

A simple two-step electrochemical synthesis of graphene sheets film on the ITO electrode as supercapacitors

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Abstract In this study, a simple and controllable two-step electrochemical process is described for the synthesis of graphene sheets (GS) film on a cleaned indium tin oxide (ITO) sheet electrode. Namely, the main procedures involve the electrophoretic deposition (EPD) of graphene oxide (GO) film onto ITO electrode and the subsequent in situ electrochemical reduction (ECR) of GO to generate GS film. X-ray photoelectron spectroscopy (XPS) measurement demonstrates that most of the oxygen-containing functional groups in GO film have been removed after ECR. By electrochemical measurements, the maximum specific capacitance of the prepared GS film electrode was calculated to be 156 F g^{-1} , besides, the capacitance retention of the material remained 78% after 400 times of cycling, showing a promising prospect as supercapacitor materials.

Keywords Graphene sheets · Electrophoretic deposition · Supercapacitors

1 Introduction

Supercapacitor (also called electrochemical capacitor, electric double layer capacitor, EDLC), one of the most promising power energy storage systems, has aroused wide interests because of its potential applications ranging from mobile devices to electric vehicles. As the third generation commercial supercapacitors, carbon-based materials including activated carbon, carbon nanotubes, carbon fibers, and graphene sheets (GS), are widely employed and exhibit much higher capacitance compared with the conventional capacitors [1–5]. Among these, GS, an intriguing novel two-dimensional carbon material, has attracted more and more attention because of its unique properties such as high-surface area (the theoretic surface area of a single GS is about $2630 \text{ m}^2 \text{ g}^{-1}$), excellent mechanical stiffness and flexibility, as well as exceptional electrical properties [6–8]. Thus, GS has been considered as the high-performance electrochemical supercapacitor materials. However, it is rather difficult to obtain GS films on a conductive substrate via solution phase deposition due to bad dispersion of GS and poor adhesion to substrate. Therefore, developing a convenient and efficient route to produce GS film on the conductive substrate as supercapacitor is still a challenge. Fortunately, the GS film on an indium tin oxide (ITO) sheet electrode has been realized via electrophoretic deposition (EPD) technique and the subsequent in situ electrochemical reduction (ECR) process; [9–14] however, the electrochemical properties of the obtained films have not been referred to and need further groove for.

In this study, by combining EPD process with in situ ECR of the GO, GS film has been achieved on the ITO sheet successfully, which was confirmed by X-ray photoelectron spectroscopy (XPS) investigation and field emission scanning electron microscope (FE-SEM) observation;

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and then, the electrochemical properties of the obtained GS films are measured and analyzed in detail by characterizations of cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), and chronopotentiometry measurements.

2 Experimental section

In this study, GO was firstly prepared based on the previous report [9]. A cleaned ITO conductive glass sheet and a stainless steel plate were employed as the positive electrode and the negative electrode, respectively. EPD technique was applied to fabricate GO films on the ITO electrode. Under an applied potential of 150 V for 45 s, the GO films were deposited in the GO aqueous suspension with the concentration of 0.6 mg mL^{-1} at the room temperature. At last, in situ ECR of GO was performed on a CHI660C electrochemical workstation in the 0.1 M KCl aqueous solution by the constant potential reduction method.

The surface morphology and microstructure of the prepared samples were investigated by characterizations of FE-SEM (JSM-6701F) and XPS (PHI-5702, Physical Electronics, USA). CV and EIS measurements were performed with a CHI660C electrochemical workstation using a three electrode system. GS film-coated ITO sheet, platinum wire, and Ag/AgCl electrode were employed as working electrode, counter electrode, and reference electrode, respectively. The electrolyte is 0.1 M Na_2SO_4 solution. EIS was recorded under the following conditions: AC voltage amplitude of 5 mV, frequency range of 10^5 –0.01 Hz, and open circuit potential. Galvanostatic charge/discharge testing was carried out from -0.2 to 0.8 V at different current density using CHI660C electrochemical workstation and Land Battery workstation.

3 Results and discussion

Owing to the existence of plentiful of polar oxygen-containing functional groups on the edges and planar surfaces of the individual GO sheets, [15, 16] a stable and well-dispersed GO aqueous suspension with brown color can be achieved with the aid of ultrasonication, as clearly shown in Fig. 1a. Measured with a Zetaplus analyzer, the zeta potential of GO aqueous suspension is about -64.7 mV at pH 7.0. Making use of EPD technique, the GO film was successfully deposited on the surface of the positive ITO electrode. Then, constant potential reduction process was applied to obtain the GS film. Namely, after

ECR process, the brown and semi-transparent GO film on ITO electrode was changed to black GS film (Fig. 1a). On the other hand, it is obvious from Fig. 1b that a typical electrochemical irreversible reaction has been occurred, demonstrating the GO has been reduced into GS successfully.

From FE-SEM images of GO and GS films shown in Fig. 2a and b, there is almost no substantial difference between them although there are more new edges and fractures generated on GS film. Figure 2a1 gives the C1 s XPS spectrum of GO film, indicating a considerable degree of oxidation occurs. Obviously, the C1 s peaks are composed of four components, corresponding to carbon atoms in different functional groups: the nonoxygenated ring C=C/C–C (284.8), C–O (hydroxyl and epoxy, 286.3 eV), C=O (carbonyl, 288.2 eV), and O–C=O (carboxyl, 290.1 eV) groups [17–19]. Upon completion of ECR step, the C1 s XPS spectrum of GS (Fig. 2b1) confirms obvious decrease of oxygenated carbon related signals at 286–290 eV. According to the calculation of the integrated areas of the C 1 s peaks, the nonoxygenated groups of C=C/C–C increase obviously from 49.1 to 74.2%, suggesting that most of the oxygen-containing functional groups have been removed [20]. On the other hand, for GO film, there is no pi-pi* shakedown feature characteristic of conjugated carbon materials appeared; while for GS sample, an obvious pi-pi* shakedown feature belonging to the conjugated carbon materials can be observed at 290.6 eV, confirming the existence of conjugated carbons. In a word, in situ ECR of GO provides a feasible opportunity for fabricating GS film on the electrode materials.

As an efficient technique, CV is often adopted to evaluate electrochemical properties of new materials for EDLC [2]. Using GS film as the working electrode, the CV plots at various scan rates of 5, 30, 50, and 100 mV s^{-1} are displayed in Fig. 3a. Obviously, the CV loop at low scan rate of 5 or 30 mV s^{-1} is close to rectangular shape, exhibiting an ideal EDLC capacitor behavior with a low contact resistance in the capacitor [21]. It is well-known that the resistance of an electrode material is an important factor influencing the supercapacitor's capacitance and the interface resistance should be minimized for a high-performance capacitor [2]. In this case, the EIS data were analyzed using Nyquist measurement and a typical Nyquist plot of the GS film was shown in Fig. 3b. From the inset in Fig. 3b, it can be seen that the plot consists of a straight line in the low-frequency region and a semicircular arc in the high-frequency region (from ~ 14650 to $\sim 8.1 \text{ Hz}$). The high frequency loop represents the electronic resistance between the GS film and current

Fig. 1 **a** optical images of the GO aqueous suspension (0.6 mg mL^{-1}) and the as-deposited GO film and GS film on ITO sheet, respectively; **b** typical $i-t$ curve for ECR of GO film on the ITO electrode in the 0.1 M KCl aqueous solution at -0.9 V

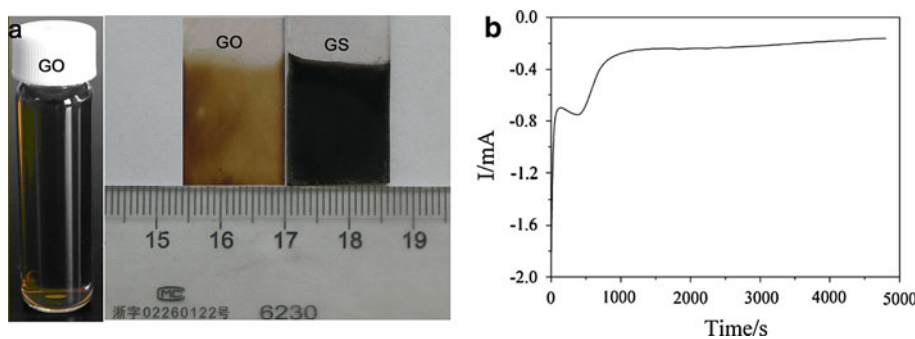
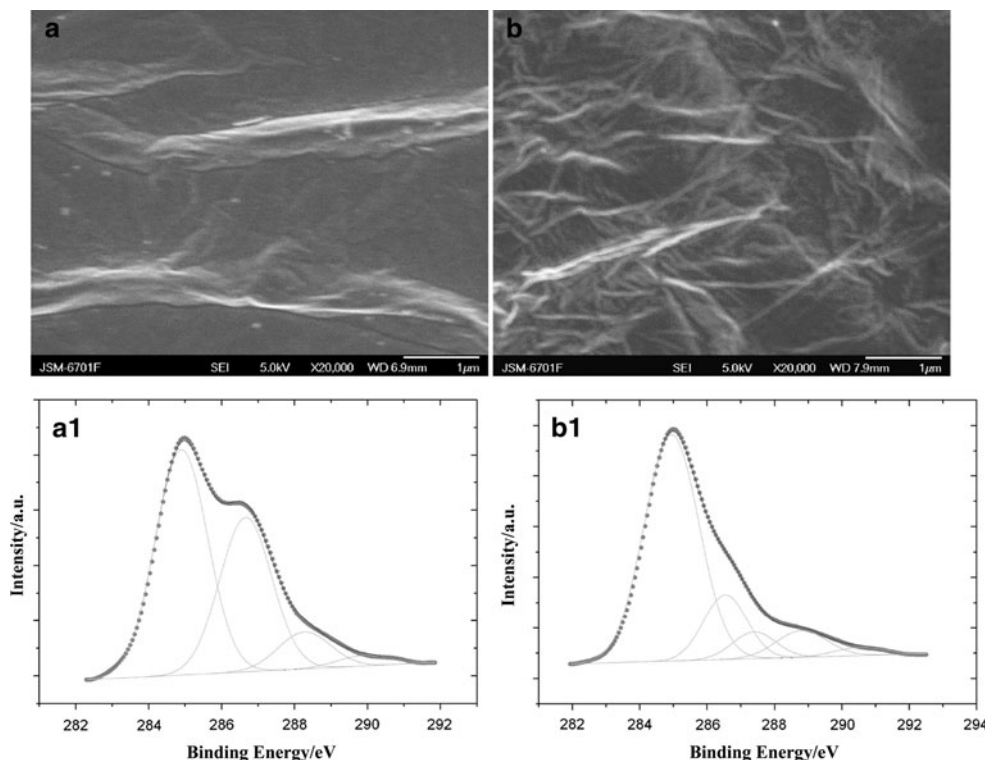


Fig. 2 FE-SEM images of the prepared GO **a** and GS **b** films; C 1 s XPS spectra of GO **a1** and GS **b1** films



collector, as well as the GS film itself. The straight line (near-vertical) at low-frequency region represents ions diffusion behavior and the very steep shape reveals the swift ion diffusion in solution and the adsorption onto the electrode surface [22].

At different current densities, the charge–discharge properties of the GS film electrode were investigated by chronopotentiometry in $0.1 \text{ M Na}_2\text{SO}_4$ aqueous solution in a potential window of $-0.2 \sim 0.8 \text{ V}$ and the corresponding results were shown in Fig. 3c. According to the specific capacitance (C_{spec}) equation

$$C_{\text{spec}} = I / (m(dV/dt))$$

where m (0.14 mg , which was obtained by the weight method) is the mass of the GS electrode, I is the applied current, and dV/dt can be obtained from the slope of the

discharge curve, [23] the calculated specific capacitance of the GS film electrode can reach to 156 F g^{-1} at 150 mA g^{-1} . Moreover, cycle life of the GS film electrode was evaluated by variation of specific capacitance with cycle number at a constant current density of 750 mA g^{-1} and the corresponding result was shown in Fig. 3d. It is clearly observed that the specific capacitance still remains a high level of 93 F g^{-1} after 400 times of cycling, illustrating the prepared GS film electrode possesses the excellent stability and lifetime as the supercapacitor material.

In summary, the as-prepared GS film on the ITO electrode by a two-step electrochemical process shows good performance as the EDLC supercapacitor materials. Moreover, this simple method also can be controllably realized on other conducting substrates such as metals, conducting polymers, etc.

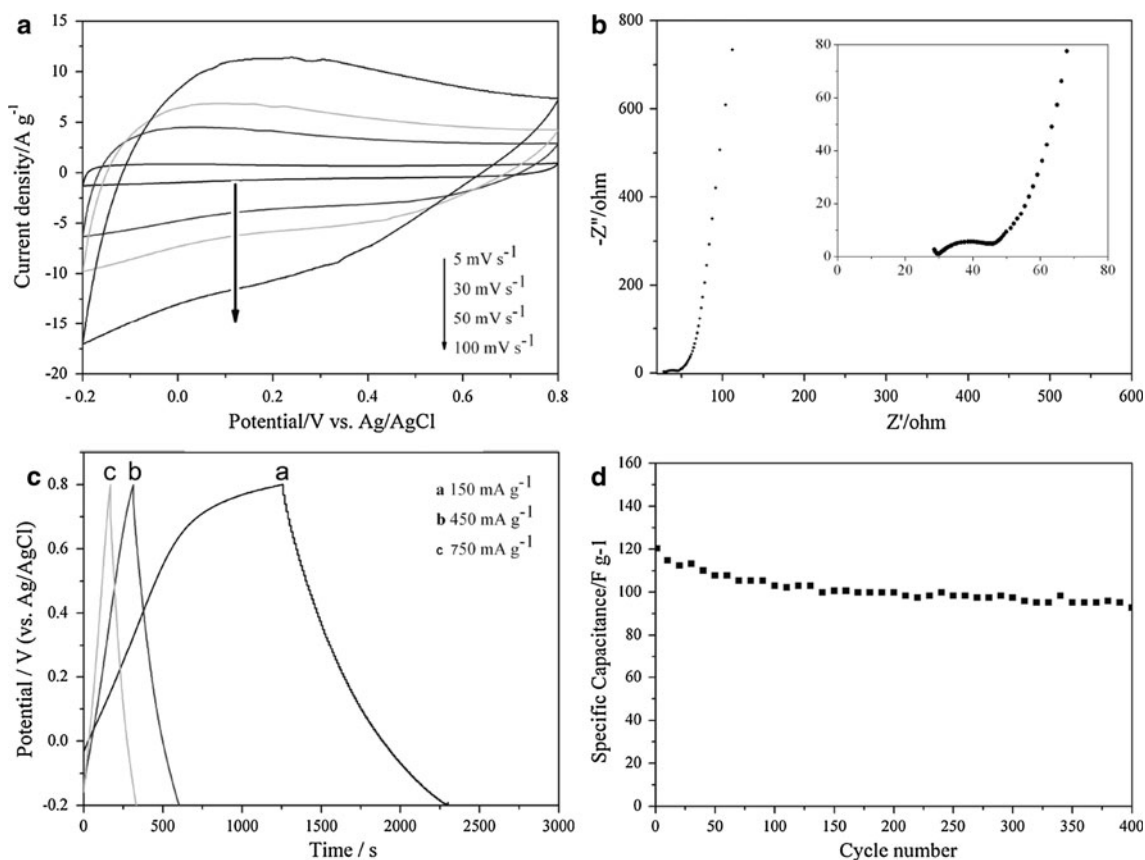


Fig. 3 CV **a** and Nyquist **b** plots of GS films in 0.1 M Na₂SO₄ electrolyte; **c** Galvanostatic charge/discharge curves of GS films at different current densities; **d** the specific capacitance change at a constant current density of 750 mA g⁻¹ as a function of cycle number

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References

- An KH, Kim WS, Park YS et al (2001) *Adv Funct Mater* 11:387
- Jiang FT, Fang YZ, Xue QS et al (2010) *Mater Lett* 64:199
- Kim C (2005) *J Power Sour* 142:382
- Merino C, Soto P, Vilaplana-Ortego E et al (2005) *Carbon* 43:551
- Huang CW, Wu YT, Hu CC et al (2007) *J Power Sour* 172:460
- Novoselov KS, Geim AK, Morozov SV et al (2004) *Science* 306:666
- Cuong TV, Pham VH, Tran QT et al (2010) *Mater Lett* 64:765
- Hernandez Y, Nicolosi V (2008) *Nat Nanotech* 3:563
- Liu S, Zeng J, Wang JQ et al (2010) *J Power Sour* 15:4628
- Wu ZS, Pei S, Ren W et al (2009) *Adv Mater* 21:1
- Lee V, Whittaker L, Jaye C et al (2009) *Chem Mater* 29:3905
- Hasan SA, Rigueur JL, Harl RR et al (2010) *ACS Nano* 4:7367
- Pumera M (2009) *Chem Rec* 9:211
- Pumera M (2010) *Chem Soc Rev* 39:4146
- Kotov NA, Dekany I, Fendler JH (1996) *Adv Mater* 8:637
- Cassagneau T, Guerin F, Fendler JH (2000) *Langmuir* 16:7318
- Jeong HK, Lee YP, Lahaye RJWE et al (2008) *J Am Chem Soc* 130:1362
- Szabo T, Berkesi O, Forgo P et al (2006) *Chem Mater* 18:2740
- Shin HJ, Kim KK, Benayad A et al (2009) *Adv Funct Mater* 19:1987
- Zhou Y, Bao QL, Tang LAL et al (2009) *Chem Mater* 21:2950
- Wang Y, Shi ZQ, Huang Y et al (2009) *J Phys Chem C* 113:13103
- Kim C, Ngoc BTN, Yang KS et al (2007) *Adv Mater* 19:2341
- Burke A (2000) *J Power Sour* 91:37