



Nitrogen/manganese oxides co-doped nanoporous carbon materials: Structure characterization and electrochemical performances for supercapacitor applications



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ABSTRACT

Nitrogen-doped nanoporous carbon materials with large BET surface area ($1322.5 \text{ m}^2 \text{ g}^{-1}$) and pore volume ($0.87 \text{ cm}^3 \text{ g}^{-1}$) have been achieved by a synchronous carbonization/nitridation process, simply using potassium biphthalate and azodicarbonamide as carbon/nitrogen sources, respectively. The above carbon materials have been further impregnated with MnO_x nanocrystallites that comes from the thermal decomposition of $\text{Mn}(\text{NO}_3)_2$. Taking the **carbon-2:1-Mn** sample as an excellent example, it also has large BET surface area ($1160.1 \text{ m}^2 \text{ g}^{-1}$) and pore volume ($0.77 \text{ cm}^3 \text{ g}^{-1}$) and exhibits high nitrogen/manganese contents of 4.13%, and 3.30%, respectively. The **carbon-2:1-Mn** sample delivers excellent capacitances of 564.5 and 496.8 F g^{-1} at the current density of 0.5 and 1.0 A g^{-1} , respectively, as well as superior cycling stability of 96.10% even after charging/discharging for 5000 times. The present method of incorporating cheap MnO_x substance into carbon matrix is efficient and also easy for large scale production of carbon nanocomposites, especially possessing large BET surface area and high pore volume.

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1. Introduction

Supercapacitors are energy storage devices that possess high power density, long cyclic stability, low equivalent series resistance (ESR) and can be charged and discharged rapidly, which can bridge the gap between electrolytic capacitors and rechargeable batteries [1]. They have been implemented in many applications requiring many rapid charge/discharge cycles, where they are used for recovery energy from braking, short-term energy storage or burst-mode power delivery [2]. Several types of ECs can be distinguished, depending on the charge storage mechanism as well as the active materials used, primarily including electrostatic double-layer capacitances (EDLCs), electrochemical pseudocapacitance or a combination of both instead.

EDLCs, the most common devices at present, utilize carbon-based active materials with high surface areas up to $3000 \text{ m}^2 \text{ g}^{-1}$ [3]. Most porous carbons include carbon nanotubes (CNTs) [4], carbon aerogels [5], templated carbons [6], activated carbons [7] and graphenes emerging as hot issues since the year of 2004 [8], whose porosities strongly correlative with the electrochemical behaviors differentiate greatly relying on the synthesis protocols adopted. Apart from CNTs with lower BET surface areas of $120 \sim 500 \text{ m}^2 \text{ g}^{-1}$, most of other porous carbon materials can reach up to high ones of $1000 \sim 3000 \text{ m}^2 \text{ g}^{-1}$, whose specific capacitances are of $100 \sim 350 \text{ F g}^{-1}$ when measured in aqueous electrolytes and those of $60 \sim 200 \text{ F g}^{-1}$ in organic electrolytes [9].

As the specific capacitance of carbon materials mainly derives from EDLCs, pure carbon-based capacitors cannot meet the requirements in high energy storage field. An alternative method to enhance the capacitance is to incorporate additional contributions from pseudo-capacitance [10]. In terms of transition metal oxides possessing mixed valences such as MnO_2 , NiO, Fe_3O_4 , Co_3O_4 , they have been demonstrated for supercapacitor application due to the superior pseudo-capacitive behavior, practical availability, environmental compatibility and lower cost especially in contrast

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to the expensive and rare material RuO_2 [11]. Among these metal oxides, manganese oxides, basically including MnO , Mn_3O_4 , Mn_2O_3 , MnO_2 with different allotropes, exhibit the advantages of low cost, no toxicity, easy to obtain and high specific capacitances and therefore has been taken for granted as the most promising materials in application of supercapacitors [12]. For example, MnO_2 with α -, β -, γ -, δ -, and λ -type crystal structures exhibit specific capacitances of $70 \sim 150 \text{ Fg}^{-1}$ at a scan rate of 5 mVs^{-1} [13]. Besides, an enhanced specific capacitance (279 Fg^{-1} at 1 Ag^{-1}), high rate capability (54.5% retention at 20 Ag^{-1}) and good cycling stability (1.7% loss after 1000 cycles) was achieved toward the α - MnO_2 nanowires with sub-10 nm diameters [14].

However, the limitation incurred by the manganese oxides MnO_x is also evident to us. Most of the pseudo-capacitance comes from surface redox reactions and only the first few nanometers from the surface layer are utilized in the faradic processes, as well as partial dissolution of MnO_x in the electrolyte during cycling [15], thereby resulting in lower capacitance than that of the theoretical values of MnO_2 reported as 1370 Fg^{-1} [11], or 1100 Fg^{-1} [16]. Furthermore, the low surface area and poor electronic conductivity of MnO_x give rise to unsatisfactory rate capability and thus limits their applications as electrode materials for high power supercapacitors [15]. On the other hand, porous carbon materials have shown high surface areas and good electrical conductivities. As a

consequence, the incorporation of MnO_x onto carbon matrix can not only increase the effective utilization of the active materials, but also improve the electrical conductivity of the composites [17]. The combination between MnO_x and carbon matrix can be generally divided into binary system of CNTs- MnO_2 [18], graphene- MnO_2 [19,20], and ternary system of MnO_2 -CNTs-conducting polymer [21], MnO_2 -CNTs-textile [22]. On the whole, further exploring an available way to combine MnO_x and carbon matrix with higher electrochemical performances in a simple, scalable but efficient approach still seems to be interesting and challenging for materials scientists.

In this work, we have successfully incorporated certain amount of manganese oxides into nitrogen-doped porous carbons by a two-step reaction synthesis method. Nitrogen-doped porous carbons were first gained from potassium biphthalate and azodicarbonamide by a synchronous carbonization/nitridation process. Next, the as-obtained carbon materials were impregnated with $\text{Mn}(\text{NO}_3)_2$ and further decomposed to form manganese oxides at elevated temperatures. The carbon materials before/after incorporated with manganese oxides were systematically investigated by means of XRD, TEM, Raman and BET techniques. In addition, the electrochemical behaviors of the pristine porous carbons as well as the derivatives incorporated with manganese oxides were measured by a three-electrode system, using 6 M KOH solution as electrolyte.

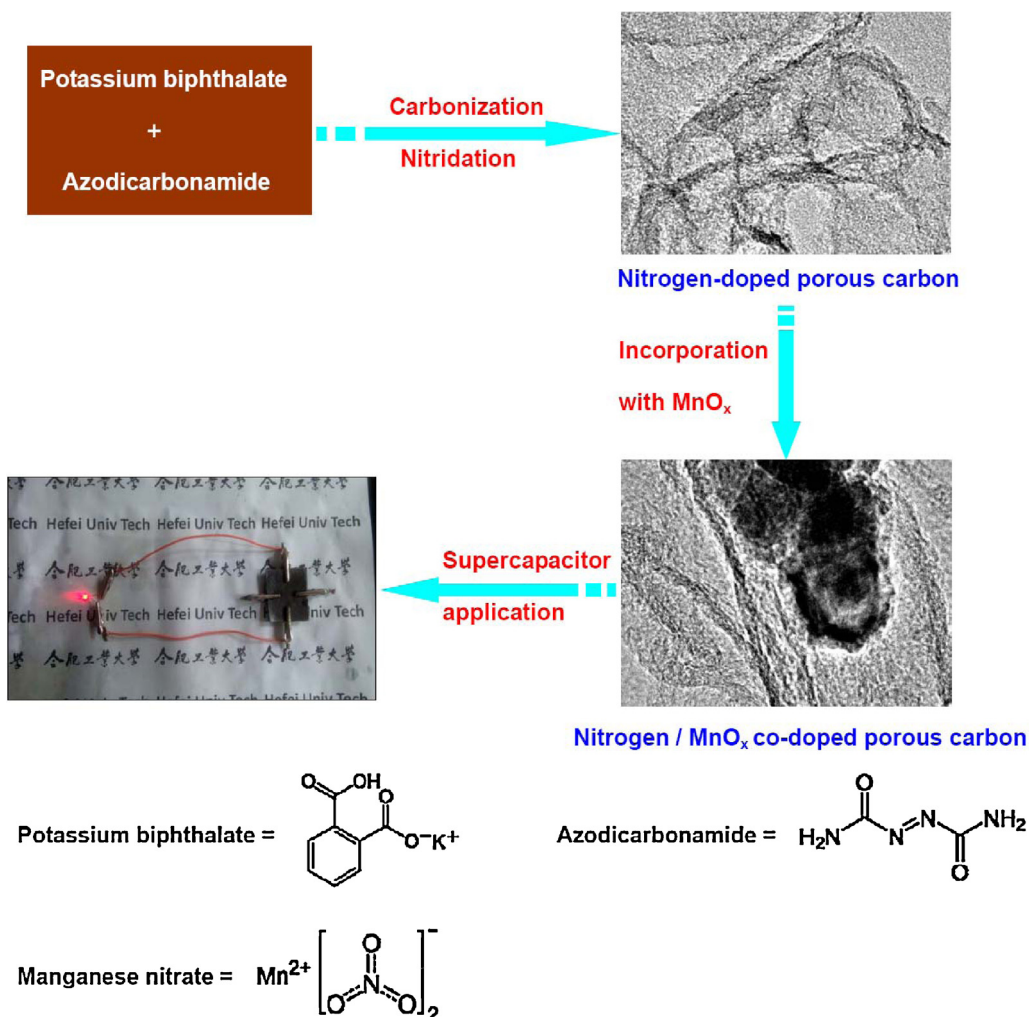


Fig. 1. Schematic diagram for the synthesis of nitrogen/ MnO_x co-doped porous carbon materials, using potassium biphthalate as carbon source, azodicarbonamide as nitridation agent (i.e., nitrogen source), and manganese nitrate as manganese source.

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