Enhanced performance of HRGO-RuO₂ solid state flexible supercapacitors fabricated by electrophoretic deposition

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Abstract

Ruthenium oxide (RuO₂) nanomaterials exist as excellent materials for electrochemical capacitors. However, they tend to suffer from low mechanical flexibility when cast into films, which makes them unsuitable for flexible device applications. Herein, we report an environmentally friendly and solution-processable approach to fabricate RuO₂-based composite electrodes for flexible solid state supercapacitors. The composites were produced by anchoring RuO₂ nanoparticles onto holey reduced graphene oxide (HRGO) via a sol-gel method, followed by the electrophoretic deposition (EPD) of the material into thin films. The uniform anchoring of ultra-small RuO₂ nanoparticles on the two-dimensional HRGO sheets resulted in HRGO-RuO₂

hybrid sheets with excellent mechanical flexibility of HRGO. EPD induced a layer-by-layer assembly mechanism for the HRGO-RuO₂ hybrid sheets, which resulted in a binder-free, flexible electrode. The obtained HRGO-RuO₂ flexible supercapacitors exhibited excellent electrochemical capacitive performance in a PVA-H₂SO₄ gel electrolyte with a specific capacitance of 418 Fg⁻¹ and superior cycling stability of 88.5% capacitance retention after 10,000 cycles. In addition, these supercapacitors exhibited high rate performance with capacitance retention of 85% by increasing the current density from 1.0 to 20.0 Ag⁻¹, and excellent mechanical flexibility with only 4.9% decay in the performance when bent 180°.

1. Introduction

Flexible solid state supercapacitors have attracted increasing interest as next-generation energy storage devices for flexible and wearable electronics [1-3]. In comparison to conventional supercapacitors, flexible solid state supercapacitors have several advantages including small size, low weight, ease of handling, excellent reliability, and a wider range of operating temperatures [3]. One of the most important criteria of flexible solid state supercapacitor is that the electrode must have certain mechanical flexibility. Carbon materials, such as carbon fibres, carbon nanotubes (CNTs) and graphene, have been widely explored as flexible electrodes due to their good electrical conductivity and exceptional structural and mechanical properties [4-10]. Among those materials, graphene is considered as the most promising candidate because of its large surface area, and excellent conductivity [3,11]. However, graphene sheets are prone to restack with each other via π - π stacking interactions and Van der Waals forces to form irreversible agglomerates, resulting in a loss of the effective surface area and a much lower mass diffusion rate [12,13]. One of the most effective approaches to prevent the restacking of graphene is to use guest materials, such as nanoparticles, CNTs and conducting polymers, as spacers [14]. In our previous study, ultra-small ruthenium oxide nanoparticles were anchored on the surface of reduced graphene oxide (RGO) sheets, which effectively prevented the restacking of the RGO. The subsequently fabricated supercapacitor exhibited excellent electrochemical capacitive properties [15]. In another recent study, Xu et al. [13] reported a scalable, defect-etching strategy to improve the surface area and mass diffusion rate of RGO by creating nanopores across the entire basal plane of the RGO sheets. Interestingly, this strategy was highly effective not only for three-dimensional hierarchical RGO hydrogels but also for RGO free-standing papers in which RGO sheets are highly restacked.

To date, preparing flexible carbon material-based electrodes with robust mechanical properties and excellent electrochemical performance remains a major challenge, particularly with conductive substrates functioning as the current collector [3]. Various fabrication techniques have been explored to prepare CNT and graphene-based flexible electrodes, including slurry casting, spray-coating, print-coating, and electrophoretic deposition (EPD) [3,16-20]. EPD is arguably the most attractive technique because of its notable advantages, such as its versatility, high deposition rate, long-range morphological uniformity, wide-range thickness adjustment, size-scalability, and cost-effective equipment [21,22]. In this study, we report the EPD of holey reduced graphene oxide-ruthenium oxide (HRGO-RuO₂) nanomaterials on gold-coated poly(ethylene terephthalate) (PET) electrodes for implementation in flexible solid state supercapacitors. The obtained HRGO-RuO₂ supercapacitors exhibited excellent electrochemical capacitive performance within a PVA-H₂SO₄ gel electrolyte, yielding a specific capacitance of 418 F g⁻¹ at a current density of 1.0 A g⁻¹ and an outstanding cycling stability of 88.5 % capacitance retention after 10,000 cycles. The HRGO-RuO₂ system also demonstrated a high rate performance and minor capacitive evolution when the supercapacitors were bent over angles as large as 90° and 180°.

2. Experimental

2.1 Preparation of HRGO-RuO₂

Graphene oxide (GO) was prepared by the modified Hummers method, using expanded graphite as the starting material [15]. The as-prepared GO was diluted to a concentration of 2.0 mg mL⁻¹ and sonicated for 30 min. The holey graphene oxide (HGO) was prepared by hydrogen peroxide etching of GO, following Xu's method [13]. Briefly, 10 mL of H₂O₂ (30 wt. %) was added to 200 mL of the GO solution, the mixture was then heated at 95° C and stirred for 4 h.

The obtained HGO was then centrifuged and washed 3 times with DI water to remove the excess of H_2O_2 .

The HRGO- RuO_2 was prepared following our previous report [15]. 312 mg ruthenium trichloride hydrates ($\text{RuCl}_3 \cdot x\text{H}_2\text{O}$, Ru content of 40-49 wt. %) was added into 200 mL of HGO solution (1.0 mg mL^{-1}) under mixing. The suspension was then neutralized with 1M NaOH solution and stirred for 12 h at room temperature to obtain HGO- RuO_2 . The pH of HGO- RuO_2 suspension was then adjusted to 12 by adding NaOH, and the suspension was aged at 90°C for 12 h for deoxygenation of HGO. The obtained HRGO- RuO_2 suspension was repeatedly centrifuged and washed with DI water (4 times) to remove the residual NaCl and NaOH. Finally, the HRGO- RuO_2 was diluted to a concentration of 0.75 mg mL^{-1} and sonicated for 30 min to create a homogeneous solution.

2.2 Electrophoretic deposition of HRGO- RuO_2

The EPD of HRGO- RuO_2 on flexible gold coated PET substrate (200 nm gold deposited by electron-beam evaporation) was performed using home-built system consisting of Keithley 2410 SourceMeter controlled by a LabView program. The anode gold coated PET (2.0 x 6.0 cm) was mounted vertically parallel to an identical size 316 L stainless steel (McMaster Carr) counter cathode with a separation of 1.0 cm. A **direct current (DC)** voltage of 4.0 V was applied after fully dipping the electrode into the GO solution, and remained the same until the electrode was withdrawn from the solution. The HRGO- RuO_2 deposited on gold coated PET substrate was air dried for 1 h and then annealed at 120°C for 2 h.

2.3 Characterizations

The morphologies of the HRGO–RuO₂ materials were characterized by scanning electron microscopy (SEM, Hitachi 4800S) and transmission electron microscopy (TEM, JEOL 1400). Zeta potential measurements were performed on Malvern Zetasizer (Nano-ZS, Malvern Instrument).

2.4 Flexible solid state supercapacitor cell assembly and electrochemical measurements

H₂SO₄-PVA gel electrolyte was prepared by adding 1 g of PVA into 10mL of deionized water and the mixture was heated to 85°C under stirring until it became clear. Subsequently, 0.277 mL of concentrated H₂SO₄ was added to the mixture to create 0.5 M H₂SO₄-PVA gel electrolyte [10].

The H₂SO₄-PVA gel electrolyte was poured on the surface of HRGO-RuO₂ electrode and dried in air for 12 h to form a solid electrolyte membrane. The two identical electrodes were then pressed together to allow the electrolyte membranes to combine into one thin separating layer and form an integrated device which was flexible and robust.

The electrochemical capacitive performance of flexible solid state HRGO-RuO₂ supercapacitor was characterized by cyclic voltammetry, galvanostatic charge–discharge and electrochemical impedance spectroscopy. Cyclic voltammetry measurements were performed on a potentiostat/galvanostat PARSTAT 2273 (Princeton Applied Research), and galvanostatic charge–discharge tests were conducted on an Arbin battery tester BT2000 (Arbin Instrument) in the potential range of 0-1.0V. Electrochemical impedance spectroscopy tests were performed over a frequency range from 0.01 Hz to 100 kHz at an open circuit potential with an AC perturbation of 10.0 mV. The specific capacitance was calculated according to the following equation:

$$C_{sp} = 4(I\Delta t/m\Delta V)$$

where C_{sp} is the specific capacitance, I is the constant discharge current, Δt is the discharging time, m is the mass of two electrodes, and ΔV is the voltage drop upon discharging.

3. Results and discussion

Fig. 1 Schematic illustration of the preparation procedure of the flexible solid state HRGO-RuO₂ supercapacitor.

The synthesis of HRGO-RuO₂ and the preparation of the flexible electrodes by EPD are illustrated schematically in Fig. 1. HGO was prepared by mild oxidation of GO using hydrogen peroxide [13]. Subsequently, anchoring the ultra-small RuO₂ nanoparticles on the surface of HRO and reducing HGO into HRGO were performed by combining the in-situ sol-gel synthesis of RuO₂ and the alkaline deoxygenation of HGO, following our previous report [15]. The obtained HRGO-RuO₂ was easily dispersed in water with mild sonication. The zeta potential measurement of HRGO-RuO₂ dispersion revealed the zeta potential value to be -37.2 mV (Fig.

S1), confirming the thermodynamic stability and the negative average charge of the HRGO-RuO₂ dispersion, both of which facilitate the EPD process. The EPD of HRGO-RuO₂ on a flexible gold-coated PET substrate was performed by applying a DC voltage of 4.0 V for 500 seconds (Fig. S2). Under an applied electric field engendered between the two electrodes, the negatively charged HRGO-RuO₂ species electrophoretically deposited onto the positive electrode (Fig. S3(a)). The HRGO-RuO₂ that was deposited on gold-coated PET substrate was dried in the air for 1 h and then annealed at 120 °C for 2 h to remove both the absorbed and chemically bound water from the RuO₂ nanoparticles. This step improved the capacitive performance of RuO₂ [15]. The mass of the HRGO-RuO₂ deposited was approximately 0.7 mg cm⁻² (Fig. S3(b)). Finally, two identical HRGO-RuO₂ electrodes were assembled into a flexible solid state supercapacitor cell using 0.5 M H₂SO₄-PVA gel electrolyte (Fig. S4).

Fig. 2 (a & b) SEM images of freeze-dried HRGO-RuO₂, (c & d) TEM images of HRGO-RuO₂ (yellow and red circles were used to highlight the representative RuO₂ nanoparticles and the in-plane nanopores, respectively), and (e & f) SEM images of the surface of HRGO-RuO₂ film electrochemically deposited on gold coated PET.

The morphologies of the as-prepared HRGO-RuO₂ and HRGO-RuO₂ films, electrophoretically deposited onto gold-coated PET substrates, were characterized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM), as shown in Fig. 2.

The SEM images of the freeze-dried HRGO-RuO₂ revealed large HRGO sheets with diameters up to a few tens of microns. Each sheet was fully decorated with ultra-small RuO₂ nanoparticles (Fig. S5). The TEM images in Fig. 2d and Fig. S6 further revealed that the mean size of RuO₂ nanoparticles was 1.0-2.0 nm and were homogeneously anchored on the HRGO sheet surface. Numerous in-plane pores with sizes 1.0-4.0 nm were observed across the entire basal plan of HRGO-RuO₂ (Fig. S6), which was consistent with previous reports [13]. The SEM images in Fig. 2 (e & f) and Fig. S7 show the surface of the HRGO-RuO₂ film that was electrophoretically deposited on gold-coated PET, which was quite flat with numerous small wrinkles. The HRGO-RuO₂ sheets appeared to lie flat and parallel to the electrode's surface, suggesting the stacked, compactly-formed, layer-by-layer deposition of the HRGO-RuO₂ sheets [21].

The electrochemical capacitive performance of these flexible solid state HRGO-RuO₂ supercapacitors was characterized by cyclic voltammetry (CV), galvanostatic charge–discharge (GCD), and electrochemical impedance spectroscopy (EIS). Fig. 4a shows CV curves of HRGO-RuO₂ within the potential window 0-1.0 V at various scan rates. The CV curves were quasi-rectangular, which can be attributed to the pseudocapacitive behaviour of RuO₂ nanoparticles. Note that no redox peak was observed, indicating that a fast reversible redox reaction occurred on the surface of ultra-small RuO₂ nanoparticles [15]. The CV curves were slightly distorted when the scan rate increased from 20 to 500 mV s⁻¹, suggesting excellent capacitive behavior with very low internal resistance from the electrodes. Consistently, the GCD curves of HRGO-RuO₂ had a symmetrical triangular shape, implying good capacitive characteristics. The IR drop at the beginning of the discharge was very small and was observed only at high current densities (≥ 10 A g⁻¹, Fig. S10), suggesting very low equivalent series resistances (ESR).

Fig. 3 (a) CV curves at different scan rates, (b) GCD curves at different current densities, (c) specific capacitance, and (d) cycling stability of HRGO-RuO₂.

The specific capacitances of HRGO-RuO₂ that were calculated from the discharge curves are shown in Fig. 3c. The specific capacitances of HRGO-RuO₂ were 418.5 and 353.6 F g⁻¹ at current densities of 1.0 and 20.0 A g⁻¹, respectively; these specific capacitances are comparable to the best ever reported for RGO-RuO₂ (Table 1). Note that the specific capacitance retained 84.5 % of its initial value as the current density increased from 1.0 to 20 A g⁻¹, indicating excellent rate performance. Both the high specific capacitance and the excellent rate performance of HRGO-RuO₂ can be attributed to a combination of the high capacitance of the pseudo-capacitive ultra-small RuO₂ nanoparticles and the unique features of HRGO when an abundance of in-plane nanopores exist. Such features improve the surface area and the ion diffusion rate. The cycling stability of HRGO-RuO₂ was evaluated using GDC at a current density of 4.0 A g⁻¹ up to 10,000 cycles. As shown in Fig. 3d, the specific capacitance gradually decreased by ~10 %

of its initial value within the first 1000 cycles. Thereafter, the specific capacitance remained essentially constant for the next 9000 cycles, confirming HRGO-RuO₂'s excellent long-term electrochemical stability.

Table 1. Specific capacitances of RGO–RuO₂ supercapacitors

Material	RuO ₂ content	Cell type	Electrolyte	Specific capacitance	Ref.
a-RGO-RuO ₂	72.6 wt%	Two-electrode	1M H ₂ SO ₄	509 F g ⁻¹ at current density of 1.0 A g ⁻¹	15
RGO-RuO ₂	86.9 wt%	Two-electrode	2M H ₂ SO ₄	400 F g ⁻¹ at current density of 1.0 A g ⁻¹	23
RuO ₂ /GNs	36 wt%	Two-electrode	30 wt% KOH	365 F g ⁻¹ at scan rate 5 mV s ⁻¹	24
RuO ₂ /RGO	75 wt%	Three-electrode	1M H ₂ SO ₄	497 F g ⁻¹ at current density of 0.5 A g ⁻¹	26
GRA-6	45 wt%	Three-electrode	1M H ₂ SO ₄	471 F g ⁻¹ at current density of 0.5 A g ⁻¹	29
RuO ₂ /RGOH	15 wt%	Three-electrode	1M H ₂ SO ₄	345 F g ⁻¹ at current density of 1.0 A g ⁻¹	30
RuO ₂ -f-HEG	25 wt%	Two-electrode	1M H ₂ SO ₄	265 F g ⁻¹ at scan rate 10 mV s ⁻¹	31
HRGO-RuO ₂	51.2 wt%	Flexible, solid state	PVA/H ₂ SO ₄	418.5 F g ⁻¹ at current density of 1.0 A g ⁻¹	This work

To extend the investigation of the capacitive performance and the mechanical flexibility of HRGO-RuO₂ supercapacitors, CV data at the scan rate of 100 mV s⁻¹ were acquired as the capacitors were bent at angles of 90° and 180°, as shown in Fig. 4a. The shape of the CV curves, when the supercapacitors were subjected to bending, remained nearly unchanged; the current densities of the CV curves decreased insignificantly as the bending angle increased, suggesting excellent mechanical stability under flexion for HRGO-RuO₂. Fig. 4b shows that the specific capacitance of HRGO-RuO₂ slightly decreased from 418.5 to 403.4 and 398.0 F g⁻¹,

corresponding to 3.6 and 4.9 % decays as functions of bending angle from 0.0 to 90 and 180°, respectively. This superior mechanical stability of HRGO-RuO₂ can be explained by the layer-by-layer assembly of HRGO-RuO₂ sheets, facilitated by EPD.

Fig. 4 (a) CV curves at scan rate of 100 mV s⁻¹, (b) specific capacitance of HRGO-RuO₂ under various bending angles; (c) Bode plot, and (d) Nyquist plot of HRGO-RuO₂.

Use of EIS was expanded to characterize the electrochemical behaviour of HRGO-RuO₂. The Bode plot in the Fig. 4c displays a phase angle value of -80° at low frequency; this phase angle's value, which is close to that of an ideal capacitor (-90°), also implies HRGO-RuO₂ excellent capacitive behaviour [8,27]. Moreover, at a phase angle of 45°, the characteristic frequency f_0 , which is the point where the capacitive and resistive impedances are equal, is ~2.14Hz corresponding to a time constant τ_0 ($\tau_0 = 1/f_0$) of 0.46s. This is much lower than most commercially available electrochemical capacitors ($\tau_0 = 10$ s), which affirms the existence of enhanced ion transport within the electrodes [28]. The Nyquist plot in Fig. 4d was nearly vertical

and did not possess the expected semicircle geometry at high frequencies, further confirming the system's excellent capacitive behaviour and the fast ion diffusion [27]. Fast ion diffusion in HRGO-RuO₂ can be attributed to the abundance of nanopores across the surface of the HRGO sheets, which shortens the ion diffusion pathway through the electrode [13,28]. The ESR value, ascertained from the intersection of the data in the Nyquist plot and the real impedance axis (Z'), was only 0.7 Ω . The low ESR value can be attributed to a combination of the low contact resistance, due to the binder-free layer-by-layer assembly of HRGO-RuO₂ sheets (via EPD) on the gold-coated PET current collector, and low ion diffusion resistance due to the shortening of the ion diffusion pathway throughout the electrode by the nanopores.

4. Conclusions

In summary, we have developed a scalable approach for the fabrication of HRGO-RuO₂ electrodes for flexible, solid state supercapacitor applications using electrophoretic deposition. The hydrogen peroxide solution-based etching of GO resulted in abundant in-plane nanopores across the HGO sheets. The combination of a sol-gel synthesis and the alkaline deoxygenation of HGO produced ultra-small RuO₂ nanoparticles, homogeneously anchored on the surface of HRGO sheets. Electrophoretic deposition effectively drove the HRGO-RuO₂ sheets to assemble in a layer-by-layer format to yield compact films with excellent mechanical flexibility. These flexible solid state HRGO-RuO₂ supercapacitors, operating within a PVA-H₂SO₄ gel electrolyte, exhibited high specific capacitance of 418.5Fg⁻¹ at a current density of 1.0Ag⁻¹, and excellent cycling stability with 88.5% capacitance retention after 10,000 cycles. These supercapacitors also exhibited high rate performance with capacitance retention of 85 % by increasing the current density from 1.0 to 20.0Ag⁻¹, and excellent mechanical flexibility with only 4.9% decay in the performance when bent 180°. The excellent capacitive properties of flexible HRGO-RuO₂

electrode can be attributed to the combination of high capacitance of pseudocapacitive ultra-small RuO₂ nanoparticles, the unique features of HRGO with abundant in-plane nanopores, and the electrophoretically assembled layer-by-layer structure of HRGO-RuO₂ sheets. This study demonstrates the exciting potential of EPD for the industrially favourable and scalable fabrication of high-performance graphene based composites for flexible solid state energy storage devices.

Acknowledgements

This work was supported in part by the U.S. Department of Energy, Office of Science, Office of Workforce Development for Teachers and Scientists (WDTS) under the Visiting Faculty Program (VFP). The research used resources of the Center for Functional Nanomaterials, which is a U.S. DOE Office of Science Facility, at Brookhaven National Laboratory under Contract No. DE-SC0012704.

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