



Short communication

## Facile synthesis and electrochemical performance of manganese dioxide doped by activated carbon, carbon nanofiber and carbon nanotube



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### ABSTRACT

Manganese dioxide (MnO<sub>2</sub>) composite materials doped by activated carbon (AC), carbon nanofiber (CNF) and carbon nanotube (CNT) were synthesized via a facile route. The effects of AC, CNF and CNT doping on the structure, composition, electrochemical properties and performances of the modified materials were investigated by X-ray powder diffraction (XRD), scanning electron microscopy (SEM), cyclic voltammetry (CV), galvanostatic charge–discharge and electrochemical impedance spectroscopy (EIS) experiments. Results show that these carbon material dopants do not affect the microstructure of MnO<sub>2</sub>, but CNF and CNT doping can optimize the crystal microstructure, modify the particle morphology, decrease the charge transfer resistance, and thus improve the electrochemical performance of the MnO<sub>2</sub> composite materials. Among all the doped samples, AC doped MnO<sub>2</sub> (MnO<sub>2</sub>/AC) has better performance than the other samples. The MnO<sub>2</sub>/AC composite electrode has a specific capacitance of 375 F g<sup>-1</sup> at a discharge current of 100 mA g<sup>-1</sup> within a potential range of 0 to 0.8 V (vs. Ag/AgCl) in 1 mol L<sup>-1</sup> Na<sub>2</sub>SO<sub>4</sub> solution, which is 2.2 times higher than that of the pristine MnO<sub>2</sub> electrode. EIS results show that AC-doping can significantly decrease the equivalent series resistance and charge transfer resistance, which is favorable for the insertion/extraction of ions in supercapacitors.

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### 1. Introduction

As an advanced energy storage device, supercapacitors have been drawn much attention in recent years due to their higher power density and longer cycle life compared with conventional capacitors and rechargeable batteries [1–3]. Based on working mechanism, supercapacitors can be classified into two categories [4,5]. The first one is called as electric double-layer capacitors (EDLCs), including various carbon materials (e.g., activated carbon (AC) [6], carbon nanofiber (CNF) [7], carbon nanotubes (CNT) [8], carbon aerogels [9], graphite [10] and graphene [11]) with large specific surface area, which utilize the capacitance resulting from the charge separation at the electrode/electrolyte interface, whereas the other one is pseudocapacitors, and its capacitance typically is 10–100 times higher than EDLCs [12], which obtain the pseudocapacitance by the fast reversible faradaic redox reactions occurring within the active materials [13–16]. It is reported that various metal oxides (e.g., ruthenium oxide [17], cobalt oxide [18], nickel hydroxide [19], nickel oxide [20], manganese dioxide (MnO<sub>2</sub>) [21], vanadium oxide [22]) and conducting

polymers (e.g., polyaniline [23], polypyrrole [24] and polythiophene [25]) have been employed to develop an advanced pseudocapacitors.

As it is well known, amorphous hydrated ruthenium dioxide (RuO<sub>2</sub> × H<sub>2</sub>O) exhibits excellent capacitive properties with a high specific capacitance of 720 F g<sup>-1</sup> [18,26]. However, high cost as well as toxicity limit its commercialization. As a result, developing cheap material with acceptable electrochemical performances has become a challenge. In a case of the transition-metal oxides, MnO<sub>2</sub> has received considerable attention for supercapacitors due to its low cost, abundance, high electrochemical activity and more environmental friendliness [26]. Furthermore, MnO<sub>2</sub> electrode materials can function well in neutral electrolytes, much safer than the strong acidic electrolytes used in RuO<sub>2</sub> or alkaline electrolytes used in NiO and Ni(OH)<sub>2</sub> based supercapacitors. The theoretical capacitance of the reduction of MnO<sub>2</sub> to MnOOH can reach as high as 1370 F g<sup>-1</sup> in a potential window of 0.8 V calculated on the basis of Faraday' law [27], but the values reported in the literatures [28–30] are usually in a range of 100–300 F g<sup>-1</sup>, which is by far lower than the theoretical value. It is well known that MnO<sub>2</sub> is a semiconductor material, and pseudo-capacitive reaction is an electrochemical behavior occurring at material surface, that is, only a very thin surface layer can involve the charge-storage process. However, the “bulk” materials do not undergo such a reaction, thus leading to lower specific capacitance [31,32]. Hence, ultrathin MnO<sub>2</sub> films could be expected to deliver a high specific capacitance. For example, Zhang et al.

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[33] prepared MnO<sub>2</sub> film by polystyrene template electrodeposition method from MnSO<sub>4</sub> aqueous solution, and the maximum specific capacitance was as high as 1018 F g<sup>-1</sup> at the current density of 500 mA g<sup>-1</sup>, which is close to its theoretical value. However, the specific capacitance is strongly dependent on the MnO<sub>2</sub> film thicknesses which limited its practical application [32]. One effective way to improve the electrochemical performance of MnO<sub>2</sub> is the incorporation of conductive additive with a high surface area, such as AC [34], CNT [35], carbon aerogels [14,26], graphite [14,26], and carbon fibers (CF) [27]. In this case, it increases active material utilization and electrical conductivity [36]. For instance, Zhang et al. [37] synthesized birnessite-type MnO<sub>2</sub>/AC nanocomposites via the direct reduction of KMnO<sub>4</sub> with AC in an aqueous solution, and the nanocomposites deliver a specific capacitance of 50.6 F g<sup>-1</sup> with a maximum energy density of 28.1 Wh kg<sup>-1</sup> in 1 M Na<sub>2</sub>SO<sub>4</sub> aqueous solution. Cheng et al. [16] prepared nanostructured MnO<sub>2</sub>/graphene composite electrodes, and the specific capacitance can reach to 328 F g<sup>-1</sup> at the current density of 1 mA g<sup>-1</sup>. Wang et al. [21] have prepared MnO<sub>2</sub>/CNT composites using cathodic electrodeposition of MnO<sub>2</sub> on CNT, and the electrode showed good capacitive behavior with a specific capacitance of 356 F g<sup>-1</sup> at a scan rate of 2 mV s<sup>-1</sup> in the 0.5 M Na<sub>2</sub>SO<sub>4</sub> electrolyte. Bokkyu et al. [38] reported the improved MnO<sub>2</sub> capacitance by electrodeposited MnO<sub>2</sub> on CF. Recently, Jiang et al. [39] also synthesized one dimensional highly graphitic carbon-tipped manganese oxide/mesoporous carbon/manganese oxide hybrid nanowire, and the galvanostatic charge-discharge testing indicated that the specific capacitance was up to 266 F g<sup>-1</sup> at 1 A g<sup>-1</sup>, which is much higher than the pristine MnO<sub>2</sub> nanowires (157 F g<sup>-1</sup>). For all these methods, the used additives are with good electronic conductivity and high specific surface area. However, these methods reach some obvious disadvantages of complex, energy consumption, high cost and pollution process.

It is significant to develop a quick and simple route to control the grain sizes and surface morphologies of MnO<sub>2</sub>, with good supercapacitor performance. In this work, a facile low temperature solid reaction method was employed to synthesize AC, CNF and CNT doped MnO<sub>2</sub> composites by chemical redox between potassium permanganate and manganese (II) chloride tetrahydrate. The effects of AC, CNF and CNT doping on the structure, morphology and electrochemical supercapacitive properties of MnO<sub>2</sub> composites have been investigated.

## 2. Experimental

### 2.1. Synthesis

Pure and doped MnO<sub>2</sub> with AC, CNF and CNT, marked as MnO<sub>2</sub>, MnO<sub>2</sub>/AC, MnO<sub>2</sub>/CNF and MnO<sub>2</sub>/CNT, respectively, were prepared by a facile low temperature solid reaction method through chemical redox of potassium permanganate with manganese (II) chloride tetrahydrate (3:2 mole ratio). After well grinding in a mortar, 7 wt.% AC, CNF and CNT were added at room temperature. Then ground for 1 h, and the mixture was transferred into a thermostatic water bath of 80 °C for 24 h. The obtained mixture was washed with distilled water, and dried in an oven at 80 °C for 12 h. Afterwards, the product was subjected to acid-treatment in 2 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> solution at 80 °C for 2 h, and then the product was washed thoroughly with distilled water, and dried at 200 °C for 5 h. After that the product was ground for 1 h and then black powder was obtained. Subsequently, the MnO<sub>2</sub>, MnO<sub>2</sub>/AC, MnO<sub>2</sub>/CNF and MnO<sub>2</sub>/CNT samples were successfully synthesized.

### 2.2. Characterization

The crystal structure of the obtained MnO<sub>2</sub>, MnO<sub>2</sub>/AC, MnO<sub>2</sub>/CNF and MnO<sub>2</sub>/CNT samples was analyzed with X-ray diffraction (XRD) via a Bruker D8 X-ray diffractometer. The morphologies of samples were performed by scanning electron microscopy (SEM) (SEM, JEOL JSM-6490LV).

### 2.3. Electrochemical tests

The work electrodes consist of the as-prepared sample, conductive agent and bind polytetrafluoroethylene with weight ratio of 75:20:5. The prepared samples, SP and PTFE were fully mixed and ground, then a proper amount of anhydrous ethanol (dispersant agent) was added into the powder mixture to achieve homogeneous slurry, followed by painting the prepared slurry onto a nickel foam current collector. Finally, the painted current collector was dried at 100 °C for 12 h in vacuum and pressed at a pressure of 10 MPa to form a reliable electrode. The mass loading is about 18.6 mg (9.3 mg/cm<sup>2</sup>).

All electrochemical measurements were conducted in a 1 mol L<sup>-1</sup> Na<sub>2</sub>SO<sub>4</sub> at room temperature. Cyclic voltammetry (CV) measurements were performed on a RST-5000 electrochemical workstation in a three-electrode cell set-up, using the prepared sample as the working electrode, AC as the counter electrode and Ag/AgCl as the reference electrode. The CV response of the electrodes was recorded between 0 and 0.8 V (vs. Ag/AgCl) at a scan rate of 2, 5, 10, 20 and 50 mV s<sup>-1</sup>. The galvanostatic charge-discharge tests were conducted using a NEWARE 5 V/10 mA instrument. The electrochemical impedance spectroscopy (EIS) was carried out on a RST-5000 electrochemical workstation in the frequency range of 0.01 Hz–100 kHz with an amplitude of 5 mV.

## 3. Results and discussion

### 3.1. Structure and morphology

Fig. 1 shows the X-ray diffraction (XRD) patterns of the MnO<sub>2</sub>/AC, MnO<sub>2</sub>/CNF and MnO<sub>2</sub>/CNT samples in comparison with as-prepared pure MnO<sub>2</sub>. The weak and broad peaks seen in Fig. 1(a)–(c) indicate the amorphous nature and the small size of the as-prepared samples. The amorphous parts are beneficial to exhibiting much higher specific capacitance than the crystalline parts, and in some cases it also shows excellent cycling performance. This is because the highly amorphous structure can not only favor the electrolyte to insert into or to expel out from the MnO<sub>2</sub> matrix, but also appropriately increase contact between the electrolyte and electrode materials. The representative diffraction peaks positioned at 12.8°, 18.1°, 28.8° and 37.5° correspond to the (110), (200), (310) and (211) planes, respectively, which can be indexed to α-MnO<sub>2</sub> (JCPDS 44-0141) [14]. As shown in Fig. 1(b) and (c), no extra peaks related to AC and CNF compounds are observed, and all h k l reflections were labeled along with the Miller indices of MnO<sub>2</sub> phase, indicating that the AC and CNF doping does not have any significant effect on the crystal structure of MnO<sub>2</sub>, which is consistent

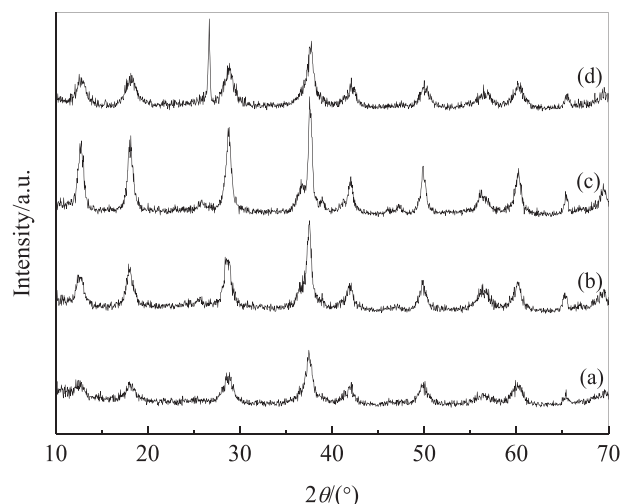


Fig. 1. XRD patterns for (a) MnO<sub>2</sub>, (b) MnO<sub>2</sub>/AC, (c) MnO<sub>2</sub>/CNF, and (d) MnO<sub>2</sub>/CNT.

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