Reduced graphene oxide based ternary nanocomposite cathodes for high-performance aqueous asymmetric supercapacitors

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ABSTRACT

Ternary nanocomposites have attracted increasing attention as efficient supercapacitor electrode materials. Here we report, the synthesis of a ternary hybrid nanocomposite by the introduction of crystalline RuO$_2$ nanoparticles loaded carbon nanocoils (CNCs) as spacers in reduced graphene oxide (RGO). The RGO-(RuO$_2$/CNCs) composite electrode exhibits a high specific capacitance of 725 F g^{-1} at a scan rate of 20 mV s^{-1} in three-electrode configuration. When used in symmetric two electrode configuration, it shows a specific capacitance of 436 F g^{-1} at a constant current density of 1 A g^{-1}, which is nearly three times higher than that of pure RGO based electrode. An aqueous asymmetric supercapacitor fabricated using RGO-(RuO$_2$/CNCs) as the positive electrode and RGO as the negative electrode is operational in an electrochemically stable potential window of 2 V. The asymmetric capacitor exhibits a high energy density of 45 Wh Kg^{-1} at a power density of 1 kW kg^{-1} and retains an energy density of 41 Wh Kg^{-1} even at a high power density of 40 kW kg^{-1}.

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1. Introduction

From portable electronics and transportation systems to backup systems that complement renewable sources such as solar and wind, the demand for energy storage is expected to grow substantially well into the foreseeable future [1,2]. Supercapacitors can act as a promising energy- storage alternative for rapidly growing electronic industry [3,4]. But their lower energy density as compared to batteries is still a significant problem, which needs to be addressed for making these devices useful for everyday applications [3,5]. The energy density of supercapacitors can be expressed as $E = \frac{1}{2}\,CV^2$, where C is the device capacitance and V is the potential window of operation. This expression indicates that the energy density of supercapacitors can be improved either by improving the device capacitance using an electrode material with high surface area, excellent electrical conductivity, and high specific capacitance or by widening the electrochemically stable potential window [3,6]. The asymmetric configuration of electrodes in aqueous electrolytes or the use of organic/ionic liquid electrolytes help in extending the potential window of operation [7].

Reduced Graphene Oxide (RGO), due to its high electroactive surface area, good chemical stability, large in-plane conductivity, and excellent flexibility, has attracted significant research attention as the electroactive material for supercapacitor electrodes [8–10]. However, these electrodes exhibit a low specific capacitance value ($<$200 F g^{-1}), as the graphene layers tend to agglomerate during the electrode preparation due to the π-π stacking and strong van der Waals interactions between individual layers, leading to a reduction in electrochemically active surface area [9,11]. The restacking of graphene layers can be considerably reduced by the introduction of spacers between the layers. Both nanocarbon materials showing electric double layer capacitive (EDLC) behavior and pseudocapacitive materials (transition metal oxides or conducting polymers) showing faradaic behavior can act as efficient spacers for this purpose [12–18]. The spacers ensure high electrochemical utilization of graphene layers and also contribute to the total capacitance of the system [19].

Among the different pseudocapacitive materials, ruthenium oxide (RuO$_2$), with its high theoretical specific capacitance (up to 2200 F g^{-1}), proton-electron mixed conductive nature, wide potential window, ability to store charges reversibly, long cycle life, and high rate capability, is considered as the most promising candidate for supercapacitor applications [12,20,21]. But high cost limits its practical applications, which can greatly be overcome by loading this material on a porous and conductive nanocarbon

support. Reports suggest that when a pseudocapacitive nanomaterial is used in combination with a nanocarbon, synergistic effects of the combination enhances the electrochemical performance of the functional nanomaterials. If such a nanohybrid is introduced as the spacer between the graphene layers, the resultant ternary nanocomposite obtained can serve as a promising supercapacitor electrode material with excellent conductivity and high electroactive surface area[12,20]. Carbon nanofibers with helical morphologies, widely known as carbon nanocoils (CNCs) possess excellent electrical conductivity, high porosity, and oxidation resistance nature [22–26]. These qualities make them an ideal carbon support for the dispersion of pseudocapacitive nanomaterials [23,26].

The thermodynamically stable potential window of the electrolyte decides the operating voltage of the supercapacitor. Because the thermodynamic window of water is 1.23 V, water-based electrolytes work with a relatively small equivalent series resistance (ESR) in a maximum potential window of 1 V [27]. By contrast, the operational voltage varies from 3 to 5 V for the organic electrolyte. But the high equivalent series resistance (ESR) value prevents from attaining high power density value for organic electrolyte based supercapacitors [28]. Moreover, low conductivity, high cost, toxic nature, and the tendency to become unstable in the presence of activated carbon based electrodes make them less attractive for practical applications. The operational potential window of aqueous supercapacitors can be widened by designing asymmetric configurations. Aqueous electrolytes are having the added advantages of low cost, high ionic conductivity, environmentally safe nature, stability in the air, and non-inflammability [29].

Herein, we aim to study the spacer effect of $RuO_2/CNCs$ in RGO for maximizing the capacitance of the latter. The introduction of spacers significantly improves the electroactive surface area of the RGO-($RuO_2/CNCs$) composite, without a detrimental loss of electrical conductivity. The composite electrode exhibited a specific capacitance of $725\,F\,g^{-1}$ at a scan rate of $20\,mV\,s^{-1}$. Systematic comparison of the performances of symmetric supercapacitor based on RGO-($RuO_2/CNCs$) composite electrodes and an asymmetric supercapacitor comprised of a RGO-($RuO_2/CNCs$) composite cathode and an RGO anode (with a cell voltage of 2 V) demonstrates the obvious enhancements in both energy and power densities in the asymmetric design.

2. Experimental

2.1. Synthesis of RGO-(RuO₂/CNCs) ternary nanocomposites

The RGO-($RuO_2/CNCs$) composite was synthesized by the ultrasonication of RGO and $RuO_2/CNCs$. RGO was prepared by the hydrothermal reduction of graphite oxide (GO) synthesized using modified Hummer's method. 37.5 mL of $0.5\,mg\,mL^{-1}$ GO aqueous solution (basic, pH $\sim$ 10) prepared by probe ultrasonication (160 W) for 1 h was sealed in a 50 mL teflon-lined autoclave and maintained at 180 °C for 6 h. It was then cooled to room temperature; the resultant black product was filtered and washed using DI water. For the synthesis of $RuO_2/CNCs$, 1 g of $RuCl_3$. $3H_2O$ was added to a uniform dispersion of CNCs in water (200 mg in 500 mL, pH $\sim$ 7). The mixture was refluxed at 120 °C for 6 h. After the reaction, the precipitate was separated, dried, and calcined at 300 °C, leading the formation of $RuO_2/CNCs$. RGO and $RuO_2/CNCs$ composites in the ratio 8:2 by weight were dispersed in 200 mL of distilled water by ultrasonication for 5 h to obtain a homogeneous RGO-($RuO_2/CNCs$) suspension. Finally, the solid was filtered, and washed several times with distilled water and alcohol, dried at 80 °C for 5 h in a vacuum oven.

2.2. General characterization of composites

The nanocomposites were characterized by a powder X-ray diffraction system (XRD, PAN analytical X'pert Pro) equipped with Cu Kα radiation (λ=0.15406 nm) and the composition of RuO_2/CNCs was analyzed using thermogravimetric analysis (EXSTAR TG/DTA 6200). BET surface areas of the materials were measured using surface area and porosimetry system 'Micromeritics' (Micromeritics ASAP 2020) at 77 K. The surface morphology and microstructure of the nanomaterials were investigated using scanning electron microscopy (SEM, JEOL JSM-5600 LV) and transition electron microscopy (TEM, FEI, Tecnai G^2 30LaB$_6$, ST with EDAX) analyses. The elemental presence was identified using energy dispersive X-ray analysis (EDAX).

2.3. Preparation of electrodes and electrochemical measurement

Symmetric capacitors were fabricated using the nanocomposites. Supercapacitor electrodes of 1 cm^2 area were prepared using RGO and RGO-($RuO_2/CNCs$) by the following procedure. The active material was mixed with polytetrafluoroethylene (PTFE) binder in a mass ratio of 95:5 and dispersed in ethanol by ultrasonication. The resulting mixture was coated onto the conductive carbon cloth (ELAT, Nuvant Systems Inc.) substrate, which was followed by drying at 100 °C for 12 h in a vacuum oven. Two symmetric electrodes, separated by a thin polymer separator (Celgard® 3501) in 30 wt % KOH aqueous electrolyte, were sandwiched in a standard electrochemical cell (ECC-std, EL-Cell GmbH). Each electrode contained ~**4 mg** of active material, and this mass was used in the calculation of specific capacitance of the symmetric supercapacitors.

Specific capacitance values of RGO and RGO-($RuO_2/CNCs$) electrodes were also measured in three electrode configuration. This measurement was conducted in 30 wt % KOH aqueous electrolyte, with a platinum foil and an Ag/AgCl respectively as the counter and the reference electrodes and the (RGO-(RuO_2/CNCs) or RGO) based electrode as the working electrode. The RGO-($RuO_2/CNCs$)//RGO asymmetric supercapacitor is constructed using RGO (mass = 5.6 mg) as the negative electrode material and RGO-($RuO_2/CNCs$) (mass = 2 mg) as the positive electrode material, Celgard® 3501 membrane as the polymer separator, and 30 wt% KOH as the aqueous electrolyte medium. The loading mass ratio of active materials in the electrodes was estimated by the charge balancing principle, details of which are explained in Section 3.

The electrochemical properties of the supercapacitor electrodes were studied by cyclic voltammetry (CV), galvanostatic charge/discharge (CD) and electrochemical impedance spectroscopy (EIS) measurements. All these measurements were carried out at room temperature using a VMP3 Biologic electrochemical workstation. EIS measurements were conducted at a dc bias of 0 V in the frequency range from 100 kHz to 1 mHz with a sinusoidal signal of 10 mV. EIS data was analyzed using complex plane impedance plots (Nyquist plots).

Specific capacitance (C_{sp}) of symmetric supercapacitors were calculated from the cyclic voltammogramms and charge-discharge curves according Eqs. (1) and (2)

$$C_{sp} = {}^{sp}\frac{2}{m}C_{cell} = \frac{2i}{ms} \tag{1}$$

where 'i' is average cathodic current of CV loop and 's' is the scan rate.

$$C_{sp} = \frac{2}{m}C_{cell} = \frac{2}{m} \times \frac{I}{\left(\frac{\Delta V}{\Delta t}\right)} \tag{2}$$