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Metal sputtered graphene based hybrid films comprising tin oxide/reduced graphene oxide/Ni as electrodes for high-voltage electrochemical capacitors

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ABSTRACT

The high voltage aqueous electrochemical capacitor (EC) is a promising energy storage device because of eco-friendliness and high electrochemical performance with a wide operational voltage and high energy density. However, it typically experiences a stability problem that includes cell aging and capacitance loss. Here, to overcome the stability issue, a thin metal layer of Ni is created on one side of a SnO_2/reduced graphene oxide (rGO) hybrid film to produce a binder-free film of SnO_2/rGO/Ni. Due to the formation of the highly conductive metal layer of Ni, the fabricated film can be well interconnected with the current collector and have lower contact resistance and open-circuit potential compared with untreated SnO_2/rGO film, which results in a remarkable enhancement of electrochemical performance, including a wide operational voltage (1.8 V), semi-permanent cycle-life (95% retention after 10k cycles), and ultrahigh volumetric energy density with a high power density, all of which are superior values compared to bare SnO_2/rGO film based devices. We anticipate that the fabricated SnO_2/rGO/Ni film could be utilized as a promising electrode for high voltage ECs, and our simple surface engineering technique will provide an effective electrode design for the fabrication of high performance thin-film ECs.

1. Introduction

Aqueous electrolyte based high voltage ECs have been considered as next-generation energy storage devices due to their eco-friendly nature and high electrochemical performance with a wide operational voltage and high energy density [1–3]. To achieve a wide operational voltage in an aqueous electrolyte, the electrode materials of the devices must have a higher overpotential of the hydrogen and oxygen evolutions than 1.23 V. However, when acidic or basic aqueous electrolytes have been used as an electrolyte with a symmetric cell configuration, it normally has an operational voltage below 1 V [4]. Unlike these electrolytes, sulfate based neutral electrolytes, such as Li_2SO_4, K_2SO_4 and Na_2SO_4, are known to have a higher overpotential of more than 1.23 V, which widens the operational voltage of the device [2,3,5]. Fic et al. found that when the device was tested in a highly concentrated Li_2SO_4, the activated carbon (AC) based symmetric supercapacitor exhibited a stable device operation until a potential of 2.2 V [3]. However, such a high operational voltage was only accomplished when a noble current collector such as gold was used, and therefore, current collector corrosion and cell aging phenomena were not sufficiently considered to evaluate its electrochemical performance [1,6]. Furthermore, due to the low packing density of AC based electrodes (typically 0.5–0.7 g cm^{-3}), they had limited volumetric energy densities, and hence, were not suitable as electrodes for compact capacitive energy storage devices [7–9].

To address this challenge, another allotrope of carbon material, a reduced graphene oxide (rGO) film that was immersed in a non-volatile solvent of sulfuric acid was proposed [7]. Due to the high packing density of the rGO film (~1.3 g cm^{-3}) [7], it exhibited remarkably high areal and volumetric capacitances (C_A and C_V, respectively) compared to other types of carbon materials, such as the AC and powder form of rGO [7,8]. However, the highly stacked feature of the film produced a limited electrolyte transport in the film, and the compact binder-free rGO film electrode only showed a remarkable energy density when it operated in an immersed

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electrolyte within the film. Very recently, we created a densely-packed hybrid film comprising SnO_2 nanoparticles (NPs) within rGO interlayers, which formed a heterostructure film of SnO_2/rGO [8]. Because of the role of effective spacers of SnO_2 NPs in the heterostructure film, this film based supercapacitor showed a superior electrochemical performance in all aqueous electrolytes, including neutral, acidic and basic electrolytes, while maintaining a compact film geometry [8]. Interestingly, due to exhibiting a stable device operation in the sulfate based electrolytes, it is expected that the SnO_2/rGO film can be operated at a potential above 1.23 V as similar to the AC based supercapacitor. Therefore, we investigated that the hybrid film could work well in an electrolyte of Li_2SO_4. Unfortunately, stability issues, such as cell aging and capacitance loss, occurred when it was tested above a potential of 1.6 V; this result was similar to that in a recent study [1,5,10]. Furthermore, when the thickness of the hybrid film was increased by more than 3 μm, the capacitance loss phenomenon dramatically appeared at fast scan rates, which is a typical feature of film based ECs [8,9,11].

In this work, to solve these stability problems of film based electrodes, cell aging and capacitance loss, we applied a metal sputtering process of nickel (Ni) in the fabrication process of SnO_2/rGO films as a model system. During the process, a thin Ni layer (around 300 nm) was formed on one side of a densely packed SnO_2/rGO film, which maintained the highly stacked heterostructure film consisting of the thin Ni layer on one side of the SnO_2/rGO film. In this SnO_2/rGO/Ni film, we anticipated that the Ni layer would act as an electron transport pathway, that is, a current collector, and hence it could either make a good electrical interconnection between the film and the current collector or dramatically reduce the contact resistance and open-circuit potential of the entire electrode, which would enhance its rate performance and cyclic stability. Surprisingly, together with these advantages, the film based device shows a stable operation up to 1.8 V, which resulted from a decrease in the open-circuit potential of the device through formation of a conductive Ni layer on the SnO_2/rGO film. The detail performance enhancement and behind mechanism of our SnO_2/rGO/Ni film based supercapacitor would be systematically investigated through the material and electrochemical characterizations.

2. Experimental procedure

2.1. Fabrication of the films consisting of SnO_2/rGO/sputtered Ni layer

Graphite oxide was obtained from the chemical oxidation of graphite (SP1, Bay carbon, 70 μm of average diameter) by a modified Hummer's method [12]. After that, graphene oxide (GO) solution was prepared by sonicating the graphite oxide powder in deionized (DI) water for 1 h with a concentration of 1 mg mL^{-1}. To form SnO_2/rGO hybrids, we adapted a simple chemical method that recently developed by our group [8]. Briefly, Sn precursor ($SnCl_2 \cdot 2H_2O$, Sigma-Aldrich) was dissolved in DI water with a concentration of 1 mg mL^{-1} and added to the GO solution. Next, hydrochloric acid (0.02 M in DI water, Sigma-Aldrich) was slowly added to the solution with adjusting a pH around 1, which resulted in the formation of SnO_2/GO hybrid. Using vacuum filtration of the solution through a PTFE membrane filter paper (0.22 μm, Millipore), a freestanding SnO_2/GO film was easily peeled off from the filter paper. For the reduction of GO to rGO, the film was thermally annealed at 200 °C for 1 h in a muffle furnace, which can create a compact film of SnO_2/rGO hybrid. The SnO_2/rGO film was clipped with two holey stainless steel plates to put the film in the vacuum chamber of a sputtering system (A-Tech System, Ltd.). Using this system, the Ni layer (thickness around 300 nm) was deposited on a side of the film. The Thickness of the Ni layer was engineered by the duration time of sputtering. Finally, the SnO_2/rGO/Ni film was punched with a desired size around 13 mm diameter for the assembly of supercapacitor as an electrode.

2.2. Material and electrochemical characterizations

The weight percent of SnO_2 NPs in the SnO_2/rGO film was obtained using thermal gravimetric analysis (TGA, Netzsch TG 209 F3) with a heating rate of 10 °C min^{-1} from room temperature until 900 °C in the air atmosphere. For surface and cross-section images of the fabricated films, scanning electron microscopy (SEM, Philips XL30SFG) and transmission electron spectroscopy (TEM, JEOL JEM-2100F) were utilized. For the material characterizations, X-ray diffraction (XRD) and Raman spectra were obtained using a multi-purpose thin-film X-ray diffractometer (D/Max-2500, Rigaku) and a dispersive Raman system with a 514-nm laser (LavRAM Aramis, Horiba Jobin Yvon), respectively. The electrical sheet resistances of all films were measured by using a four-point-probe instrument (CMTSR2000N, Advanced Instrument Technology). The electrochemical performance of SnO_2/rGO based films was evaluated using a two electrode cell kit (EL-Cell, ECC-Aqu, Germany) in 1 M Li_2SO_4 (99%, Junsei). All electrochemical measurements were performed under ambient conditions using an electrochemical instrument (Bistat, Biologic Science Instruments). The electrochemical impedance spectra were obtained with a potential of 0 V in the frequency range of 100 kHz to 10 mHz, with a sinusoidal wave of 10 mV.

2.3. Calculation of the (areal and volumetric) capacitance, energy and power densities

The areal and volumetric capacitances, C_A and C_V, were calculated using the following equations:

$$C_A = \frac{2}{A\nu\Delta V}\int IdV \tag{1}$$

$$C_V = \frac{2}{Vol.\nu\Delta V}\int IdV \tag{2}$$

where A and Vol. are the area and volume of the active electrode, respectively, ν is the scan rate, I is the discharge current, and ΔV is the working voltage.

The energy and power density of the films regarding to total area and volume of the electrodes were calculated from the following equations:

$$E_A = \frac{1}{8}C_A\Delta V^2, \quad P_A = \frac{I\Delta V}{2A} \tag{3}$$

$$E_V = \frac{1}{8}C_V\Delta V^2, \quad P_V = \frac{I\Delta V}{2Vol.} \tag{4}$$

3. Results and discussion

3.1. Fabrication of the metal sputtered SnO_2/rGO/Ni hybrid film

We recently developed a simple solution based synthetic route to create hybrid films with a SnO_2/rGO heterostructure that had uniformly dispersed SnO_2 NPs within the film [8]. We found that the content of the SnO_2 NPs in the hybrid film was below around 30 wt%, which could produce a binder-free self-standing SnO_2/rGO film. The weight percent of SnO_2 in the hybrid film was further