



# Preparation of sandwich-like ternary hierarchical nanosheets manganese dioxide/polyaniline/reduced graphene oxide as electrode material for supercapacitor

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## HIGHLIGHTS

- Sandwich-like ternary hierarchical nanosheets MnO<sub>2</sub>/PANI/RGO are fabricated.
- MnO<sub>2</sub>/PANI/RGO exhibit high specific capacitance of 1090.2 F g<sup>-1</sup> at 0.5 A g<sup>-1</sup>.
- MnO<sub>2</sub>/PANI/RGO retains 82.3% initial capacity after 5000 cycles at 0.5 A g<sup>-1</sup>.
- Ternary hierarchical nanosheets improve electrochemical properties.

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## ABSTRACT

In this paper, a new class of sandwich-like ternary hierarchical nanosheets is fabricated by a facile, reproducible, and scalable two-step strategy. Conducting polymer polyaniline (PANI) is coated on reduced graphene oxide (RGO) to form PANI/RGO hybrid nanosheets. Then, nanoflaky manganese dioxide (MnO<sub>2</sub>) *in situ* grows on PANI/RGO hybrid nanosheets to obtain ternary hierarchical nanosheets MnO<sub>2</sub>/PANI/RGO by simply mixing PANI/RGO and KMnO<sub>4</sub> under mild condition. The electrochemical behavior shows that MnO<sub>2</sub>/PANI/RGO electrode material is a typical pseudo-capacitance. In comparison with RGO, PANI, and PANI/RGO hybrid nanosheets, MnO<sub>2</sub>/PANI/RGO composites display the highest specific capacitance of 1090.2 F g<sup>-1</sup> at 0.5 A g<sup>-1</sup> in three-electrode configuration. They maintain 82.3% initial capacitance after 5000 consecutive cycles at 0.5 A g<sup>-1</sup>. The excellent electrochemical performance is attributed to nanometer-sized flaky MnO<sub>2</sub> *in situ* growth on the surface of PANI/RGO, which can enhance electrode/electrolyte interface areas, provide high electroactive regions and short diffusion lengths, and protect the structure of composites effectively. Thus, the sandwich-like ternary hierarchical nanosheets of MnO<sub>2</sub>/PANI/RGO are excellent electrode material in supercapacitor with high specific capacitance and the long-term cycle stability, which is helpful in developing new kinds of portable energy storage devices.

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## 1. Introduction

Nowadays, electrochemical double-layer capacitors supercapacitors (EDLCs) have attracted extensive attention owing to their high power density, fast charge/discharge rates, and long cycle lifetime [1–5]. However, the low energy density of EDLCs has limited their application in commercialized devices. Carbon-based active electrode materials are the most common EDLCs. Compared to carbon electrode materials, pseudocapacitive electrode materials, such as transition-metal oxides [6–11] and conducting polymers

[12–16], have higher specific capacitances and energy densities, therefore, can meet the requirement of high-performance supercapacitors.

Recently, many attempts have been devoted to the use of electronically conducting polymers as electrode materials in supercapacitors such as polyaniline (PANI), polypyrrole (PPY) [13], poly(ethylenedioxythiophene) [15], polythiophene [16] and its substituted counterparts. However, it is a challenge to fabricate high power supercapacitors using conducting polymer because the swelling and shrinkage of conducting polymer may occur during the charge/discharge processes, thus, leading to capacity degradation. The combination of conducting polymer with various carbon materials including carbon nanotubes and graphene has been proved to be attractive to reinforce the stability of conducting

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polymer [17–23]. Gupta et al. reported the electrochemical polymerization of PANI/single-wall carbon nanotube (SWCNT) composites with the highest specific capacitance of  $485 \text{ F g}^{-1}$  obtained for 73 wt% PANI in a three-electrode cell [17]. Compared with carbon nanotubes, graphene or graphene oxide nanosheets are predicted as an excellent scaffold due to their high surface area, remarkable mechanical property and excellent conductivity [18–27]. Wang et al. synthesized fibrillar PANI doped with graphene oxide sheets with the specific capacitance of  $531 \text{ F g}^{-1}$  compared to  $216 \text{ F g}^{-1}$  of individual PANI in a three-electrode system [24].

Carbon materials/conducting polymers belong to binary composite materials. Recently, ternary composites have attracted extensive concern of researchers due to giving full play to their respective advantages to improve the comprehensive performance of materials [28–40]. The inclusion of transition metal oxides, such as manganese dioxide ( $\text{MnO}_2$ ), will further enhance the specific capacitance. Specific capacitance of multiwall carbon nanotube-poly(styrene sulfonate) (MWCNT-PSS)/poly(3,4-ethylenedioxythiophene) (PEDOT)/ $\text{MnO}_2$  nano-composite electrode was found as high as  $375 \text{ F g}^{-1}$ . In contrast, specific capacitance of MWCNT-PSS/ $\text{MnO}_2$  and MWCNT-PSS nano-composite electrodes is  $175 \text{ F g}^{-1}$  and  $15 \text{ F g}^{-1}$ , respectively [29]. Liu et al. synthesized  $\text{MnO}_2$  nanospheres/carbon nanotubes/conducting polymer ternary composites. Specific capacitance of the ternary composite electrode can reach  $427 \text{ F g}^{-1}$ . The electrode exhibited exceptional cycling stability and retained over 99% of its initial charge after 1000 cycles [30]. Yu et al. developed a “conductive wrapping” method to obtain graphene/ $\text{MnO}_2$ /conducting polymer (GMP) systems. Compared with carbon nanotubes or conducting polymer, specific capacitance of the electrodes has substantially increased by ~20% and ~45%, respectively [33]. Moreover, these ternary composite electrodes have also exhibited excellent cycling performance with >95% capacitance retention over 3000 cycles [33]. Other ternary composites, such as graphene nanosheet/carbon nanotube/polyaniline (GNS/CNT/PANI) [31], graphene/CNT-PANI [35,36], they all exhibited the excellent electrochemical performance of ternary composites compared with binary compounds.

In this paper, we succeeded in synthesizing sandwich-like ternary hierarchical nanosheets  $\text{MnO}_2$ /PANI/RGO by simply mixing PANI/RGO and  $\text{KMnO}_4$  under mild conditions. This synthetic strategy might be instructive for the design of ternary hierarchical nanocomposites. The morphology, microstructure and electrochemical performances of ternary hierarchical nanosheets were investigated. Electrochemical results show that they possess excellent electrochemical properties. Their ideal material form and superior electrochemical performances are helpful in developing new kinds of portable energy storage devices.

## 2. Experimental

### 2.1. Materials preparation

All chemicals with analytical reagent grade were purchased from Sinopharm Chemical Reagent Company used as received without further purification. Reduced graphene oxide was purchased from Nanjing JiChang Nano Technology Co., Ltd. Double distilled water was used to prepare all solutions.

### 2.2. Characterization

Transmission Electron Microscopy (TEM) observation was performed on a Philips TECNAI-12 instrument. High-resolution TEM (HRTEM) and high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) were conducted using a FEI Tecnai G2 F30 STWIN (USA) operating at 200 kV. Scanning electron

microscope (SEM) was applied to investigate the morphology, which was carried out with Hitachi S-4800 (Japan). X-ray Powder Diffraction (XRD) data were obtained with a graphite monochromator and  $\text{Cu K}\alpha$  radiation ( $\lambda = 0.1541 \text{ nm}$ ) on a D8 advance super-speed powder diffractometer (Bruker). The X-ray photoelectron spectroscopy (XPS) experiments were carried out on a Thermo Escalab 250 system using  $\text{Al K}\alpha$  radiation ( $h\nu = 1486.6 \text{ eV}$ ). The test chamber pressure was maintained below  $2 \times 10^{-9}$  Torr during spectral acquisition. The energy-dispersive X-ray (EDX) analysis was performed on a KEVEX X-ray energy detector. Fourier Transform infrared (FT-IR) spectra for the different samples were recorded on a Bruker Tensor 27 FTIR spectrometer operated at a resolution of  $4 \text{ cm}^{-1}$ . Ultraviolet–visible (UV–vis) absorption spectra were measured on a UV-2550 PC UV–visible spectrometer (Shimadzu, Japan). Electrochemical impedance spectroscopic (EIS) experiments were performed with an Autolab Electrochemical Analyzer (Ecochemie, Netherlands).

### 2.3. Preparation ternary hierarchical nanosheets $\text{MnO}_2$ /PANI/RGO

In this paper, we used a new strategy to prepare ternary hierarchical nanosheets  $\text{MnO}_2$ /PANI/RGO. A thin PANI shell was coated on the surface of RGO to form PANI/RGO nanosheets by *in situ* polymerization. Firstly, RGO (20 mg) was suspended in 50 mL distilled water under ultrasonic irradiation and mechanical stirring. Then, aniline (100  $\mu\text{L}$ ) in the presence of concentrated HCl (0.1  $\text{mol L}^{-1}$ , 10 mL) was added into the mixture. The solution was mechanical stirred for 2 h at room temperature. An aqueous solution of ammonium peroxydisulfate (APS) (0.3 g of APS in 5 mL of  $\text{H}_2\text{O}$ ) was added into the above mixture instantly to start the oxidative polymerization under magnetic stirring, and the reaction was allowed to proceed for 12 h at room temperature. After the reaction, the black precipitate was separated and washed successively with  $\text{H}_2\text{O}$  and EtOH three times. The product was dried in vacuum for 12 h at  $60^\circ\text{C}$  to obtain PANI/RGO hybrid nanosheets.

Next, PANI/RGO hybrid nanosheets (20 mg) were suspended in 10 mL distilled water under ultrasonic irradiation and mechanical stirring. Then,  $\text{KMnO}_4$  (20  $\text{mmol/L}$ , 100  $\mu\text{L}$ ) was added into the suspension under magnetic stirring for 30 min at room temperature. The reaction mechanism has been explained by some references [41,42]. PANI on RGO surface was used as reductant and  $\text{KMnO}_4$  was used as oxidant. In the initial stage,  $\text{MnO}_2$  nuclei were inclined to be deposited on surfaces of PANI possibly due to the large surface energy of PANI and interactions between PANI and  $\text{MnO}_2$ . With reaction ongoing, directional growth along the wrinkles of PANI led to the formation of the nanoflaky  $\text{MnO}_2$  supported on the surface of PANI/RGO hybrid nanosheets. Lastly, the black precipitate was separated by centrifugation and washed successively with  $\text{H}_2\text{O}$  and EtOH three times. The final product was dried in vacuum for 12 h at  $60^\circ\text{C}$  to obtain the desired sandwich-like ternary hierarchical nanosheets  $\text{MnO}_2$ /PANI/RGO. The different  $\text{MnO}_2$  loading amounts of  $\text{MnO}_2$ /PANI/RGO composites were prepared by varying the addition amount of  $\text{KMnO}_4$  into the solution of PANI/RGO.

### 2.4. Electrochemical measurements

The working electrodes, including RGO, PANI nanorods, PANI/RGO and  $\text{MnO}_2$ /PANI/RGO, for evaluating the electrochemical properties were fabricated by mixing 70 wt% of samples with 15 wt% acetylene black and 15 wt% polyvinylidene difluoride (PVdF) in an agate mortar. 1-Methyl-2-pyrrolidinone (NMP) was added into the mixture to form slurry. The slurry was coated (area of coating:  $1 \text{ cm}^2$ ) on a pretreated battery-grade polished Ni foil ( $7 \text{ cm} \times 1.5 \text{ cm}$ , 0.2 mm thick) and vacuum-dried at  $60^\circ\text{C}$  for 8 h.

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