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Original Research

# Influence of graphene microstructures on electrochemical performance for supercapacitors

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**Abstract**

The influence of variant graphenes on electrochemical performance for supercapacitors was studied comparatively and systematically by using SEM, FTIR and Raman spectroscopy, cyclic voltammetry (CV), galvanostatic charge/discharge and electrochemical impedance spectroscopy (EIS). The results revealed that: 1) the nitrogen-doped graphene (N-G) electrode exhibited the highest specific capacitance at the same voltage scan rate; 2) the specific capacitance of the N-G reached up to 243.5 F/g at 1 A/g, while regular graphite oxide (GO) was 43.5 F/g and reduced graphene oxide (rGO) was 67.9 F/g; 3) N-G exhibited the best supercapacitance performance and the superior electrochemical properties, which made it an ideal electrode material for supercapacitors.


*Keywords:* Graphene; Nitrogen doping; Microstructure; Supercapacitor

## 1. Introduction

As a new type of energy storage devices, supercapacitors exhibit both high capacitance and large energy density, which bridge the gap between conventional capacitors and rechargeable batteries, and have advantages in applications, such as electronic communication, transportation, aerospace and other fields [1–3]. Electrode materials are the key component of supercapacitor, and determine its main performance parameters [4–7]. Recently, graphene, a new carbon material with one-atom thick layer 2D structure, has been recognized as an ideal material for electrochemical energy storage, due to its unique properties of high electrical conductivity, large surface area, and chemical stability, etc. [8–12].

Some researches have been reported about the graphene-based supercapacitors. Rao and his co-workers [13] prepared graphene by three methods and compared their capacitive behaviors. With aq. $H_2SO_4$ as the electrolyte, the specific capacitance of samples prepared by exfoliation of graphite oxide reached up to 117 F/g, while samples prepared by transformation of nano-diamond and the decomposition of camphor had lower values as 35 F/g and 6 F/g. Stoller et al. [14] synthesized chemical modified graphene by reducing graphene oxide sheets with hydrazine hydrate, and its specific capacitances were 135 F/g and 99 F/g in aqueous and organic electrolytes respectively. Chen et al. [15] fabricated the graphene with few layers by using hydrobromic acid as reductant, and the maximum specific capacitance reached to 348 F/g, which was the highest value of the chemical modified graphene so far. Jeong et al. [16] developed supercapacitors based on nitrogen-doped graphene, which exhibited a specific capacitance up to 280 F/g, i.e. about 4 times higher than that of pristine graphene. Thus it can be seen that the graphene sheets with different types or microstructures have great influences on the performance of supercapacitors.

In this paper, variant graphenes involving graphite oxide (GO), reduced graphene oxide (rGO) and nitrogen-doped graphene (N-G) were prepared and their microstructures have been characterized. Then these graphenes were fabricated as electrode materials of

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supercapacitors. For comparisons, their electrochemical properties including cyclic voltammetry (CV), galvanostatic charge/discharge and electrochemical impedance spectroscopy (EIS) were measured under the same experimental conditions. Clearly, the influences of the different graphene microstructures on electrochemical performance for supercapacitors were deeply revealed, and it is expected to provide the theoretical and experimental basis for further study on graphene-based energy storage devices.

## 2. Experimental

### 2.1. Preparation of graphite oxide

Graphite oxide (GO) was synthesized from natural graphite powders by a modified Hummers method [17] including following steps : 1) A pretreatment was used to obtain GO with fully oxidation and less impurities, i.e., graphite powder (1.0 g), $K_2S_2O_4$ (0.5 g) and $P_2O_5$ (0.5 g) were mixed into concentrated $H_2SO_4$ (2–4 mL), and the mixture was continually stirred in 80 °C water bath for 6 h, and then the product was filtrated by deionized water for several times and dried at 60 °C. 2) The pre-oxidized graphite was dispersed into 30 mL 98% $H_2SO_4$, and then 4 g $KMnO_4$ was slowly added while stirring and cooling with ice-water bath. 3) The solution was transferred into 35 °C water bath. 4) 30 mL deionized water was added into the solution after 2 h, and maintained in the temperature range of 80–90 °C for 1 h. After that, 30% $H_2O_2$ solution was added until the color of the suspension turned to bright yellow. 5) The GO was finally obtained after pickling, washing, filtration and drying.

### 2.2. Preparations of graphene and N-doped graphene

#### 2.2.1. Preparations of graphene

1) 0.5 g of the prepared GO was dispersed into 1 L deionized water with the aid of ultrasonication to obtain 0.5 mg/mL GO dispersion. 2) 30 mL of the dispersion was put into a Teflon lined stainless-steel autoclave, and then the autoclave was sealed and maintained at 180 °C for 3 h in an electric oven. 3) The product was collected and washed with deionized water for several times, followed by drying at 80 °C to obtain reduced GO.

#### 2.2.2. Preparations of N-doped graphene (N-G)

1) Taking out 30 mL of the prepared GO dispersion and adding the ammonium hydroxide as the nitrogen dopant. 2) After stirring for 30 min, the resultant mixture was transferred into a Teflon lined stainless-steel autoclave, and treated under the same experimental conditions as above. 3) Finally, the black product was collected and washed with deionized water for several times, followed by drying at 80 °C to obtain N-G.

### 2.3. Characterizations

The microstructures and morphologies of the samples were characterized by using the following facilities of scanning electron microscope (SEM, S-4800, Hitachi, Japan); transmission electron microscope (TEM, JEM-2010, JEOL, Japan); X-ray photoelectron spectroscope (XPS, ESCALAB 250Xi, Thermo Fisher Scientific, USA) with Al Kα radiation of 1486.6 eV as the excitation source; Fourier transform infrared (FTIR) spectrometer with scanning range of 400–4000 $cm^{-1}$ (FT-IR, Nicolet iS10, Thermo fisher, USA) and laser scanning confocal micro-Raman spectrometer (LabRAM HR, HORIBA, France) with a laser excitation wavelength 488 nm and scans on an extended range (1000–3000 $cm^{-1}$).

### 2.4. Electrode preparation and electrochemical measurements

#### 2.4.1. Electrode preparation

Nickel foam was used as the current collector, and electrode materials were GO, rGO and N-G. The preparation process was as follows: 1) Nickel foam was cut into rectangle sheets (20 mm*10 mm); 2) the mixture containing 80 wt% active material, 10 wt% conductive carbon black and 10 wt% PVDF was well mixed with appropriate amount of N-methyl-2-pyrrolidone (NMP), and grinded for 1 h to obtain the dark paste; 3) the paste was casted on nickel foam and dried in a vacuum oven at 80 °C for 12 h; 4) finally, the electrode was obtained by pressing at 10 MPa for 1 min. The mass of active materials on each working electrode was about 1.5 mg.

#### 2.4.2. Electrochemical measurements

All the experimental measurements were carried out in a three-electrode system, in which the nickel foam as working electrode, platinum as counterelectrode, and saturated calomel electrode (SCE) as reference electrode, and 6 M KOH was used as aqueous electrolyte solution. The electrochemical performances involving cyclic voltammetry (CV), galvanostatic charge/discharge and electrochemical impedance spectroscopy (EIS) were measured by using the Electrochemical Working Station (CHI660D, Shanghai Chenhua, China). The cyclic voltammetry (CV) was recorded with a voltage range from −0.1 V to −1.1 V, and the electrochemical impedance spectroscopy (EIS) was recorded in the frequency range of 0.1–100,000 Hz by applying an AC voltage with 5 mV perturbation.

## 3. Results and discussion

### 3.1. Microstructures characterizations of graphenes

Fig. 1 shows the SEM and TEM images of the GO, rGO and N-G. Clearly, graphite oxide (GO) showed single or a few layer microstructure with wrinkles and defects on the surface, which may be due to large amount of functional groups, such as hydroxyl, carboxyl on the edge, and carboxyl and epoxide groups in the inner part. These groups expanded the interlayer distance of graphite, and destroyed its integrated layer microstructure, which resulted in the wrinkle phenomenon. However, the reduced graphene oxide (rGO) presented a different morphology as fluffy and transparent layers with rich wrinkles and fluctuation. The fluctuation was essential to sustain the thermodynamic stability of graphene, due to its 2D crystal structure. These disordered graphene sheets could connect as a 3D porous network, which was conducive to the contact of electrolyte and electrode materials. Comparing to regular graphene, the nitrogen-doped graphene (N-G) exhibits the similar microstructure, such as, fluffy