Freestanding and flexible Graphene wrapped MnO_2/MoO_3 nanoparticles based asymmetric supercapacitors for high energy density and output voltage

Supporting Information

Experimental section

Fabrication of Graphene Oxide (GO) Synthesis:

GO was prepared by oxidation of natural graphite powder by using a modified Hummers' method[1]. Briefly, sulfuric acid (23 mL) was stirred at ice-bath and the mixture of graphite(1 g) and sodium nitrate(0.5 g) was added. Potassium permanganate(3.0 g) was added slowly under vigorous agitation, it is very important to keep the temperature of suspension lower than 10℃. Successively, 35℃ of water-bath will be need for the reaction system for 2 h until it was formed a thick paste. Under vigorous agitation, deionized water(46 mL) was added continuously and slowly to keep the temperature lower than 98℃, after finish it, the reaction system was transferred to 98℃ oil-bath for about 15 min ,turning the color of the solution from brown to yellow. 300 mL 3% hydrogen peroxide solution was added to make graphite powder oxidation more fully for 30 min. The resulting solution was filtered and washed with 3% HCl aqueous solution (300 ml).The resulting solid was dispersed in water by ultrasonication for about 1.5 h to make a GO aqueous dispersion (1 mg/mL).

Fabrication freestanding Graphene/MnO_2 films:

It is easy to prepare the MnO_2 nanoparticles by modified hydrothermal reduction method.[2] Briefly, 0.5 g $KMnO_4$ dissolve in 30 ml deionized water, then 10 ml ethylalcohol add to the solution under mild mechanical stirring, the MnO_2 nanoparticles are obtained after vacuum suction filtration, and then wash 3 times with deionized water. After completely dry, the particles are grinded 30 min until black powders become homogeneous. 25ml GO solution (1 mg/ml) is added in 100 ml (0.2 mg/ml) MnO_2 dispersion liquid under suitable stir, turbid liquid is heat at 95℃ to pre-reduced. The Flexibility of final samples relate to the pre-reduced time (Fig. 1). After then, freestanding film will be get by vacuum suction filtration.

Fabrication freestanding Graphene/MoO_3 films:

The MoO_3 powers are dispersion by ultrasonic treatment, then the turbid liquid is filtrated and washed by deionized water to remove impurities. The resulting solid was dispersed afresh in water to make a MoO_3 nanoparticles aqueous dispersion (0.8 mg/ml). Then, 25ml GO solution (1 mg/ml) was added under mild mechanical stirring. After pre-reduced 10 h, the freestanding MoO_3@GO film is obtained after vacuum suction filtration.

Fabrication flexible Asymmetric supercapacitors

When the films are dried completely, they are cut to a suitable area, all

films are prepared by annerling at 500℃ for 2h in Ar_2 atmosphere to reduce graphene oxide. After then, they are cut to a suitable area and then coated on the Polyethylene terephthalate oxalic ester (PET). The MnO_2@rGO positive electrode and MoO_3@rGO negative electrode were pressed together and separated by a porous filter separator with 1 mol LiCl electrolyte.

Characterization and electrochemical measurement

The morphologies, structure, and chemical composition of the samples are characterized by high-resolution field emission SEM (FEI Nova Nano-SEM 450), TEM(FEI Titan G2 60-300), and XRD (PANalytical B.V. X'Pert PRO). All the electrochemical measurements are carried out in a two-electrode system at room temperature using Autolab PGSTAT302N (Metrohm AG) with 1 mol LiCl electrolyte. The electrochemical impedance spectroscopy is carried out at 10 mHz to 100 kHz with a potential amplitude of 10 mV. The electrochemical tests of the individual electrode are performed in a three electrode cell, in which carbon electrode and Ag/AgCl electrode was used as the counter and reference electrodes, respectively. The electrochemical measurements of the ASC were carried out in a two electrode cell at room temperature in 1 M LiCl electrolyte. All of the above electrochemical measurements are carried out by a biologicMP3 electrochemical workstation.

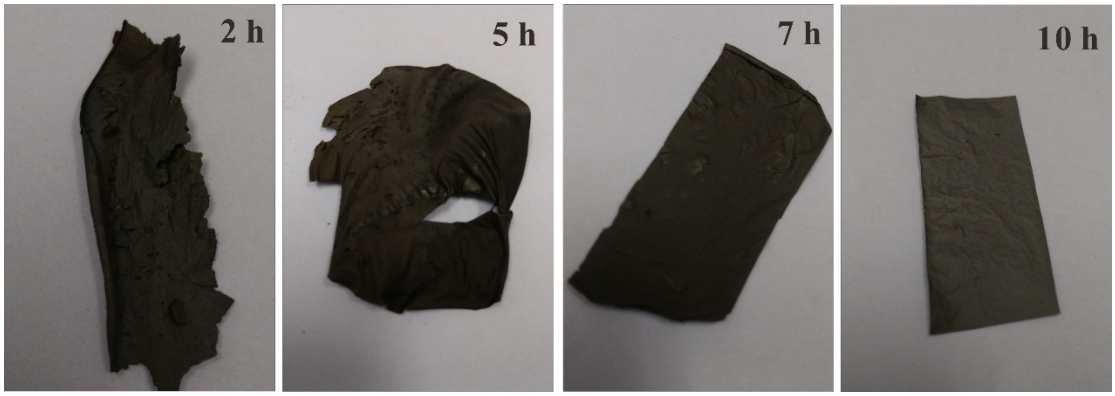

Fig.1 The influence on freestanding film by different time

Electrochemical impedance spectroscopy study analysis of the electrode materials

In order to characterize the conductivity, we draw two curves of electrochemical impedance spectroscopy study analysis about MnO_2@rGO and MoO_3@rGO. Fig.2 shows the Nyquist plots of MnO_2@rGO and MoO_3@rGO films and Modeled equivalent circuit of electrochemical impedance spectroscopy. The frequency range from 100 kHz to 0.01 Hz. In the equivalent circuit, a solution resistance (R_S) connects in series with a constant phase element (CPE), and the CPE connects in parallel with the charge transfer resistance (R_{CT}) and pseudocapacitance (C_P). The solution resistance refers to the resistance from the electrolyte, the CPE account for the double –layer capacitance and the charge transfer resistance (also called Faraday resistance) corresponds to the total resistance at the interface between the electrode an the electrode. Experimental results show that R_S is insensitive to the

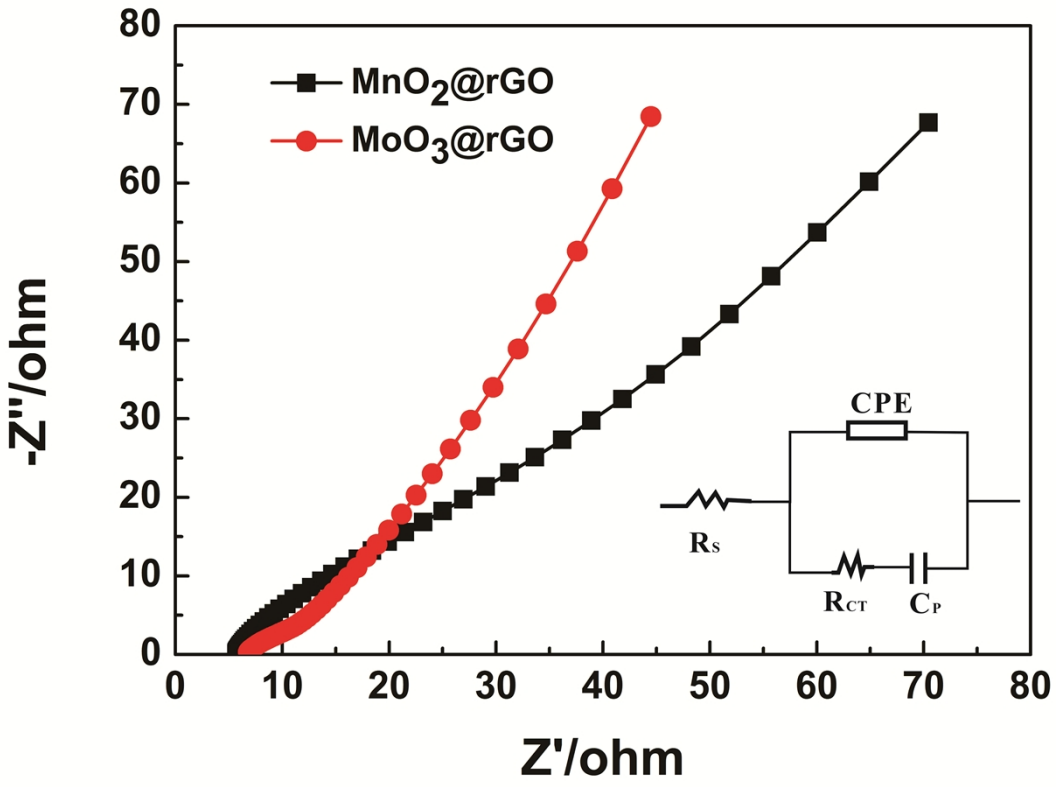

Fig.2 Nyquist plots of MnO_2@rGO and MoO_3@rGO films and Modeled equivalent circuit of electrochemical impedance spectroscopy.

surface condition of the electrode[3]. According to Nyquist plots, for MnO_2@rGO film, the value of R_S is around 6 Ω; for MoO_3@rGO film, the value of R_S is around 7 Ω.

Mechanical strength of the electrode materials

In order to characterize the flexibility of electrode materials, we design the experiment about the influence of deformation effect on resistance. Fig.3 display the photographs of MnO_2@rGO film and MoO_3@rGO film. Fig.3c and d show only 1% change of total resistance of MoO_3@rGO film. For MnO_2@rGO film, Fig.3e and f reveal 7.8% change of total resistance .They are all show good electrical performance with 180° deformation.

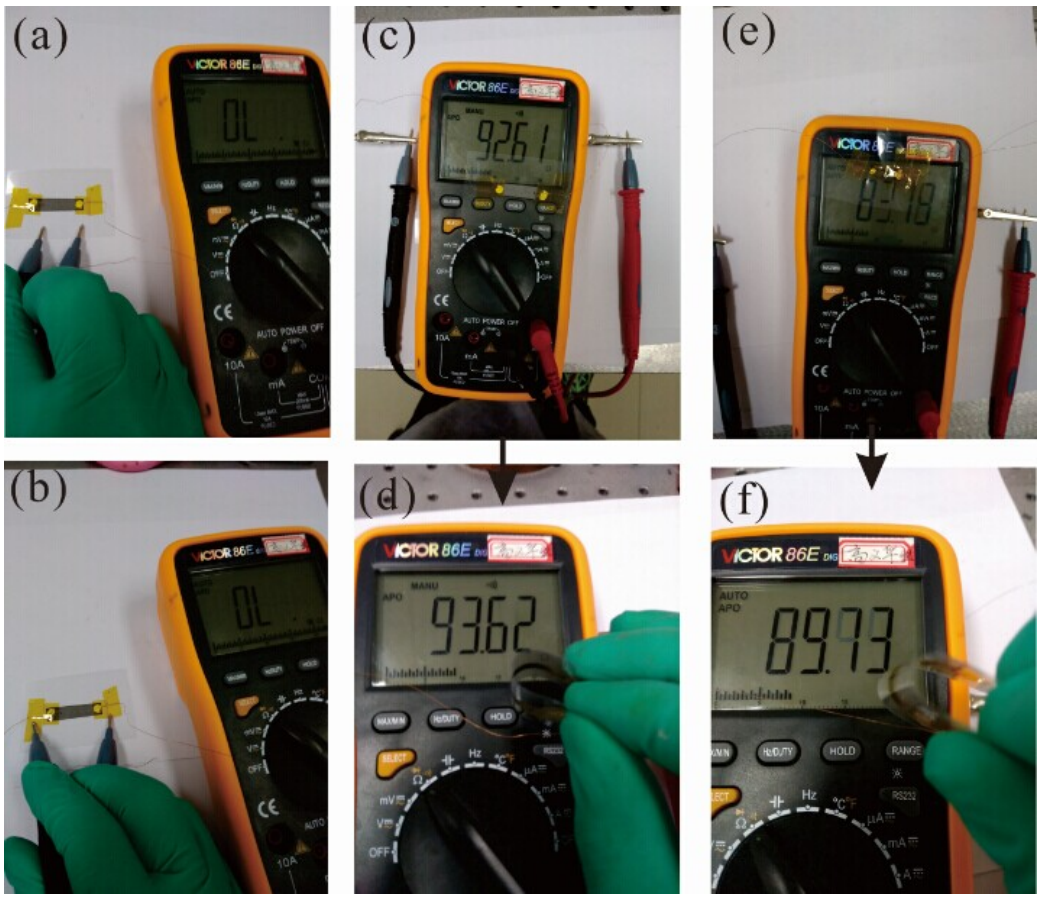

Fig.3 The influence of deformation on resistance.

Notes and references

[1]. Li, C.; Shi, G., Functional Gels Based on Chemically Modified Graphenes. *Advanced materials* **2014**.

[2]. R. Jiang, T. H., Y. Tang, J. Liu, L. Xue, J. Zhuang and A. Yu,Electrochimica Acta, Generation of B-Doped Graphene Nanoplatelets Using a Solution Process and Their Supercapacitor Applications. *ASC Nano* **2009,** *7* (1), 7173-7179.

[3]. Wei Chen, R. B. Rakhi, Liangbing Hu, Xing Xie, Yi Cui, and H. N. Alshareef, *Nano Lett.,* **2011,** 11 (12), 5165–5172