

Preparation of graphene oxide/polypyrrole/multi-walled carbon nanotube composite and its application in supercapacitors



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ABSTRACT

We report a novel method for preparing graphene oxide/polypyrrole/multi-walled carbon nanotubes (MWCNTs) composites (PCMG). The MWCNTs are treated by sulfuric acid, nitric acid and thionyl chloride, and then composite with graphene oxide and PPy by in situ polymerization. Transition electron microscopy (TEM), scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD) results show that in 3-D structure of PCMG composites, PPy chains act as the “bridge” between graphene oxide and chlorinated-MWCNTs. Electrochemical tests reveal that the PCMG1-1 composite has high capacitance of 406.7 F g^{-1} at current density of 0.5 A g^{-1} , and the capacitance retention of PCMG1-1 composite is 92% after 1000 cycles.

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1. Introduction

Supercapacitors have attracted enormous attention in recent years due to their great advantages including high power density, long cycle life, reversibility, and small environmental impact. [1–3]. At present, carbon-based materials (e.g., active carbon [3], carbon nanotubes [6,7], and graphene [5,8]) are widely applied as electrode materials for supercapacitors because of their excellent conductivity, huge surface area, and robust mechanical strength. However, as a kind of double-layer capacitance electrode materials, the specific capacitance of carbon-based materials is lower than those of other materials, such as metal oxides and hydroxide [9]. As a counterpart, conducting polymers possess many advantages (e.g., high conductivity, large storage capacity, and reversibility [10,11]) that make them promising materials for supercapacitors. Unfortunately, their electrochemical performances tend to fade for swelling and shrinking during cycling [9]. Given the complementary profiles of carbon-based materials and conducting polymers in terms of specific capacitance and mechanical strength, numbers of researchers have been focusing on developing electrode materials based on their composites to better the performance of supercapacitors [3–5].

Graphene oxide (GO), a significant carbon-based material, has attracted extensive attention for its unique 2-D structure and properties. GO contains ample oxygen functional groups on their

sheets and edges. These oxygen groups act as active spots, providing strong reactivity of GO sheets with polymers and thus making it easy fabricating GO-based 2-D composites [12]. For instance, recently, Wang et al. fabricated GO/polyaniline (PANI) composites with high specific capacitance by in situ polymerization [12,13]. The maximum specific capacitance reached up to 746 F g^{-1} when the mass ratio of graphene oxide and aniline was 1:200 [12]. However, GO is less self-conductive [14], which is disadvantageous for supercapacitors. Another carbon-based material, carbon nanotube (CNT) is a traditional 1-D electrode material for supercapacitors. Since agglomeration and insolubility of CNTs in water restrict their homogeneous dispersion in polymer matrix [16], much research is concentrated on the modification of CNTs and the application on supercapacitors thereafter [15]. For instance, sulfonated multi-walled carbon nanotubes (MWCNTs)/PANI nanorods 1-D composites have been prepared by Zhu et al. [17] Apart from the specific capacitance as high as 515.2 F g^{-1} , this composites showed a good cycling stability (below 10% capacity loss after 1000 cycles). This was attributed to functionalized CNTs that afforded the huge specific area and suitable pore size for electrolyte ion transport [9].

Compared with 1-D or 2-D composites, 3-D composites possess many advantages when applied in supercapacitors, such as hierarchical porosity, high contacting efficiency, and ease of handling [18]. In recent reports, researchers are trying to fabricate the CNTs/graphene (GS)/polymer 3-D composites. The GS/CNTs/PANI composites have been successfully prepared by Yan et al. [19] The specific capacitance of this composites reached up to 1035 F g^{-1} , just a little lower than that of GS/PANI composites

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Table 1
Grouping of the samples.

Name	$m_{GO+CM}:m_{Py}$ ^a	$m_{GO}:m_{CM}$ ^b
PCMG1-1	1:25	1:1
PCMG1-2	1:50	1:1
PCMG2-1	1:25	2:1
PCMG2-2	1:50	2:1
PCMG3-1	1:25	1:2
PCMG3-2	1:50	1:2
PCMG1-3	1:12.5	1:1
PCM-1	1:25	Without GO
PCM-2	1:50	Without GO
PG-1	1:25	Without CM
PG-2	1:50	Without CM
CMG	Without Py	1:1

^a the mass ratio of CM+GO and Py.

^b the mass ratio of GO and CM.

(1046 F g⁻¹), but much higher than that of pure PANI (115 F g⁻¹). At the same time, this composite showed good cycling stability (after 1000 cycles, the capacitance decreased by only 6%). Sandwiched nanostructure PANI/multi-walled carbon nanotubes (MWCNTs)/GS composites have been prepared by Zhou et al. [20] The specific capacitance of these composites was up to 259.4 F g⁻¹ in an organic electrode and 490.1 F g⁻¹ in 1 M H₂SO₄. In addition, other conducting polymer/carbon material 3-D composites have been prepared, for example, PPy/carbon, PANI/cross-linked carbon network and graphene/CNT-PANI, and all of them possess high specific capacitance and cycle stability [21–23]. In particular, the GS/PPy/CNT composites have been prepared by Lu [24] and Peng [25], the specific capacitance of this composites reached up to 361 and 178 F g⁻¹, respectively. However, the effects of mass ratios of polymer, GS and CNTs on the electrochemical properties of such composites have not been investigated intensively.

In this work, we report the synthesis of a novel three-component composite, polypyrrole (PPy)/chlorinated-MWCNTs (CM)/GO composites (PCMG), for the first time to the best of our knowledge. The composite was prepared through in-suit polymerization method and we further systematically explored the effect of the three componets' mass ratio on the property of electrochemical capacitance and chemical structure of PCMG composites. We find that the introduction of fewer amounts of GO and CM into PPy will greatly improve the electrochemical performance of PPy.

2. Experimental section

2.1. Materials

Graphite powder (325 mesh) was purchased from Kaitong Co. Ltd. (Tianjin, China). MWCNTs powder was purchased from Institue of Chemical Physics (Chengdu, China). Py monomer was purified by distillation under reduced pressure before use. Other reagents were commercially available and analytically graded. Solutions were prepared with distilled water.

2.2. Preparation of CM

CM was prepared from MWCNTs via the following method [26,27]. Firstly, preoxidized MWCNTs powder was synthesized through reaction of pristine MWCNTs (2 g), sulfuric acid (300 mL) and nitric acid (100 mL). The reaction mixture was maintained at 70 °C for 2 h, filtrated, washed with HCl solution (5%), dried in air, and generated the acid-treated MWCNTs (AM). After that, the AM were refluxed in 200 mL thionyl chloride at 70 °C for 12 h.

Finally, removing thionyl chloride by distillation and drying in a vacuum for 24 h.

2.3. Preparation of PCMG composites

GO was prepared according to the previous report [28]. PCMG composites were prepared by in-suit polymerization. In a typical experiment, 19.4 mg GO was dispersed in 50 mL of deionized water with 0.5 h sonication, followed by the addition of 19.4 mg CM ($m_{GO}:m_{CM} = 1:1, m_{GO+CM}:m_{Py} = 1:25$) with vigorous stirring for 10 min. And then, 1.118 g sulfamic acid (SA) and 1 mL Py were added into the mixture and stirred at room temperature for 10 min. Afterwards, 50.00 mL 0.30 M FeCl₃ solution was added drop by drop to the mixture to start the polymerization. The reaction was performed under nitrogen protection for 0.5 h. The final product was dried under vacuum at 50 °C for 12 h to obtain the PCMG1-1 composites as a black powder. PPy/CM (PCM, without GO), PPy/GO (PG, without CM), pure PPy (without GO and CM) and CM/GO (CMG, without Py) samples were also prepared for comparison. According to the difference of proportions, the samples are referred to different groups shown in Table 1. In addition, we also prepared of PPy/AM composites (PAM, the mass ratio of AM and Py was same to PCM-1, just CM was replaced by AM) for comparison.

2.4. Structure characterization

The morphology of samples was observed by a scanning electron microscopy (SEM, S-4300, Hitachi Co., Ltd. Tokyo, Japan) and transition electron microscopy (TEM, H-8110, Hitachi Co., Ltd. Tokyo, Japan). The crystallographic structures of the samples were observed by a powder X-ray diffraction system (XRD, XRD-6000, Shimadzu Co., Ltd. Kyoto, Japan) equipped with Cu K α radiation. The molecular structure of the composites was identified by Fourier transform infrared spectroscopy (FTIR, JRT-7000; JASCO, Japan). Nitrogen adsorption/desorption isotherms were collected at liquid-nitrogen temperature (-196 °C) with a Micromeritics ASAP 2020. All samples were outgassed under vacuum at 80 °C overnight prior to measurement. The specific surface area was calculated according to the BET method. The molecular structure of the composites was identified by X-ray photoelectron spectroscopy (XPS, PHI-5000, Perkin-Elmer Corp., USA).

2.5. Electrochemical tests

The test electrodes were prepared by mixing the samples, polytetrafluoroethylene (10 μ L), and ethanol (50 μ L), and grinding

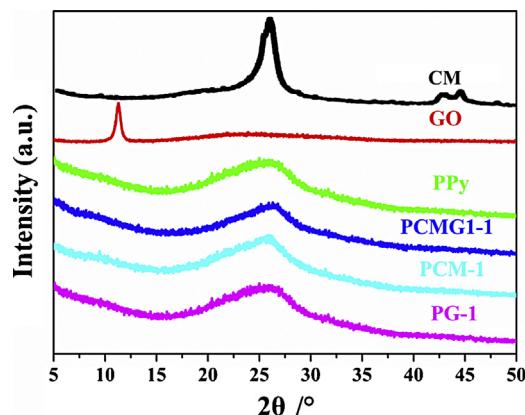


Fig. 1. XRD patterns of CM, GO, PPy, PCMG1-1, PCM-1 and PG-1.

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