Facile synthesis and effective measurement method for scale-like CoMn$_2$O$_4$/rGO electrode in supercapacitor

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Abstract. Scale-like CoMn$_2$O$_4$/reduced graphene oxide (rGO) have been successfully synthesized via a facile hydrothermal and annealing process. When evaluate its potential as electrode material for supercapacitor, effective measurement method of electrochemical performance was implemented. The result shows the electrode has high specific capacitance, excellent rate capability and long cycle life.

1. Introduction
Supercapacitor (SC), also known as electrochemical capacitors, is a promising next generation energy storage device. Due to its high charge-discharge rate, excellent coulomb efficiency, long cycle life and wide operating temperature range [1], SC has good application prospects. However, compared to secondary battery, the energy density of SC still has room for improvement. The key factor affecting energy density is electrode material. Therefore, developing new electrode materials and effective measurement methods of electrochemical performance is urgent.

2. Experimental
2.1. Preparation of active material
All the reagents used were analytical grade. Graphene oxide (GO) sheets were prepared by a modified Hummers method [2]. In preparation procedure, 10 mg GO sheets were added into 40 mL deionized water and dispersed by sonication process for 30 min. Then, 0.5 mmol Co(NO$_3$)$_2$·6H$_2$O (145.5 mg), 1 mmol MnSO$_4$·H$_2$O (169 mg), 2.5 mmol (350.35 mg) hexamethylenetetramine (HMT) and 0.45 mmol (132.3 mg) trisodium citrate dihydrate (TSC) were dissolved in the above GO suspension with sonication for 10 min. Next, the result solution was heated to 90°C in oil bath with continuous stirring for 6 h. Afterwards, the solution was naturally cooled to ambient temperature. The black product was
gathered via centrifugation, washed thoroughly with ethanol and dried at 60°C for 12 h. The obtained powders were calcined in N₂ at 450°C for 3 h with a heating rate of 1°C min⁻¹. Finally, the CoMn-precursor/GO was converted to the CoMn₂O₄/rGO nanocomposite.

2.2. Electrochemical measurements
The electrode was assembled by the procedure as follow. First, active material (CoMn₂O₄/rGO), conductive additive (carbon black) and polymer binder (polyvinylidene fluoride) were dissolved in N-methyl-2-pyrrolidinone (NMP) solvent with a mass ratio of 7:2:1 to produce homogeneous slurry. After that, the resulting slurry was pasted uniformly onto nickel foam and followed by drying overnight under vacuum at 120°C. Capacitive performance of the electrode was measured using an CHI 660E electrochemical workstation in a three-electrode system. A Pt foil and a saturated calomel electrode (SCE) were used as the counter electrode and reference electrode, respectively. In addition, 6 M KOH solution served as electrolyte. Energy storage characteristic of the electrode was investigated by cyclic voltammetry (CV) and galvanostatic charge-discharge (GCD) techniques. Electrochemical impedance spectroscopy (EIS) was tested in the frequency range from 0.1 Hz to 10 kHz with an ac perturbation of 5 mV. The specific capacitances were evaluated by the formula below [3].

\[ C = \frac{I \cdot \Delta t}{m \cdot \Delta V} \]  (1)

where \( I \) represents the discharge current (A), \( \Delta t \) is the total discharge time (s), \( m \) is the mass of active materials (g) and \( \Delta V \) is the discharge potential range (V).

3. Result and discussion
3.1. Characterization of the CoMn₂O₄/rGO composite
Surface morphology of the CoMn₂O₄/rGO composite was characterized using FESEM (Figure 1). It can be seen that the rGO sheets were uniformly decorated with a large amount of ultrathin CoMn-precursor nanosheets. After annealing at 450°C in N₂ atmosphere, the CoMn-precursor was transformed into CoMn₂O₄ and the original morphology was maintained. The closer observation of CoMn₂O₄ nanosheets reveals that scale-like ultrathin CoMn₂O₄ nanosheets anchored on the surface of rGO substrate and connect to each other to form the extended network structures (Figure 1B). Owing to the rGO substrate, this kind of hybrid structure is supposed to have good flexibility and mechanical strength which can effectively buffer the volume change of electrode material during charging-discharging cycles [4]. More details of structure features of the CoMn₂O₄/rGO were
characterized by TEM (Figure 2). As illustrated in Figure 2A, CoMn$_2$O$_4$ nanosheets grown on the surface of rGO. From the closer observation (Figure 2B), CoMn$_2$O$_4$ nanosheets consists of nanoparticles. Measured interplanar spacing is 0.249 nm, 0.205 nm, 0.152 nm that correspond to the (440), (222) and (400) crystal planes of CoMn$_2$O$_4$ (Figure 2C and 2D). The SAED pattern (inset of Figure 2D) proves the good polycrystallinity of the product.

3.2. Electrochemical measurement

To explore electrochemical properties of CoMn$_2$O$_4$/rGO as electrode material in supercapacitor, the tests of CV, GCD, cycling stability and EIS were performed. Figure 3A shows the CV curves of the CoMn$_2$O$_4$/rGO electrode at various scan rates from 2 mV·s$^{-1}$ to 100 mV·s$^{-1}$. It is obvious that a couple of distinct redox peaks exhibit in all cycles due to the reversible redox processes [5]. As the scan rate increases, the shapes of the curves show negligible changes, suggesting that the material allows rapid redox reactions and has good capacitive characteristic [5]. The positions of redox peaks shift slightly due to the increase of internal diffusion resistance in the electrochemical redox reactions. The GCD measurements were performed at different current densities from 2 to 20 A·g$^{-1}$ within the potential of 0-0.4 V (vs. SCE). The corresponding discharge curves are presented in Figure 3B. As can be seen, each discharge curve has a potential plateau that confirm the pseudocapacitive behavior of the CoMn$_2$O$_4$/rGO electrode. The calculated specific capacitances of the electrode are 1000.8 F·g$^{-1}$, 771 F·g$^{-1}$, 656 F·g$^{-1}$, 585 F·g$^{-1}$, 546 F·g$^{-1}$, 414.2 F·g$^{-1}$ and 357.6 F·g$^{-1}$ for discharge current densities of 2 A·g$^{-1}$, 5 A·g$^{-1}$, 10 A·g$^{-1}$, 15 A·g$^{-1}$, 20 A·g$^{-1}$, 40 A·g$^{-1}$ and 50 A·g$^{-1}$ (Figure 3C), respectively. From the figure, it can be seen that the specific capacitance appears a certain degree of attenuation with the increase of the current density. This is because the internal resistance of the electrode leads to a large potential drop and the Faraday reaction between the electrode material and electrolyte is insufficient. The cycling performance of the CoMn$_2$O$_4$/rGO electrode was tested at 5 A·g$^{-1}$. The result in Figure 3D
illustrates that the specific capacitance is 771 F·g⁻¹ at the first cycle and, after 1000 charge-discharge cycles, it slightly reduces to 721 F·g⁻¹. Meanwhile, 93.6% of the capacitance is retained, indicating an excellent cycle life of the CoMn₂O₄/rGO electrode for supercapacitors. However, the specific capacitance of the CoMn₂O₄ aggregates electrode decreased from 530 F·g⁻¹ to 400 F·g⁻¹, only 75.5% of the original capacitance is kept at 1000th cycle. By comparison, the CoMn₂O₄/rGO electrode has a higher cycle stability, which is due to its unique structure. The EIS plots of the CoMn₂O₄/rGO electrode before and after charge-discharge cycles at open circuit voltage in the frequency range of 0.1 Hz to 10 kHz are show in Figure 4. The equivalent series resistance is about 0.5 Ω before and after cycling, which is basically unchanged. In enlarged view of the plots at high-frequency region (inset of Figure 4), the charge-transfer resistance R_{CT} has been significantly increased after 1000 cycles of charge-discharge. This is the reason that the specific capacitance has decreased after cycles.

4. Conclusion
Scale-like CoMn₂O₄/rGO have been successfully synthesized through a simple hydrothermal and annealing process. Effective measurement method of electrochemical performance was implemented to evaluate it as a potential electrode material for supercapacitor. The result shows the electrode has high specific capacitance, excellent rate capability and long cycle life.

Reference
[1] P Simon and Y Gogotsi 2008 Nature Materials. 7 845-854
[2] D C Marcano, D V Kosynkin, J M Berlin, A Sinitskii, et al. 2010 ACS Nano. 4 4806-14
[3] Y Z Jiang, Z H Li, B B Li, J Y Zhang and C M Niu 2016 J. Power Sources. 320 13-19
[4] Sun Y, Wu Q, Shi G. 2011 Energ. Environ. Sci. 4 1113-32
[5] Shen L F, Yu L, Yu X Y, Zhang X G and Lou X W 2015 Angew. Chem.-Int. Edit. 54 1868-72