Symmetric Supercapacitor Based on Reduced Graphene Oxide in Non-Aqueous Electrolyte

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Reduced graphene oxide (RGO) is prepared by thermal exfoliation of graphite oxide in air. Symmetric RGO/RGO supercapacitors are constructed in a non-aqueous electrolyte and characterized. The values of energy density are 44 Wh kg\(^{-1}\) and 15 Wh kg\(^{-1}\), respectively at 0.15 and 8.0 kW kg\(^{-1}\). The symmetric supercapacitor exhibits stable charge/discharge cycling tested up to 3000 cycles. The low-temperature thermal exfoliation approach is convenient for mass production of RGO at low cost and it can be used as electrode material for energy storage applications.

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Graphene oxide (GO) was prepared by a modified Hummer’s method. In a typical synthesis, 92 mL of sulfuric acid (98 wt%) was taken in a 500 mL conical flask, which was kept in an ice bath. 2 g of graphite powders and 2 g of NaNO\(_3\) were added to the above solution. 6 g of potassium permanganate was slowly added to the mixture and stirred for 2 h at room temperature. The mixture was filtered and washed with 5% HCl and deionized water until no sulfate ions in the filtrate were detected, the solid was dried in a vacuum oven for 24 h. The thermal exfoliation of GO was carried out by keeping small quantity of GO in a pre-heated furnace (200°C) under argon atmosphere. After 10 min, the volume of the GO sample expanded for several times and few-layered partially exfoliated reduced graphenes were obtained.

The Powder X-ray diffraction (XRD) pattern were recorded using Bruker D8 advance X-ray diffractometer and Raman spectra were measured by a Horiba Jobin Yvon LabRam HR spectrometer. Surface area and pore size distribution of the samples were measured using micromeritics surface area analyzer model ASAP 2020. The microstructures of the materials were examined by using scanning electron microscopy (SEM) model Sirion and transmission electron microscopy (TEM) model JEOL JEM 2100F.

For the fabrication of electrodes, the active material (RGO, 85 wt%), conductive material (Acetylene black, 10 wt%) and polyvinylidene fluoride (PVDF, 5 wt%) were mixed and ground in a mortar. Few drops of n-methyl pyrrolidinone (NMP) were added to a mortar. The mixture and stirred for 2 h at room temperature. To the above mixture 2 g of graphite powders and 2 g of NaNO\(_3\) were added to the above mixture and stirred for 2 h at room temperature. The mixture was filtered and washed with 5% HCl and deionized water until no sulfate ions in the filtrate were detected, the solid was dried in a vacuum oven for 24 h. The thermal exfoliation of GO was carried out by keeping small quantity of GO in a pre-heated furnace (200°C) under argon atmosphere. After 10 min, the volume of the GO sample expanded for several times and few-layered partially exfoliated reduced graphenes were obtained.

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Results and Discussion

Fig. 1a shows the XRD patterns of GO and RGO. The diffraction peak at 10.6° corresponds to GO. After the heat-treatment at 200°C in air, the characteristic peak observed for RGO at 24.4° indicates the formation of RGO. The Raman intensity of D band increased while that of G band decreased and the I\(_D\)/I\(_G\) ratio is found to be 1.1. It is mainly attributed to the formation of vacancies and topological defects caused by the release of CO and CO\(_2\) during decomposition. The specific surface area of RGO is found to be 395 m\(^2\) g\(^{-1}\) with a pore size distribution at 3.1 nm. The SEM micrograph of RGO (Fig. 1b)

Experimental

Graphene oxide (GO) was prepared by a modified Hummer’s method. In a typical synthesis, 92 mL of sulfuric acid (98 wt%) was taken in a 500 mL conical flask, which was kept in an ice bath. 2 g of graphite powders and 2 g of NaNO\(_3\) were added to the above solution. 6 g of potassium permanganate was slowly added to the mixture and stirred for 2 h at room temperature. The mixture was filtered and washed with 5% HCl and deionized water until no sulfate ions in the filtrate were detected, the solid was dried in a vacuum oven for 24 h. The thermal exfoliation of GO was carried out by keeping small quantity of GO in a pre-heated furnace (200°C) under argon atmosphere. After 10 min, the volume of the GO sample expanded for several times and few-layered partially exfoliated reduced graphenes were obtained.

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Figure 1. (a) XRD patterns of GO and RGO, (b) SEM, and (c) TEM photographs of RGO.

shows that there is a large exfoliation of graphene layers exhibiting a multi-layer structure. Under low magnification TEM the RGO look like wrinkled transparent flakes (Fig. 1c) and at high magnification (Fig. 1c, inset) it resembles a transparent ultra thin film with a few thin ripples within the plane.

Figure 2a presents the CV curves of a symmetric supercapacitor operating at cell voltage between 0 and 3 V, and cycled at different scan rates in the range 10–100 mV s⁻¹. The CVs exhibit a rectangular shape with a good reversibility, which is a characteristic of a pure capacitive behavior. As per energy storage mechanism, both anions (PF₆⁻) and cations (Li⁺) are adsorbed on the graphene sheets during charging process, whereas the process is reversed during discharge. It is obvious to notice that increasing sweep rate leads to a decrease in the net charge under the curve. At the high scan rates the surface of the active material (RGO) is only involved in the electrochemical reaction rather than the bulk, which results in a decrease in specific capacitance.

Galvanostatic charge/discharge experiments at various current densities between 0 and 3.0 V were carried out for symmetric supercapacitor (Fig. 2b). The specific capacitance of 140, 132, 127, 121 and 116 F g⁻¹ are observed at a current density of 0.1, 0.2, 0.3, 0.4 and 0.5 A g⁻¹, respectively. The obtained values are highly comparable to the previous reports. Recently, Mhamane et al., reported the capacitance of 97 F g⁻¹ at a current density of 0.1 A g⁻¹. Also, Ruoff’s and co-workers reported the maximum capacitance of 112 F g⁻¹ in an ionic liquid electrolyte (1 M tetraethylammonium tetrafluoroborate in acetonitrile or propylene carbonate). The specific capacitance obtained in the present study is significantly greater than the values reported in the literature for RGO prepared by the other routes. The specific capacitance values at different current density are presented in Fig. 2c. The maximum capacitance of 84 F g⁻¹ was observed at a current density of 10 A g⁻¹ indicating excellent high power capability.

Figure 2d, shows the plot of specific energy vs specific power densities. RGO based symmetric supercapacitor system is capable of delivering maximum energy density of 44 Wh kg⁻¹. At a power density of 8 kW kg⁻¹, the energy density obtained is 15 Wh kg⁻¹. The observed values in the present study are comparatively higher than that of carbon based systems.

The cycling stability of symmetric RGO/RGO cell was subjected to galvanostatic charge-discharge cycling at a specific current density of 0.2 A g⁻¹ (Fig. 3). The capacitance retention of about 86% was obtained after 3000 cycles.

Figure 2. (a) Cyclic voltammograms of the symmetric supercapacitor between 0 to 3 V at different scan rates from 10 to 100 mV s⁻¹. (b) The galvanostatic charge/discharge curves at different current densities. (c) Specific capacitance as a function of different discharge current densities, and (d) The energy density and power density calculated from the data obtained from the charge-discharge experiments.
Figure 3. The cyclic performance of the symmetric supercapacitor in the voltage window between 0 to 3 V at a current density of 0.2 A g\(^{-1}\), and first few charge/discharge cycles (inset).

Conclusions

The RGO sheets were prepared in bulk by a low-temperature thermal exfoliation of GO. A symmetric supercapacitor with cell voltage up to 3 V was studied in a non-aqueous electrolyte. The system delivered the maximum energy and power densities of 44 Wh kg\(^{-1}\) and 8 kW kg\(^{-1}\), respectively.

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References