



Strongly coupled manganese ferrite/carbon black/polyaniline hybrid for low-cost supercapacitors with high rate capability



Daosong Zha, Pan Xiong*, Xin Wang*

Key Laboratory for Soft Chemistry and Functional Materials of Ministry Education, Nanjing University of Science and Technology, Nanjing 210094, China

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ABSTRACT

Hybrid nanostructures with reliable electrochemical performances (e.g., high rate capability and long cycling lifetime) and low fabrication costs are attractive for extensive application for next-generation energy storage devices. Herein, based on the inexpensive commercial carbon black (CB), a ternary manganese ferrite/carbon black/polyaniline (MCBP) hybrid is designed and synthesized through a facile two-step approach. It is found that the synergistic effects in this strongly coupled ternary hybrid nanostructure can remarkably enhance the electrochemical performances, including the impressively high rate capability ($\sim 98\%$ capacitance retention at a current density of as high as 40 A g^{-1}) and excellent cycling stability ($\sim 80\%$ capacitance retention after 10,000 cycles at 5 A g^{-1}). A symmetric supercapacitor is fabricated using ternary MCBP hybrid, which presents excellent rate capability (over 94% capacitance retention at 10 A g^{-1}) and long cycle life ($\sim 75\%$ capacitance retention after 100,000 cycles at 5 A g^{-1}). Such a low-cost integrated ternary hybrid is a promising electrode material for commercial applications in supercapacitors.

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1. Introduction

In recent years, supercapacitors have attracted considerable attention due to increasing demand in lightweight and flexible portable energy storage devices. Supercapacitors integrate the advantages of rechargeable batteries and dielectric capacitors to achieve fast dynamic response, high power density, excellent cycling lifespan, fast charge-discharge rate and operational safety [1,2].

According to the nature of charge storage, supercapacitors can be classified into electrical double layer capacitors (EDLCs) and pseudocapacitors. Thereinto, carbon nanomaterial-based EDLCs, storing energy via reversible electrostatic adsorption of charges near the electrode/electrolyte interfaces, normally show faster charge/discharge ability and longer lifetime [3,4]. Up to now, a variety of porous carbon materials such as carbon black (CB) [5,6], onion-like carbons [7,8], carbon nanofibers (CNFs) [9–11], carbon nanotubes (CNTs) [12–14], and graphene [15–17] have been widely used as electrode materials in EDLCs due to their large surface area, good electrical conductivity, and admirable chemical stability [18,19]. Theoretically, the capacitance of EDLCs is proportional to the available surface area of porous carbon electrode materials.

However, even the interior surface of micropores can significantly increase the surface area of carbon nanomaterials up to $1000 \sim 4,000 \text{ m}^2 \text{ g}^{-1}$, the sufficient diffusion of electrolyte onto the total active surface is still difficult to be guaranteed. The incomplete utilization of the theoretical huge specific surface area lead to the capacitance of EDLCs is still around $100 \sim 300 \text{ F g}^{-1}$, resulting in the limited energy density [3,18]. Moreover, sluggish diffusion of electrolyte ions within the tortuous micropores will inevitably lead to poor rate capability at larger current densities [10,20]. Therefore, improving the energy capacity and rate capability of carbon nanomaterial-based EDLCs remains an ongoing challenge and various strategies have been proposed. One approach is to introduce well-organized mesopores network or construct well-designed carbon nanostructures for reducing diffusion resistance and improving charge transport [21–23]. However, the problem of the low ionic diffusion inside the inner pores is raised. Another approach is to design and synthesize binary hybrid nanostructures via combining carbonaceous substrates with pseudocapacitive active materials, such as transition metal oxides or conductive polymers, which can provide several-fold capacitance via fast and reversible surface redox reaction, leading to high energy density [24–26]. Nevertheless, there are still several shortcomings for these binary hybrid nanostructures. Firstly, as a result of diffusion-controlled redox reactions of pseudocapacitive active materials, the enhanced energy density often accompanies with the reduced power density, leading to low

* Corresponding author. Tel.: +86 25 84305667; fax: +86 25 8431 5054.
E-mail addresses: wangx@njust.edu.cn, xpmayangel@163.com (X. Wang).

utilization of the active material and inferior rate capability [27]. Secondly, the layers of characteristic accumulation of metal oxides particles (or polymer) within the pore channels or on the surface may shrink the surface area and increase diffusion resistance [28]. Additionally, the storage capacity is heavily depended on current rate due to the limited diffusion rate, unless intimate interactions at the carbon/metal oxides (or polymers) interfaces are manageable to ensure effective charge transport [29–31].

To solve these critical problems, a “conductive wrapping” strategy has been developed recently to wrap conductive polymer layer onto carbon nanomaterial/metal oxide binary hybrids, forming a nanocarbon/metal oxide/polymer ternary hybrid with excellent capacitance, rate capability, and cycling stability compared to those of nanocarbon/metal oxide binary hybrids [26,32–35]. The enhanced performances can be attributed to the fact that the conductive polymer wrapping method can introduce additional charge storage process to increase the total capacity, provide an additional electron transport path for effective charge transport, and act as protective layer to offer good interconnectivity and structure stability, thus showing an effective approach for high rate and cycling capability electrochemical performance. Based on this strategy, ternary hybrid nanostructures such as $\text{MnO}_2/\text{CNTs}/\text{poly}(3,4\text{-ethylenedioxythiophene})$: polystyrene sulfonate (PEDOT:PSS) [32], $\text{MnO}_2/\text{graphene}/\text{PEDOT:PSS}$ [33], graphene/ MnO_2 /polyaniline (PANI) [34], reduced graphene oxide@ MnO_2 @PEDOT-PSS [35] have been prepared for high-performance supercapacitors. Other than commonly used simple metal oxides, complex metal oxides such as spinel-type ferrites and cobaltites have been considered as promising candidates for high-performance supercapacitors, mainly due to their higher electric conductivity and electrochemical activity that arise from the synergetic effects among multiply valence cations [36–40]. Recently, our group has reported graphene/ferrites/PANI-based ternary hybrids including graphene/ CoFe_2O_4 /PANI [41] and graphene/ MnFe_2O_4 /PANI [42] as upgraded electrode materials for supercapacitors. These ternary composites exhibited large specific capacitance, good rate capability and high cycling stability, superior to those of individual components and corresponding binary hybrids. Even though, it should be noted that the above ternary hybrids are based on costly graphene or CNTs, to achieve large-scale and low-cost production has become one of the most important challenges in commercial applications. As a conventional carbon material, carbon blacks (CBs), such as Vulcan XC-72, are the most commonly used supports for energy storage in many studies and commercial applications because they possess high specific surface area, good electrical conductivity, excellent chemical and mechanical stability to ensure a better electrochemical performance, more importantly, the low cost and easy availability of CBs help reduce the overall cost of energy storage devices. Nonetheless, relatively little attention has been paid to the CB-based ternary hybrids so far. Therefore, it is of great interest to rationally design and facilely synthesize the CB-based ternary hybrids for supercapacitors. If that can be accomplished, then it may be possible to obtain some exceptional performances such as high rate capability and long cycle life, especially, find a new approach to further exploit the low-cost but high-performance carbon-based materials for energy storage devices.

Herein, we report a facile and low-cost approach to fabricate ternary MnFe_2O_4 /carbon black/PANI (MCBP) hybrid for supercapacitors. MnFe_2O_4 nanoparticles were first *in-situ* generated on the surface of CB under solvothermal condition to form the binary MnFe_2O_4 /carbon black (MCB) hybrid, which was further coated by polyaniline (PANI) through an *in-situ* polymerization process to obtain the ternary MCBP. It is found that the intimate interaction between individual components together with their synergistic effects can significantly enhance the electrochemical performances,

including the much higher rate capability and better cycling stability as compared with the binary hybrids. A symmetric supercapacitor is fabricated using ternary MCBP hybrid, which also presents excellent rate capability and long cycle life.

2. Experimental section

2.1. Synthesis of ternary MnFe_2O_4 /carbon black/polyaniline

Carbon black (Vulcan XC-72, Cabot Corporation) was pretreated with concentrated nitric acid before use. Acid treatment was employed to introduce oxygen-containing functional groups to the surface of carbon black, providing nucleation sites for deposition of MnFe_2O_4 nanoparticles [43]. All other chemicals applied in the experiment were of analytical grade and used without further purification. Binary MCB was synthesized by a two-step strategy. 120 mg of carbon black, 0.35 mmol of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ and 0.70 mmol of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ were well dispersed and mixed homogeneously into 140 mL of ethylene glycol. A stable homogeneous emulsion was obtained after adjusting pH to 10 with stoichiometric NaOH aqueous solution. The resulting mixture was sealed into a 200 mL Teflon-lined stainless steel autoclave and heated to 180 °C. After maintaining for 24 h, the mixture was cooled to room temperature naturally, the precipitate was then collected by centrifugation, washed with ethanol-water several times and freeze-dried. For comparison, a similar procedure was adopted to synthesize pure MnFe_2O_4 without the presence of CB. Ternary MCBP hybrid was fabricated via *in-situ* polymerization of aniline monomers in the presence of binary MCB. Typically, 200 mg of binary MCB and 0.167 g of ammonium peroxydisulfate (APS) were well dispersed and mixed homogeneously in 100 mL of 0.1 mol L⁻¹ *p*-toluene sulfonic acid aqueous solution under ultrasonic vibrations for 1 h. 0.067 mL of aniline was then added into the mixture dropwise under vigorous stirring, then polymerized under stirring for 24 h in the ice bath. Finally the ternary MCBP hybrid was filtered out and washed with a large amount of deionized water. For comparison, the PANI and the binary CB/PANI (CBP) were synthesized by using a similar procedure without the addition of MCB and MnFe_2O_4 , respectively.

2.2. Characterization

Morphological, microstructural and compositional analyses were performed on a JEOL JEM2100 transmission electron microscope (TEM) and a HITACHI S-4800 II field emission scanning electron microscopy (FESEM). The crystallographic structures of the as-prepared materials were characterized by X-ray diffraction using a Bruker D8 Advance diffractometer equipped with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$) and the diffraction data were recorded for 2θ angles between 10° and 80°. Thermogravimetric (TG) analyses were carried out under air atmosphere, using a TGA/SDTA 851e thermogravimetric analyzer from 50 to 700 °C at a heating rate of 10 °C min⁻¹. The chemical structure analyses of samples were carried out on a Bruker Tensor 27 Fourier transform infrared spectrophotometer (FTIR) with the wavenumber between 4000 and 400 cm⁻¹. X-ray photoelectron spectra (XPS) were conducted on a Thermo ESCALAB 250 spectrometer with an excitation source of Al K α X-ray (1486.6 eV).

2.3. Electrochemical measurements

A homogeneous slurry consisting of 80 wt% active materials, 15 wt% acetylene black and 5 wt% polytetrafluoroethylene (PTFE) was coated onto stainless steel grid in the size of 1 × 1 cm, then dried under vacuum at 60 °C for 24 h and pressed as work electrode. The mass loading of the active materials on each electrode was controlled

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