# Evaporative assembly of graphene oxide for electric double-layer capacitor electrode application

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## ABSTRACT

Graphene reduced from graphene oxide (r-GO), a potentially low-cost way of obtaining a large quantity of graphene, faces many challenges and concerns, including the challenge to retain nanoscale properties after processing and the associated environmental, safety and health concerns. This study explored the method of processing graphene oxide (GO) into microparticles by spray drying as an intermediate step for fabricating electric double-layer capacitor electrodes. We prepared GO microparticles by spray drying an aqueous solution of GO and then thermally reduced GO to r-GO. The r-GO microparticles, with a size of ~1–2 μm, had a corrugated surface morphology with alternating grooves and ridges, a microstructure resembling that of crumpled paper. Electrochemically, r-GO compared well to nano-sized activated carbon which was used as a reference. Furthermore, r-GO retained most of its specific capacitance at high current densities, mostly due to the corrugated surface morphology of r-GO microparticles. The results suggest that spray drying, a scalable manufacturing method, is a simple and promising way of processing GO for EDLC electrode application. Future research should focus on improving the surface area for high specific capacitance by mitigating the stacking of GO during spray drying.

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## 1. Introduction

Graphene received lots of attentions for electric double-layer capacitor (EDLC) application due to its outstanding properties including chemical and electrochemical stability, electrical conductivity, and high theoretical surface area (2630 m$^2$/g) [1,2]. A relatively low cost source of graphene is graphene oxide (GO), prepared by thermochemical exfoliation of graphite powder [3–7]. GO can be easily reduced to graphene (r-GO) for use as the EDLC electrode material by subsequent thermal, chemical, or flash reduction [8–11].

The GO produced by thermochemical exfoliation contains a single or a few GO layers with a thickness on the order of ~1 nm and lateral dimensions in sub-micron ranges [7,12–14]. Due to the small dimensions of GO, the processing of GO into various usable structures is a challenge. Filtration of GO dispersion through a membrane filter has been employed [2,12,14]. But this method invites some issues such as excessive stacking of GO due to van der Waals force [14] and capillary force, which undermine high surface area and electrochemical properties. Also, there are environmental, safety and health concerns in the handling of GO in its nanoscale form, as GO is potentially cytotoxic [15,16].

In this work, we studied the evaporative assembly of GO via spray drying, which has been widely used for processing ceramics, drugs, and food ingredients as a simple way of forming microparticles [17]. Small liquid droplets with GO dispersed inside were generated and dried during spray drying to form micrometer-sized GO particles which were expected to have much less handling related issues compared to the nano-sized GO. Since a certain degree of stacking of GO was predicted in the GO microparticles due to the evaporative nature of the spray drying process, the nanostructure of r-GO microparticles was characterized and electrodes from r-GO microparticles were electrochemically tested to assess the overall practicality of spray drying as a processing method for GO.

## 2. Experimental

### 2.1. Materials

Solid graphene oxide powder, prepared by a modified Hummer's method, was purchased from a commercial source (Cheap Tubes). The solid was mixed with de-ionized (DI)water at a concentration of 5 mg/mL. The mixture was then subjected to pulsed ultrasound treatment (Ultrasonic processor CPX 600, Cole-Parmer) for 20 min in a water-ice bath. The GO dispersion prepared by this procedure is a stable suspension, as shown in Fig. 1A. The size of the GO, measured using dynamic light scattering (Zetasizer Nano Series, Malvern Instruments), is on the order of hundreds of nanometers, as shown in Fig. 1B.
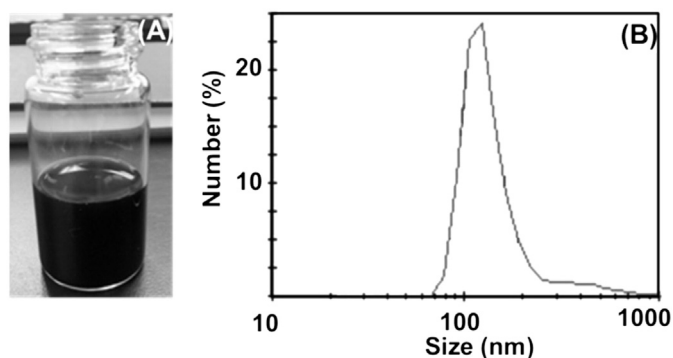
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**Fig. 1.** Stable aqueous suspension of graphene oxide (GO): (A) image of GO dispersion with a concentration of 0.5 mg/ml and (B) dynamic light scattering measurement of the size of GO.

Commercially available EDLC grade nano-sized activated carbon (DLC Super 30, Norit) was obtained as a control material for electrochemical performance measurements. The activated carbon has a reported surface area of 1400 m²/g and an average particle size of 6.3 μm [18].

### 2.2. Preparation of GO microparticles

The GO dispersion prepared above was atomized and sequentially dried using a commercial laboratory scale spray dryer (B-190 Mini Spray Dryer, Buchi). Droplets were produced using a pneumatic nozzle (cap diameter ~1.5 mm) at a gas pressure of 345 kPa. The inlet temperature was set to 120 °C and outlet temperature was read at 80 °C. The aspirator in the spray dryer was set to 100%. A flow rate of 2.74 mL/min was used to feed the dispersion to the spray dryer. GO microparticles were separated from the gas flow by a cyclone and collected in an electrically grounded container. The GO microparticles were thermally reduced at 225 °C for 12 h in air to convert them into r-GO microparticles.

### 2.3. Fabrication of electrodes and EDLC devices

The r-GO microparticles were mixed with an aqueous suspension of polytetrafluoroethylene (PTFE, 60 wt.% dispersion in H₂O, Sigma-Aldrich) which was used as a binder to form a paste with a composition of 95 wt.% r-GO and 5 wt.% PTFE. The paste was applied to titanium foil current collectors and pressed. The newly pressed electrodes and current collectors were soaked by 1 M sulfuric acid electrolyte.

A full-cell experimental EDLC was assembled from the r-GO electrodes and current collectors by stacking them with a Celgard 3401 membrane separator. The EDLC assembly were then sealed using a laminated heal-seal material (Shield Pack barrier liners, Bemis). Identical procedures were also used to assemble a control EDLC device with similar loading and dimension using activated carbon Norit DLC Super 30.

### 2.4. Characterization

The r-GO microparticles were characterized using a field-emission scanning electron microscope (FE-SEM, Auriga CrossBeam Workstation, Carl Zeiss) and a transmission electron microscope (TEM, CM20, Philips). Brunauer–Emmett–Teller (BET) surface area and pore properties were determined from multipoint N₂-physisorption measurement at 77 K using a physisorption analyzer (Autosorb iQ, Quantachrome Instruments). The electrochemical performance of the EDLCs was characterized with cyclic voltammetry (CV) and constant current charge/discharge measurements (Model 4304 system, Maccor).

## 3. Results

### 3.1. Structure of r-GO microparticles

GO microparticles were prepared from GO aqueous solution by spray drying. r-GO microparticles, with a size of ~1–2 μm, were obtained after GO microparticles were thermally reduced at 225 °C. The r-GO microparticles exhibited corrugated surface morphology with alternating grooves and ridges, as shown in the SEM images (Fig. 2A and B). The surface of the microparticles seemed to mainly consist of the planar surfaces of GO as the ridges on the microparticles appeared smooth. We observed that the r-GO microparticles had similar size and surface morphology compared to those of non-reduced GO microparticles.

A TEM image (Fig. 2C) indicated that the microparticles had collapsed shells without an internal solid core. The non-uniformity of the thickness shown from the TEM image was mostly due to the corrugated surface morphology of the microparticles. Fig. 2D compares the electron diffraction pattern from the microparticles (left) to that of amorphous carbon support on the TEM grid (right). The clearer rings from r-GO microparticles implied that there was a certain degree of crystallinity of the material.

The N₂ adsorption/desorption isotherm of the r-GO microparticles is shown in Fig. 3A. The adsorption isotherm was comparable to what was reported for corrugated graphene sheets [19]. BET surface area of the material was measured to be 385 m²/g. The pore size distribution of r-GO particles is shown in Fig. 3B. The peak at 1 nm was most likely corresponding to the inter-nanosheet spaces in the r-GO due to staking. The pores in this size range had a small contribution to the overall pore volume. The pores with most of the pore volume are pores >4 nm.

### 3.2. Electrochemical performance of r-GO microparticles based electrodes

As shown in Fig. 4A, r-GO microparticle-based electrodes exhibited fairly rectangular CV curves (from −0.1 V to 0.9 V) at scan rates in the range of 0.02 to 0.5 V/s, a characteristic of pure double layer capacitance mechanism. The specific capacitance ranged from ~40 F/g to 75 F/g based on the CV curves (Fig. 4B). In comparison, the specific capacitance of activated carbon tested at the scan rate of 0.02 V/s was 72 F/g.

A segment of the galvanostatic measurement from 0 V to 0.6 V window is shown in Fig. 4C. The retention of capacitance of the electrodes was determined from the charge/discharge curves. At a constant scan rate of 0.1 V/s, the specific capacitance decreased initially and began to stabilize after ~2000 cycles (Fig. 4D).

The effect of current density on the specific capacitance is shown in Fig. 4E. At a current density of 0.1 A/g, the r-GO electrodes had a capacitance of ~100 F/g. As the current density increased from 0.1 A/g to 0.56 A/g, the specific capacitance decreased to 65 F/g. The capacitance response from activated carbon is also shown in Fig. 4E. The current density had a severe effect on the specific capacitance of activated carbon, which was reduced at about 70% when the current density was increased from 0.1 A/g to 0.56 A/g. For the same current density, the r-GO electrodes exhibited higher specific capacitance than the activated carbon electrodes.

The galvanostatic charging/discharging curves (Fig. 4C) were fairly linear. The discharge slopes of the charge/discharge curves were used to estimate the specific energy and power density, plotted in Fig. 4F. The highest energy density of 3.52 Wh/kg was achieved at a power density of 0.09 kW/kg and the highest power density of 0.44 kW/kg was obtained at an energy density of 2.26 Wh/kg.

## 4. Discussion

The r-GO microparticle-based electrodes had a specific capacitance of 75 F/g at the scan rate of 0.02 V/s. This is a very promising value, compared to the specific capacitance obtained from activated carbon used in this study as a reference material and to graphene oxide derived