitance, poor rate capability and cyclic stability as well as low energy density are the big challenges for the CuS based supercapacitors, even though using composites with carbon-based conducting materials. Most of the CuS based supercapacitors exhibited <80% cyclic stability just after 1000–2000 cycles [36–38].

Therefore, the main aim of the present work is the preparation of a CD stabilized CuS nanoparticles with desired shape and size, and decoration of them into the graphene oxide (GO) hydrogel to get high performance supercapacitive material with high energy density, rate capability and cyclic stability. Herein, CD will also act as a good interacting agent with GO due to the presence of large number of surface functional groups. The present work also designed a high performance asymmetric supercapacitor device using the composite 3-D structure as positive electrode and reduced graphene oxide (RGO) as the negative electrode.

2. Experimental

2.1. Materials

D-glucose and L-ascorbic acid (Purchased from Sigma-Aldrich, Germany) were used as precursors for CD, while copper sulphate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) and sodium thiosulphate ($\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$) (Sigma-Aldrich) were used as CuS precursors. GO was prepared by modified Hummers method from natural graphite powder (Sigma-Aldrich) as reported in literature [41,42]. All other chemicals and reagents used in this study were reagent grade.

2.2. Preparation of CD stabilized CuS nanoparticles (CuS@CD)

CuS@CD was prepared by a one-pot hydrothermal reaction at 180 °C for 12 h, using a teflon-lined stainless steel autoclave reactor. Before transferring into the autoclave, 4×10^{-4} mol (100 mg) of copper sulphate was dissolved in 25 mL distilled water with

8×10^{-4} mol (198.8 mg) of sodium thiosulphate. In addition, 2×10^{-3} mol (360 mg) of glucose was dissolved in 25 mL water with 2×10^{-4} mol (35 mg) of ascorbic acid. Both the solutions were mixed homogeneously by stirring and followed by transfer into the 100 mL autoclave. After completion of the hydrothermal reaction, the autoclave reactor was allowed to cool naturally. The prepared sample was washed with distilled water using repeated centrifugation and finally dispersed in water by sonication for 10 min. Pure CD (using 360 mg of glucose and 35 mg of ascorbic acid) and pure CuS (using 100 mg of copper sulphate and 198.8 mg of sodium thiosulphate) were also prepared by the same procedure for comparative study.

2.3. Preparation of hydrogel

The hybrid hydrogel of GO with CuS@CD were prepared by the same hydrothermal reaction using teflon-lined stainless steel autoclave at 180 °C for 12 h. In this procedure, different amounts (25, 50 and 75 mg) of CuS@CD were dispersed separately with 100 mg of GO in 50 mL distilled water with the help of mechanical shearing and sonication at room temperature. Then, the solutions were transferred into teflon lined stainless steel autoclave before hydrothermal reaction. After completion of the reaction, it was cooled down to room temperature. Then the obtained GO hydrogels were washed with distilled water by submerging them into 1 L distilled water for 24 h. The prepared hydrogels were freeze-dried for 3 days in order to remove water without destroying their structure. For the comparison purpose CuS decorated GO hydrogel and pure GO based hydrogel were also prepared by similar procedure. The pure GO based, CuS and CuS@CD decorated GO hydrogels are coded as GOH, CuS-GOH and CuS@CD-GOH, respectively.

2.4. Characterization

Fourier transform infrared (FT-IR) spectra were recorded on a Nicolet 6700 spectrometer (Thermo Scientific, USA) using KBr pellets. X-ray diffraction (XRD) was carried out at room temperature on a X'pert Powder diffractometer (PANalytical, Netherlands) using $\text{CuK}\alpha$ radiation (0.154 nm) at a scan rate of 2° min^{-1} . Raman studies of the samples were carried out by a Nanofinder 30 spectroscopy system (Tokyo Instruments Co., Japan). X-ray photoelectron spectroscopy (XPS) was performed on an AXIS-NOVA spectrometer (Kratos Analytical Ltd, Manchester, UK) to characterize the chemical structure of the materials. The structural morphology, and elemental analysis (EDS) of the materials were carried out by field emission scanning electron microscopy (FE-SEM) using a JSM-6701F microscope (JEOL, Japan) installed in the Center for University-Wide Research Facilities (CURF) at Chonbuk National University and the internal structure of the nanostructures were analyzed by transmission electron microscopy (FE-TEM) using a JEM-2200 FS microscope (JEOL, Japan) in Jeonju center of KBSI. The high angle annular dark field (HAADF) scanning transmission electron microscopy (STEM) with elemental mapping of the hydrogel sample was performed by a Titan G2 60–300 (FEI, USA) with low-background double tilt holder Super-X 4SDD EDS system (Bruker, Germany).

2.5. Electrochemical analyses

The electrochemical performance was carried out in both three-electrode and two-electrode systems at room temperature by using a CH660D electrochemical workstation (CH Instruments Inc., USA) as the methods were described in our previous reports [43,44]. Prior to analysis, samples were annealed at 500 °C for 2 h in an

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