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Short Communication

Hierarchical copper selenide nanoneedles grown on copper foil as a binder free electrode for supercapacitors



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ABSTRACT

In this communication, we demonstrated the use of CuSe₂ nanoneedles grown on copper foil as a binder-free electrode for supercapacitors. Studies using X-ray diffraction, laser Raman spectroscopy and field emission scanning electron microscopy confirmed the formation of crystalline CuSe₂ nanoneedles on the surface of copper foil. Cyclic voltammetry and electrochemical impedance spectroscopy revealed the pseudocapacitive nature of the CuSe₂/Cu electrode. The galvanostatic charge–discharge analysis showed that the CuSe₂/Cu binder-free electrode delivered a high specific capacitance of about 1037.5 F/g at a constant current density of 0.25 mA/cm².

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Introduction

Supercapacitors or electrochemical capacitors have attained much interest among the various energy storage devices due to their high power density with long cycle life [1]. Supercapacitors become a bridge between batteries and capacitors via storing a large amount of charge, and deliver it at a high power rating. Supercapacitors are widely classified into two categories viz. (i) electrical double layer capacitors (EDLCs) and (ii) pseudocapacitors based upon their charge storage mechanism [2]. The mechanism of charge storage in EDLCs relies on the accumulation of electrostatic charge at the electrode/

electrolyte interface whereas pseudocapacitance arises due to reversible Faradaic reactions occurred at the electrode surface. In this decade, researchers focused on utilizing two dimensional transition metal chalcogenides (TMCs) as alternative electrodes for supercapacitors. The supercapacitive properties and mechanism of charge storage in TMCs such as MoS₂, Ni₃S₄, CoS, WS₂, and CuS nanostructures are widely investigated until now [3,4]. On the other hand, the use of TMCs such as metal selenides and tellurides towards electrochemical energy storage are not extensively studied compared to that of metal sulfides. The development of novel electrode with more energy and power density for supercapacitor applications is an emerging area of interest during

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the recent decade. In this scenario, transition metal selenides are more promising than transition metal oxides [5,6] for using as an electrode material for supercapacitors owing to their high electronic conductivity and multiple oxidation states. Very recently, few studies reported the use of metal selenides such as CoSe, and SnSe for supercapacitors [7,8]. Hitherto, there are no reports available in the literature regarding the electrochemical properties of copper selenide nanostructures. It is well known that copper-based oxides, binary metal oxides, and sulfides showed better electrochemical properties [9]. Copper selenide is a low cost semi-conducting material having applications in the field of optoelectronics, thermoelectrics, and solar cells [10,11]. The advantage of copper selenide is its various oxidation states and high electrical conductivity compared with metal oxides, which can deliver better electrochemical properties. In this study, we demonstrate the preparation of hierarchical nanostructured copper selenide grown on copper foil via hydrothermal reaction and investigated their electrochemical properties for potential use as a binder-free electrode for supercapacitor applications.

Experimental section

Materials used

Sodium selenite was purchased from Alfa Aesar, South Korea. Copper (Cu) foil was purchased from Nilaco, Japan. All chemicals used in this work are of research grade and used without further purification.

Growth of CuSe₂ on Cu foil

A one pot hydrothermal method was employed for the growth of CuSe₂ on Cu foil. The Cu foil acts as both substrate as well as Cu source and sodium selenite acts as Se source. Briefly, the Cu foil (3 × 4 cm) was cleaned with acetone, ethanol and then dried at 60 °C. An aqueous solution of 1 M sodium selenite was prepared using ultra sonication and transferred to the 100 mL Teflon lined autoclave in which the pre-cleaned Cu foil was already placed. Then, the hydrothermal reaction was performed at 120 °C for a time of 12 h. After that, the autoclave was cooled naturally to room temperature and the product was rinsed (with water, ethanol) and dried in an oven at 80 °C for 4 h.

Electrochemical measurements

The electrochemical measurements such as cyclic voltammetry (CV), galvanostatic charge–discharge (CD), and electrochemical impedance spectroscopy (EIS) were carried out in a three-electrode system on AUTOLAB PGSTAT302 N workstation using CuSe₂/Cu (1 × 1 cm²) as working electrode, saturated calomel electrode (SCE) as the reference electrode, and platinum sheet as the counter electrode. An aqueous solution of 1 M NaOH was used as electrolyte. The mass loading of the active material was calculated as 0.3 mg/cm² from the method reported in literature [12].

Results and discussion

Fig. 1(a) shows the digital photograph of the Cu foil before and after the hydrothermal reaction. It revealed that the color of the Cu foil changes from red-orange to dark black, thus confirming the formation of copper selenide on either side of Cu foil. In general, copper selenide can occur in different phases and compositions such as CuSe, Cu₂Se, CuSe₂, Cu₃Se₂, respectively [11]. The X-ray diffraction pattern of the final product (shown in Fig. 1(b)) revealed the presence of major diffraction peaks due to Cu foil at diffraction angles $2\theta = 43.68^\circ$, 50.70° , and 74.47° respectively. In addition to this, there are smaller peaks observed at diffraction angles $2\theta = 29.90^\circ$, 35.93° , 38.99° , and 61.86° corresponding to the (101), (200), (210), and (202), planes of CuSe₂ respectively [13]. The observed diffraction pattern closely matched with the standard diffraction pattern of orthorhombic CuSe₂ (JCPDS No: 82-0446). This analysis revealed the formation of CuSe₂ on the Cu foil via the hydrothermal selenization reaction. The mechanism of formation of CuSe₂ on the Cu foil is via nano-scale Kirkendall effect as similar to the previous works on growth of TMCs on metal surfaces [3,14]. The crystalline nature of the as grown CuSe₂ on Cu foil was examined by Raman spectroscopy, which is a non-destructive tool to measure crystallinity and defect levels in nanostructures [15]. The Raman spectrum of the CuSe₂ grown on Cu foil (shown in Fig. 1(c)) reveals bands at 232, 298, 356, and 440 cm⁻¹, respectively. The band observed at 232 cm⁻¹ corresponds to the Se–Se bond in the CuSe₂ and the other bands are due to the bond between Cu and Se in the CuSe₂ [13]. The field emission scanning electron micrograph (Fig. 1(d)) revealed the formation of CuSe₂ nanoneedles on the surface of Cu foil after hydrothermal reaction with high degree of uniformity. Further, the high magnification micrograph (shown in Fig. 1(e)) revealed the presence of nanoneedles with length in the range of 600–700 nm and diameter in the range of 100–200 nm, respectively. The presence of needle-like structures can provide more active sites and ion diffusion pathways, which can result in enhanced electrochemical properties.

The CV profiles for the CuSe₂/Cu electrode were measured in the potential region of 0–0.65 V at different scan rates from 5 to 100 mV/s (shown in Fig. 2(a)). The CV profiles revealed the presence of a pair of redox peaks suggesting the pseudocapacitive nature of the CuSe₂/Cu electrode. The current density is increasing with increase in scan rate from 5 to 100 mV/s in the CV curves, which suggested the presence of surface redox reactions and pseudocapacitive behavior of the CuSe₂/Cu electrode. The observed redox peaks can be due to the reversible electron transfer process that occurred at the CuSe₂/Cu electrode [16]. The specific capacitance of the CuSe₂/Cu electrode was calculated from the CV curves using the relation [17]:

$$C_{sp} = \left[\int IdV / (s \times \Delta V \times m) \right] F/g \quad (1)$$

where “C_{sp}” is the specific capacitance (F/g), “I” is the current (A), “s” is the scan rate (mV/s), “ΔV” is the potential window (V), and “m” is the mass of the active material (g). Fig. 2(b)

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