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RGO/MnO_2/polypyrrole ternary film electrode for supercapacitor

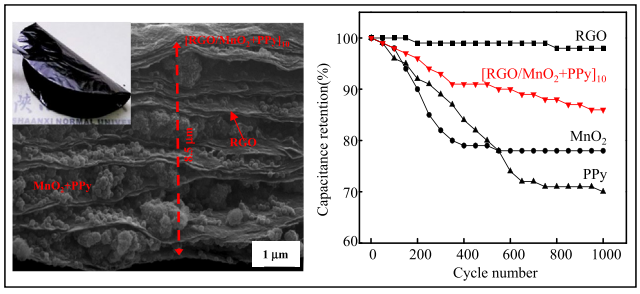
Haiyan Zhou [a, b], Zhe Yan [a, b], Xing Yang [a, b], Jing Lv [a, b], Liping Kang [a, b], Zong-Huai Liu [a, b, *]

[a] Key Laboratory of Applied Surface and Colloid Chemistry, Shaanxi Normal University, Ministry of Education, Xi'an, 710062, PR China
[b] School of Materials Science and Engineering, Shaanxi Normal University, Xi'an, 710062, PR China

HIGHLIGHTS

- RGO/MnO_2 + polypyrrole ternary film has high capacitance and good flexibility.
- Ternary film is prepared by a filtration-directed self-assembly technique.
- PPy and MnO_2 nanoparticles are embedded into the interlayer of RGO nanosheets.
- Ternary film electrode delivers a specific capacitance of 682 F g^{-1} at 5 mV s^{-1}.

GRAPHICAL ABSTRACT



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ABSTRACT

The binder-free electrode is expected for developing supercapacitor with high energy density. By using the good conductivity and forming-film property of PPy (Polypyrrole) and RGO (Reduced Graphene Oxide), as well as the high capacitance of MnO_2 and PPy, $[RGO/MnO_2 + PPy]_{10}$ ternary film electrode with high capacitance and good flexibility is prepared by a filtration-directed self-assembly technique. PPy nanoparticles (PPy) and MnO_2 nanoparticles (MnO_2) are uniformly embedded in RGO matrix constructed by the RGO nanosheets, decreasing the agglomeration of PPy and MnO_2 and the reassembling of RGO nanosheets. RGO and PPy improve the conductivity, the ion diffusion rate and the charge-transfer resistance of the $[RGO/MnO_2 + PPy]_{10}$ ternary film electrode, thus making it shows high capacitance and good flexibility. The $[RGO/MnO_2 + PPy]_{10}$ ternary film electrode with a mass ratio of RGO:MnO_2:PPy = 2:1:2 delivers the highest specific capacitance of 682 F g^{-1} at a scan rate of 5 mV s^{-1} and good cycling stability with about 86% retention of its original capacitance after 1000 consecutive cycles. The superior performance of $[RGO/MnO_2 + PPy]_{10}$ ternary film electrode is probably ascribed to the novel film structure, the synergistic effect among PPy, RGO and MnO_2 and the high packing density of PPy and MnO_2.

1. Introduction

Electrochemical capacitors (ECs) are considered as the most effective and practical technology for the energy conversion and storage [1], they can bridge the critical performance gap between the energy density of battery and high power density of conventional dielectric capacitor, which makes the rapid storage and release of energy become possible [2]. Based on the charge storage mechanisms, ECs can be classified into two categories [3]. One is the electrical double layer capacitors (EDLCs), they are usually composed of carbon materials or carbon-based hybrid materials

* Corresponding author. School of Materials Science and Engineering, Shaanxi Normal University, Xi'an, Shaanxi, 710062, PR China.
E-mail address: zhliu@snnu.edu.cn (Z.-H. Liu).

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with high surface areas and suitable pore sizes [4]. And another is pseudocapacitors, which employ electroactive conducting polymers or transition metal oxides for electrode materials [5]. Up to now, porous carbon, conducting polymers, and transition-metal oxides are promising candidates for the electroactive materials for electrochemical capacitors, but each kind of these materials has its own advantages and disadvantages [6–8]. Porous carbon materials show long cycle life and good mechanical property, but their specific capacitance is low. Although transition metal oxide electrodes show high specific capacitance, their poor electrical conductivity and structural instability hinder their applications. Moreover, conducting polymers show high specific capacitance and good flexibility, but their cycle performance in a suitable potential window of charge storage/delivery still needs to be improved. Therefore, how to exert their respective advantages and prepare the electrode materials with high capacitive performance is one of the most important issues for supercapacitors.

In order to exert their respective advantages of electrode materials, the hybrid material is expected to be designed and prepared by assembling these three types of electrode materials. Up to now, many efforts have been devoted to design advanced new electrode materials on the basis of the hybrid of porous carbon, conducting polymers, and transition-metal oxides, and a series of the multi-component hybrid electrode materials with superior capacitive performance have been prepared [9–13]. Binary composite electrode materials such as carbon-conducting polymer [14,15], carbon-metal oxide [16,17], conducting polymer-metal oxide [18,19], and ternary composite electrode materials such as carbon-metal oxide-conducting polymer [20–22] have been fabricated and investigated, and these multi-component hybrid electrode materials show superior capacitive performance [23,24].

Among the multi-component hybrid electrode materials, the film electrodes, especial the flexible and binder-free film electrodes have shown great promise in upcoming next-generation portable and flexible electronics such as roll-up displays, photovoltaic cells, and wearable devices [25–27]. Because this film architecture can reduce ion diffusion length and electron transfer resistance, and these film electrodes show ideal electrochemical performance [28,29]. Based on the highly conductive structure and good mechanical strength of graphene and the large specific capacitance of MnO_2, a novel free-standing RGO/MnO_2 nanosphere (RGO/MnO_2 NS) hybrid film has been obtained by a filtration-directed self-assembly method in our previous work, and the obtained [RGO/MnO_2]$_{10}$ film electrode with a mass ratio of RGO/MnO_2 NS = 2:1 in each layer shows not only high specific capacitance of 446 F g^{-1} at 5 mV s^{-1}, but also good flexibility and capacity retention rate [30]. Although RGO can improve the film flexibility and mechanical strength, its capacitance shall decrease. Instead the added MnO_2 can enhance the performance of the film electrode, but the film flexibility will decrease. Therefore, how to simultaneously improve the flexibility and capacitance of the RGO/MnO_2 hybrid film is a challenging work.

Polypyrrole (PPy) is an interesting conductive polymer because of its high electrical conductivity, easy synthetic procedure, enhanced thermal and chemical stability, environmental friendliness, and low cost [31]. When it is hybridized with other suitable supports, such as carbon nanotubes, graphene oxide, inorganic transition-metal oxides, and so forth, the electrode materials with better flexibility, specific capacitance, and mechanical stability can be prepared [32–34]. Therefore, when PPy is added into the as-prepared RGO/MnO_2 hybrid film, is it possible to simultaneously improve the flexibility and capacitance of the obtained hybrid film? In the present work, flexible, free-standing RGO/MnO_2 + polypyrrole ternary films are fabricated by a filtration-directed self-assembly method, and the flexibility and capacitance of the obtained hybrid film is simultaneously improved due to the addition of PPy into RGO/MnO_2 hybrid film.

2. Experimental

2.1. Materials preparation

Preparation of polypyrrole nanoparticles, birnessite-type MnO_2 nanoparticles, and RGO nanosheet suspension. Polypyrrole nanoparticles were prepared using a well-established method according to the reference [35]. Briefly, 0.1 g polyvinyl alcohol (PVA) was firstly dissolved in 20 mL deionized water at room temperature swelling for 16 h, then 60 °C swelling for 1 h, and the obtained solution is heated to 95 °C for 25 min. Then 1.24 g $FeCl_3 \cdot 6H_2O$ as oxidizing agent was added to above PVA solution, the solution gradually changes yellow. After the yellow solution was stirred for 1 h, pyrrole monomer (0.1 mol dm^{-3}, 140 μL) was added into the aqueous PVA/$FeCl_3$ solution and the polymerization was carried out at 5 °C for 4 h, then the black PPy nanoparticle suspension was obtained. The PPy nanoparticle suspension was then centrifuged at 12,000 rpm for 40 min, and the obtained PPy nanoparticles were washed several times with hot water to remove impurities, and dried at 60 °C for 6 h in air, PPy nanoparticles were finally obtained, which were abbreviated as PPy.

Birnessite-type MnO_2 nanoparticles were prepared using a solution-based ultrasonic process as reported previously [36]. Briefly, 0.316 g $KMnO_4$ and 0.7 g $MnSO_4 \cdot H_2O$ were respectively dissolved in 100 mL deionized water. Then the $KMnO_4$ solution was added into the $MnSO_4$ solution, and the obtained suspension was ultrasonicated using a KQ-600kDE Digital Ultrasonic cleaning device (600 W, 80% amplitude) for 2 h. Finally, the resultant precipitate was washed with deionized water to neutral, and dried at 60 °C for 6 h in air, birnessite-type MnO_2 nanoparticles were obtained, which were abbreviated as MnO_2.

RGO nanosheet suspension was prepared by chemical reduction method according to the reference [37]. In a typical procedure, graphite oxide (Nanjing XFNANO Materials Tech Co., Ltd) was dispersed into deionized water and treated by ultrasonic treatment for 2 h, the graphene oxide (GO) homogeneous dispersion was obtained. Then, a mixed solution of hydrazine solution (34 mL, 50%) and ammonia solution (200 mL, 25%) was added into the GO suspension (0.25 mg mL^{-1}, 100 mL), and the pH of the obtained suspension was adjusted to about 10. The obtained suspension was stirred for 30 min and then heated at 95 °C for 1 h, GO was reduced into RGO and RGO nanosheet suspension was obtained.

Preparation of RGO/MnO_2/PPy ternary film. RGO/MnO_2/Polypyrrole ternary film was assembled with RGO nanosheets, MnO_2 nanoparticles, and PPy nanoparticles by a typical filtration-directed self-assembly method [38]. The three stock suspensions of the dispersed RGO nanosheets, MnO_2 nanoparticles, and PPy nanoparticles with concentration of 0.2 mg mL^{-1} were firstly prepared. RGO/MnO_2/PPy ternary film was assembled with a 0.2 μm pore size alumina membrane (Whatman) by vacuum filtrating the above three stones in turns. After following filtration of 30-layers (10 layers RGO, 10 layers MnO_2, 10 layers PPy, and the mass ratio of RGO (0.24 mg):MnO_2 (0.12 mg):PPy (0.24 mg) = 2:1:2 in each layer), [RGO/MnO_2/PPy]$_{10}$ ternary film was obtained. While RGO/MnO_2 + PPy ternary film was prepared by vacuum filtrating RGO suspension and a mixed suspension of MnO_2 and PPy in turns. After following filtration of 20-layers (10 layers RGO, 10 layers MnO_2 + PPy, and the mass ratio of RGO (0.24 mg):MnO_2 (0.12 mg):PPy (0.24 mg) = 2:1:2 in each layer), [RGO/MnO_2 + PPy]$_{10}$ ternary film was obtained. By maintaining the mass ratio of RGO (0.24 mg)/MnO_2 (0.12 mg) = 2 and changing the mass of PPy (0.06, 0.12, 0.18, 0.30 mg) in each layer, the RGO/MnO_2 + PPy ternary films