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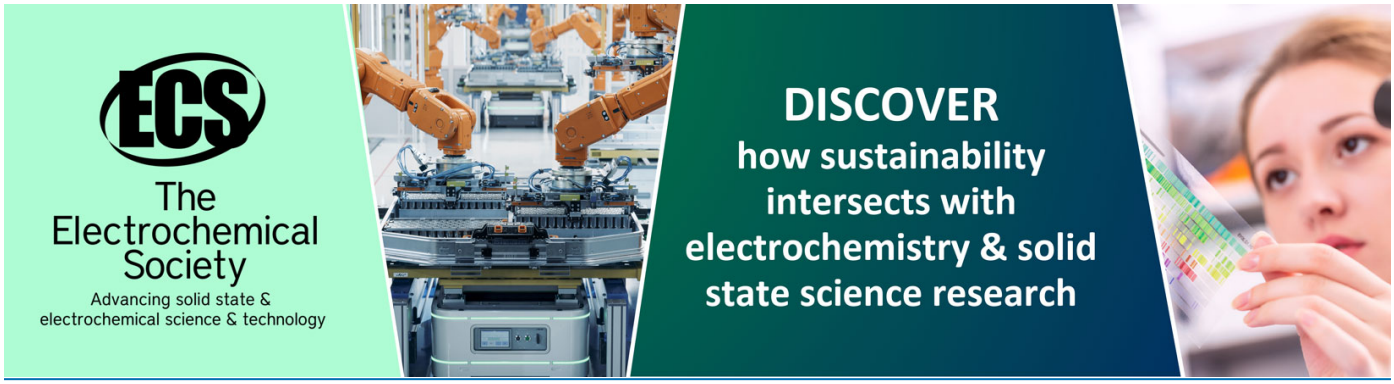

Fabrication of graphene/polydopamine/copper foam composite material and its application as supercapacitor electrode

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Abstract. In this work, a composite electrode was fabricated by chemical deposition of polydopamine (PDA) and graphene oxide (GO) on the copper foam (CF) surface, followed by annealing treatment. Owing to the cohesive effect of the PDA middle film, GO was coated on CF surface successfully, and then reduced simultaneously while annealing. The resulted rGO/PDA/CF composite electrode was directly used as a supercapacitor electrode and exhibited excellent electrochemical performance, with a high specific capacitance of 1250 F g^{-1} at 2 A g^{-1} and favorable cycle stability.

1. Introduction

Supercapacitors have drawn great interest in energy device because of their fast charge and discharge rate, long cycle lifetime and high reliability [1, 2]. Due to the difference of their storage mechanisms, supercapacitors can be classified as electronic double layer capacitors (EDLCs) and pseudocapacitors. Compared with EDLCs who store energy through reversible ions at electrode / electrolyte interface, pseudocapacitors possess higher charge-storage capacity, induced by rapid Faradaic redox reactions [3, 4].

Carbon materials are widely used in electrodes because of high specific surface area and easy accessibility. Among them, graphene has been extensively explored due to its superior conductivity, pore size distribution and excellent electrochemical performance [5-7]. However, the self-aggregation and restacking of graphene sheets occurred during the preparation process, leading to an actual specific capacitance far below its theoretical value. In order to prevent the stacking of graphene effectively, we try to reduce the graphene oxide (GO) via annealing.

Dopamine can self-polymerize and spontaneously deposit conformal polydopamine (PDA) films, which could be utilized to functionalize various material surfaces [8]. In this work, we use PDA as a middle film, because (1) the secondary amine groups on PDA layer react with hydroxyl groups on GO, and then form amide groups. Thus GO could be coated more tightly on the surface of copper foam. (2) PDA contributes to conductivity. Liu et al. found that carbon nanoparticles obtained after PDA carbonization had better conductivity [8]. Hence, PDA is a good choice to be the middle film between copper foam and GO.

In this study, copper foam (CF) acts as the electrode substrate to carry active substances and the current collector for its high conductivity. To prevent the stacking of graphene sheets effectively, GO

was first deposited on the CF surface uniformly with the assistant of PDA film and then annealed to be reduced graphene oxide (rGO), and we named the sample as rGO/PDA/CF composite electrode. It can be used as the supercapacitor electrode directly, when tested in 1 mol L^{-1} Na_2SO_4 electrolyte, it exhibited typical pseudocapacitance characteristics and excellent performance.

2. Experimental section

2.1. Preparation of composite electrode rGO/PDA/CF

GO was prepared by the oxidation of natural graphite powder according to a modified Hummers' method [9, 10]. Typically, Cu foam (2.0 cm × 1.0 cm × 0.1 cm) were ultrasonically cleaned with acetone, alcohol and doubly distilled water respectively, then dried under vacuum for 24 h. The preparation of rGO/PDA/CF electrode includes the following sections. First, the cleaned CF sheet was immersed into 20 mg mL^{-1} PDA solution whose pH was about 8.5 for 1.5 h at room temperature. Second, the as-synthesized GO was diluted to a concentration of 0.5 mg mL^{-1} suspension. The Cu foam decorated by PDA (PDA/CF) was then placed into the GO suspension for 40 min at room temperature. Thus the GO/PDA/CF composite was obtained. Finally, it was annealed at 200 °C for 1.5 h. In this way, the final electrode material, rGO/PDA/CF composite sheet was synthetized successfully.

2.2. Characterizations

Structural and phase characterizations of the electrode were done by XRD using a Bruker D8 Advance Phaser diffractometer with Cu K_α radiation at a continuous scanning mode (40 kV, 40 mA, and λ = 0.15418 nm) at a scanning rate of 3° min^{-1}. Scanning electron microscopy (SEM) images was determined using a scanning electron microscope (SEM, S-4800, Hitachi, Japan). Raman spectroscopy investigations were performed by using Witec confocal Raman microscopy (LabRAM HR Evolution) with laser wavelength of 532 nm.

2.3. Electrochemical measurement

The electrochemical performance of the GO/PDA/CF and rGO/PDA/CF composite electrodes were measured by using a three-electrode configuration with an electrochemical potentiostat (CHI 760E, CH Instruments) in the potential range of -0.03 V to -0.83 V. A 1 mol L^{-1} Na_2SO_4 aqueous solution was used as the electrolyte. Pt sheet and saturated calomel electrode were used as a counter and reference electrode, respectively. The capacitive performance of rGO/PDA/CF was characterized by cyclic voltammetry (CV), galvanostatic charge and discharge (GCD). The gravimetric specific capacitance (C) of the electrode was calculated from the following equation:

$$C = \frac{I \times \Delta t}{m \times \Delta V} \tag{1}$$

where I represents the constant discharge current, Δt represents the discharging time, m refers to the mass of active substance on the electrode and ΔV is the operating voltage.

3. Results and discussion

3.1. Morphology and composition analysis

Figure 1a confirms that CF possesses smooth surface. From figure 1b, we can see that after immersing in PDA solution, small particles are appeared on CF surface, which provide good attachment points for GO. It can be seen clearly in figure 1c, that GO was successfully deposited on the surface of PDA/CF. After annealing, GO film fits more compactly on the surface and more wrinkles can be observed, as shown in figure 1d.

Figure 2 shows the Raman spectra of GO/PDA/CF and rGO/PDA/CF composite electrodes, in which two typical peaks belonged to GO and rGO can be observed within the range of 500 to 2500 cm^{-1}. The peak at around 1600 cm^{-1} and 1350 cm^{-1} are assigned to the E_{2g} mode, i.e. G band and D

band, respectively [11]. The I_D/I_G value of GO/PDA/CF was calculated to be 0.92, while that of rGO/PDA/CF was 0.84, the decrease after annealing indicates that GO was partly reduced to rGO [12]. The XRD spectra of CF, GO/PDA/CF and rGO/PDA/CF composites are showed in figure 3a. From the figure, we can see that the sharp peaks are located at 43.6°, 50.6° and 74.3°, corresponding to metal Cu (JCPDS card no. 04-0836). In figure 3b, there are no peaks can be observed in the intercept part of the spectra in the range of 2θ = 3 - 35°. Therefore, GO/PDA/CF and rGO/PDA/CF composites synthesized in the experiment may be all amorphous phase.

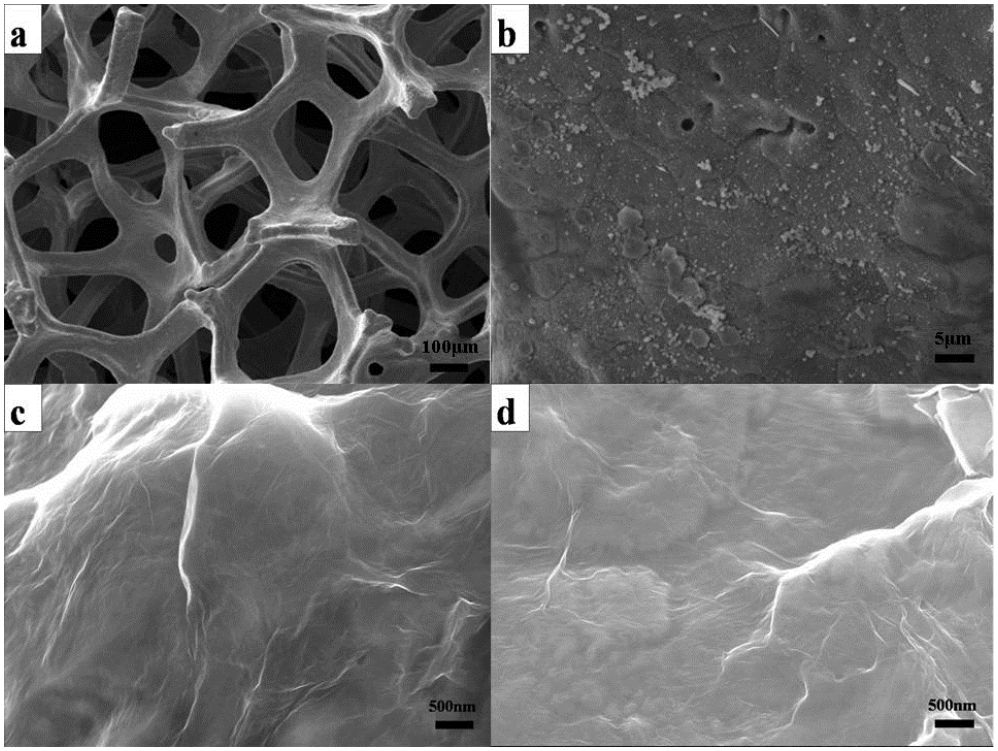

Figure 1. SEM images of different sample surfaces: (a) CF, (b) PDA/CF sheet, (c) GO/PDA/CF sheet, (d) rGO/PDA/CF sheet.

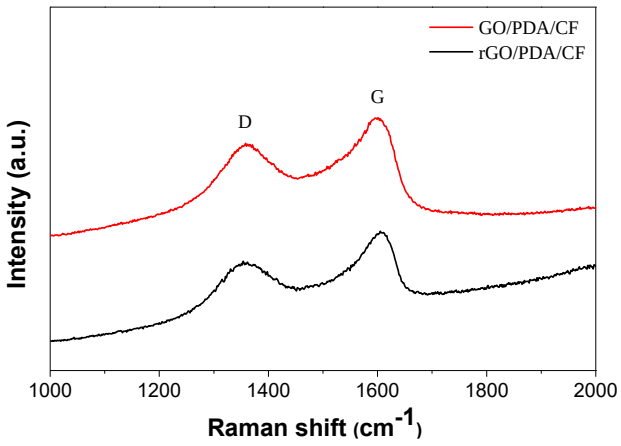

Figure 2. Raman spectra of GO/PDA/CF and rGO/PDA/CF composites.

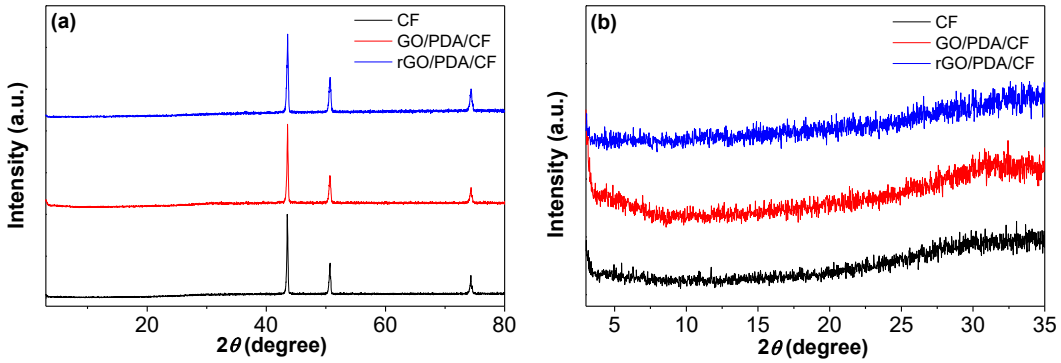

Figure 3. (a) XRD patterns of CF, GO/PDA/CF and rGO/PDA/CF composites. (b) The magnified part of the region 2θ = 3-35°.

3.2. Electrochemical performance

The electrochemical performances of GO/PDA/CF and rGO/PDA/CF composite electrodes were investigated by galvanostatic charge-discharge (GCD) tests, as shown in figure 4. The slightly nonlinear and asymmetric charging/discharging curves validate the dominant pseudocapacitance derived from Faradiac reactions [13]. On the other hand, the specific capacitance value of rGO/PDA/CF electrode is rather better than GO/PDA/CF electrode by contrast of the discharge time. This could be due to rGO reduced from GO, which can also be supported from Raman result.

The CV curves of rGO/PDA/CF composite electrode at different scan rates ranging from 5 to 100 mV s^{-1} are showed in figure 5a. All CV curves displayed broad redox peaks, suggesting the typical pseudocapacitance characteristics [14, 15]. We propose that a small amount of elemental copper was oxidized during annealing process, which results in the increase of capacitance value. The GCD curves of rGO/PDA/CF composite electrode in the current density range of 2 - 32 A g^{-1} are shown in the figure 4b. The specific capacitance of rGO/PDA/CF electrode was about 1250 F g^{-1} at current density of 2 A g^{-1}. When the current density was 4 A g^{-1}, the specific capacitance was about 760 F g^{-1}, which is much higher than 248 F g^{-1} at current density of 2 A g^{-1} in previous paper [16].

Figure 6a shows the cycling performance at 4 A g^{-1} for 1000 cycles, as illustrated that, the rGO/PDA/CF electrode showed 74.5% retention, displaying favorable cycle stability. Figure 6b illustrates cyclic voltammograms of the rGO/PDA/CF electrode under different scan rates after 1000 cycles. It is obviously that the CV curves were all close to rectangular which showed typical EDLCs behavior. This may be exactly the reason for the reduction of specific capacitance.

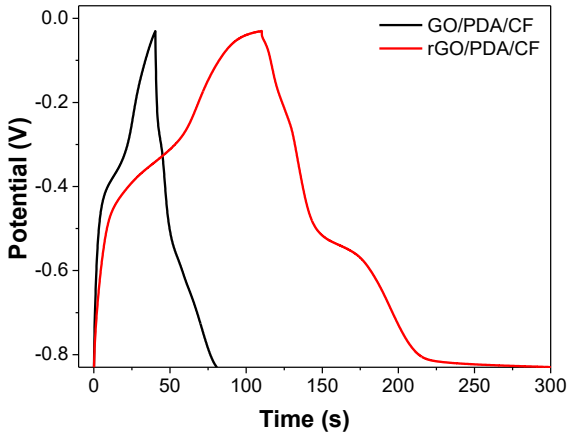

Figure 4. Discharge curves of GO/PDA/CF and rGO/PDA/CF electrodes at 4 A g^{-1}.

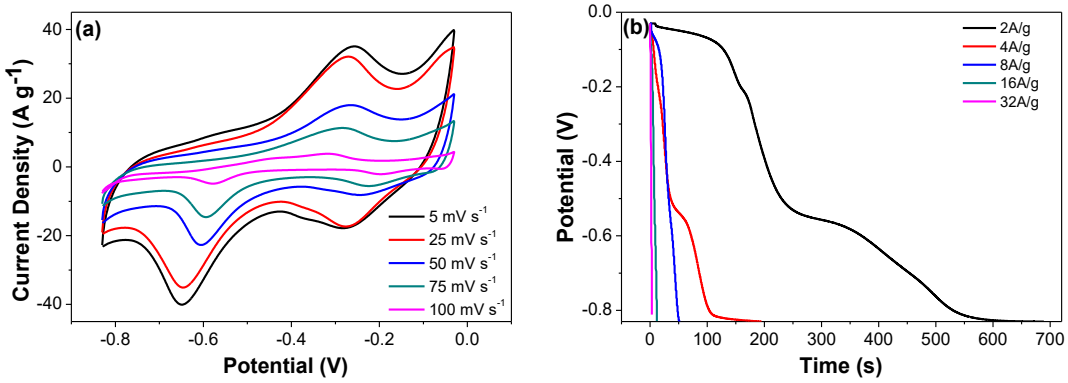

Figure 5. (a) Cyclic voltammograms of the rGO/PDA/CF electrode under different scan rates; (b) Discharge curves of rGO/PDA/CF electrode at different applied currents.

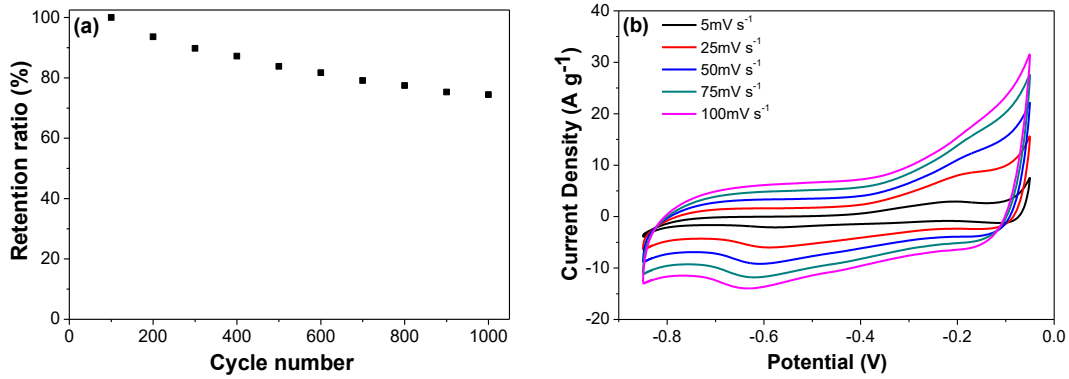

Figure 6. (a) Capacity retention versus cycle numbers for rGO/PDA/CF electrode at the current density of 4 A g^{-1}; (b) Cyclic voltammograms of the rGO/PDA/CF electrode under different scan rates after 1000 cycles.

4. Conclusion

In summary, the rGO/PDA/CF composite supercapacitor electrode has been fabricated successfully. In the experiment, GO was attached on the Cu foam by simple chemical immerse using PDA as the middle film and was reduced by annealing method. The final electrode exhibits superior specific capacitance (1250 F g^{-1} at 2 A g^{-1}) and excellent cycling stability with the capacitance retention of 74.5% after 1000 cycles.

Acknowledgements

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