Graphene-Based Supercapacitor with an Ultrahigh Energy Density

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Summary

Summarized in this manuscript are research results that are of great scientific and technological significance**.**

1. Technologically, the nano graphene-based, ionic liquid-enabled supercapacitor provides a specific energy density of **85.6 Wh/kg** (based on the total electrode weight) at room temperature and **136 Wh/kg** at 80°C, both measured at a current density of 1 A/g (corresponding to a high charge/discharge rate).
    a) These are the highest energy density values ever reported for nano carbon material-based supercapaitors dominated by the electric double layer (EDL) mechanism, with minimal contribution from any redox-type pseudocapacitance mechanism.
    b) These energy density values are comparable to that of the Ni metal hydride battery. This new technology provides an energy storage device that stores nearly as much energy as in a battery, but can be recharged in seconds or minutes. We believe that this is truly a breakthrough in energy technology.
2. Since our research group's 2006 discovery that graphene can be used as a supercapacitor electrode material, scientists around the globe have been making great strides in improving the specific capacitance of graphene-based electrodes. However, the results still fall sort of the theoretical capacitance of 550 F/g. Despite the theoretically high specific surface area of single-layer graphene (up to 2,675 m^2/g), this value has not been achieved in a real supercapacitor electrode due to the high tendency for graphene sheets to re-stack together. To this end, our research has made the following scientific

contributions:

a) In this report, we point out that the best strategy to achieve a high capacitance in graphene-based electrodes is to find a way to effectively prevent graphene sheets from sticking to one another face-to-face.

b) This face-to-face aggregation of graphene sheets can be effectively prevented if **curved graphene sheets** (instead of flat-shaped) are prepared.

c) We further confirm that this curved graphene morphology enables the formation of mesopores (> 2 nm) that are readily accessible and wettable by ionic liquids, which are significantly larger in molecular size than, for instance, KOH or H_2O in the conventionally used aqueous electrolyte. In order to take advantage of the high operating voltage of ionic liquids (> 4 volts), the pore sizes must be sufficiently large to let the ionic liquid enter the pores and form double layers of charge therein.

Some Experimental Details

Synthesis of Graphene Oxide

Graphene oxide was synthesized according to a modified Hummers method. As an example to illustrate the process, 65 mL 98% sulfuric acid was slowly added to a mixture of 5 grams of natural graphite and 2.5 grams of sodium nitrate in an ice water bath. Then, 15 grams of potassium permanganate was added, one small amount at a time. The oxidation of the mixture was allowed to proceed overnight. The mixture was diluted to 1 L, and 30% hydrogen peroxide was added slowly to quench excess potassium permanganate to give a greenish yellow suspension. The suspension was injected into a forced convention oven in which a stream of compressed air was introduced to produce a fluidized-bed situation. Upon removal of the solvent or liquid, we obtained the desired curved graphene sheets.

Fabrication of Electrode

The pH value of 1 L graphene oxide suspension (1 g/L) was tuned to 10 by 2M sodium hydroxide solution. Subsequently, 0.2 mL hydrazine monohydrate was added and the mixture was heated to 95°C and held for 2 hours. Then it was filtered and dried at vacuum oven to form graphene powder. The electrode material was coated on Al foil. The compressed electrode was dried in a vacuum oven at 120°C for 12 hours before use. Coin-size capacitor cells were assembled in a glove box using EMIMBF$_4$ ionic liquid electrolyte.

Electrochemical Testing

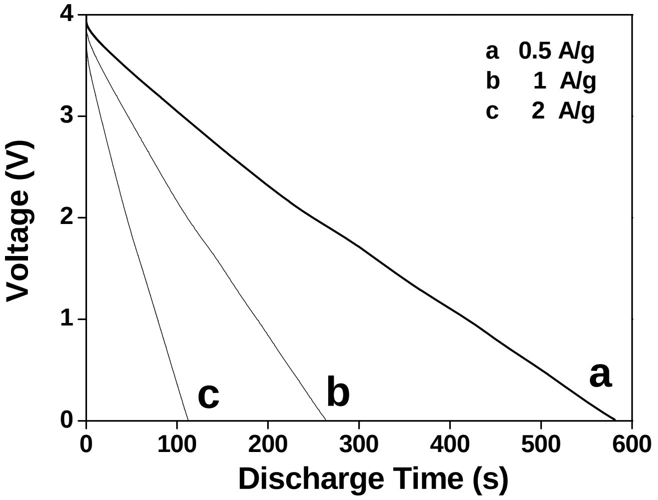
The specific capacitance was measured with galvanostatic charge/discharge tests using an Arbin SCTS system. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were conducted on a CH Instruments electrochemical workstation. The capacitance was calculated according to $C = (I \times \Delta t)/\Delta v$, where I is the constant discharging current, Δv is the voltage difference from 60% to 40% of the discharge voltage range, and Δt is the time required to go from 60% to 40% of the discharge voltage range.

Characterization of Mesoporous Graphene Nanostructure

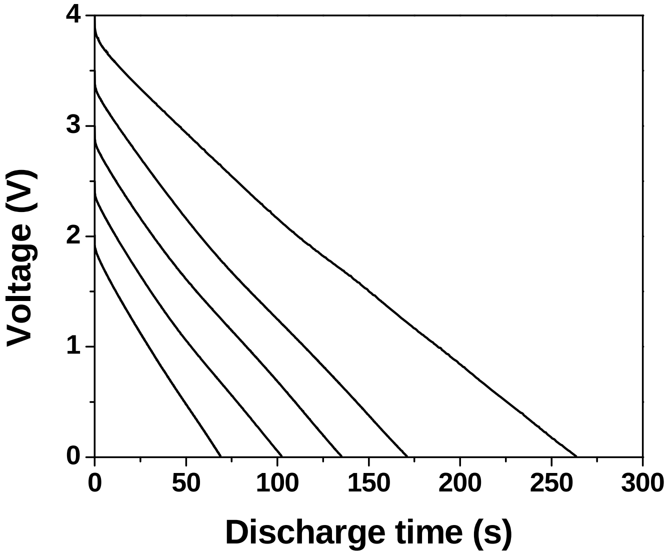
To analyze the surface area of the mesoporous graphene nanostructure, low-temperature nitrogen sorption experiments were performed by using a volumetric adsorption apparatus (Quantachrome Instruments). The volume of mesopores was derived from the data of BJH pore size distribution.

2. Results and Discussion

Supercapacitor performance



(a)



(b)

Figure S1. (a) Discharge curve at 0.5, 1 and 2 A/g current density, and (b) discharge curve at 1 A/g and 2, 2.5, 3, 3.5 and 4 V, using $EMIMBF_4$ ionic liquid electrolyte. Each electrode is 6.6 mg.

From the charge/discharge curve shown in Figure S1a at various current densities we obtained an energy density of 76.3, 85.6 and 90 Wh/kg at 2, 1 and 0.5 A/g current density, respectively. The value changes little with the variation in current density. From the discharge curve comparison of different charging voltages from 2 to 4 volts in Figure S1b, the straight discharge lines are nearly parallel to each other, indicating the good double layer performance.

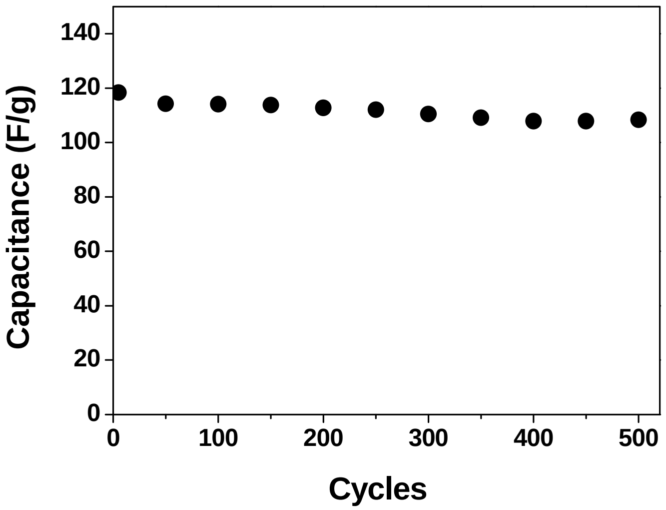


Figure S2. The specific capacitance change at a constant current density of 4 A/g as a function of cycle number of graphene.

Figure S2 indicates that the specific capacitance of the graphene supercapacitor decayed at a relatively slow rate. After 500 cycles, the initial specific capacitance was decreased less than 10%, indicating a good cycle life. Further improvements in cycle stability can be obtained if the electrode material compositions are further improved. It can be found that, even at a current density as high as 4 A/g, the energy density stills maintains a high value of 60 Wh/kg.

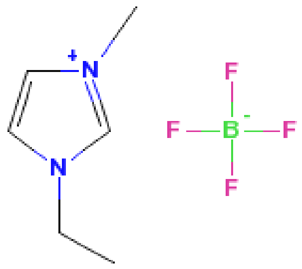


Figure S3. The molecular structure of the ionic liquid, $EMIMBF_4$.

The ionic liquid is composed of BF_4^- and its counter-ion $EMIM^+$. The motion (relocation and re-orientation) of these molecular-scale ionic species is responsible for the formation and dissociation of the double layers.

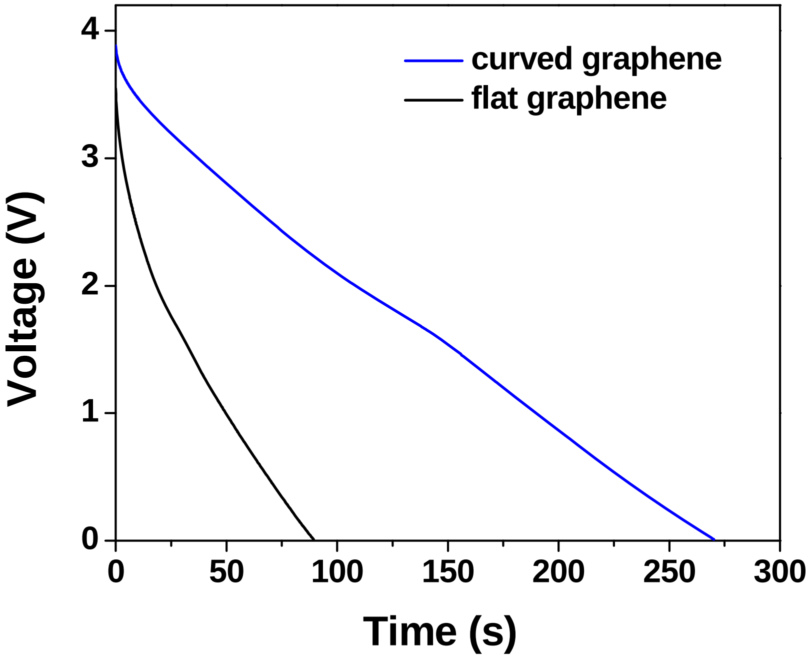


Figure S4. Discharge curves of the curved graphene electrode and the usual flat graphene electrode. Galvanostatic charge/discharge tests were conducted between 0-4 V at 1 A/g.

In order to investigate the effects of graphene morphology on cell performance, two different types of graphene material, curved and flat graphene, have been compared. The capacitances calculated from the discharge curves are 158 F/g and 48 F/g, respectively. The curved graphene sheet morphology appears to be capable of preventing graphene sheets from closely re-stacking with one another when they are packed or compressed into an electrode structure. Thus, it can maintain a mesoporous structure with a higher specific surface area of 500.6 m^2/g, which is good for electrochemical accessibility of the electrolyte and a fast diffusion rate. In contrast, the flat graphene sheets (Figure 1 (b) in the main text) prepared by conventional chemical routes tend to restack with one another face-to-face, effectively reducing the useful surface area to an average specific surface area 183.8 m^2/g. With inter-layer gaps less than 1 nm in the restacked graphene, there is insufficient space for ionic liquid diffusion, leading to poor capacitance performance. The flat shape of graphene and graphene oxide sheets is intrinsically unstable thermodynamically. This implies that a small driving force during the drying process might be all what it takes to produce curved graphene. The sheet has a tendency to get curved up from its edges if the sheet is allowed to be in a free-standing state (not supported by a solid substrate or other sheets). This can be accomplished by drying graphene oxide sheets under a gaseous flow condition (e.g. in a fluidized bed).