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A simple $Mg(OH)_2$-assisted template carbonization method to N-doped nanoporous carbon material from phenidone and the capacitive improvement with the addition of azobisformamide

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ABSTRACT

In this study, we present a simple but efficient template carbonization method to prepare nitrogen-doped nanoporous carbon material, in which phenidone acts as carbon/nitrogen sources and $Mg(OH)_2$ as hard template. The results indicate that the **carbon-1:1** sample is highly disordered with large BET surface area of 1513 $m^2 g^{-1}$, high pore volume of 2.2 $cm^3 g^{-1}$ and nitrogen content of 3.78%. As a result, it exhibits decent electrochemical behaviors, whose specific capacitance reaches up to 202.0 $F g^{-1}$ when measured at 1 $A g^{-1}$ in a three-electrode system. Moreover, azodicarbonamide has been introduced in the process of carbonization to further tailor the porosity of nanoporous carbon, named as the **carbon-1:1:1** sample. In consequence, its BET surface area has decreased to be 1261 $m^2 g^{-1}$ but the pore volume increased up to 2.8 $cm^3 g^{-1}$, together with the large enhancement of nitrogen content up to 7.05%. Besides, it thus delivers a higher specific capacitance of 281.0 $F g^{-1}$ at 1 $A g^{-1}$, mostly due to the incremental content of nitrogen species. The proposed $Mg(OH)_2$-assisted template carbonization method has provided an intriguing synthesis approach for N-doped nanoporous carbons, especially the nitrogen improvement simply by the addition of azodicarbonamide.

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1. Introduction

Because of their excellent performance but low cost, carbon materials have been widely used as electrode materials of supercapacitors, accounting for over 80% of the commercial market [1–4]. Basically, for the purpose of improving the electrochemical properties, it is crucial to enlarge carbon materials' specific areas and control their pore structures. For this reason, template carbonization method has been developed accordingly [5]. Since pioneered by Knox et al. in 1986 [6], different sorts of silicon-containing templates were reported for the synthesis of porous carbon materials, mainly including silica [7], zeolite [8] silicon alkoxide [9], which commonly use corrosive acid such as HF as removing agent. However, large-scale industrial application is still hard to achieve due to the inconvenience of removing those templates. Thus, many researchers have turned their attention to metal oxides/hydroxides, which can be easily removed by relatively moderate acid. Taking $Mg(OH)_2$ as an example, it exhibits several apparent advantages, such as commercially available, inexpensive, and easily soluble in HCl, which has been implemented as efficient template for producing nanoporous carbon materials. For instance, Zhang et al. synthesized mesoporous carbons from mixtures of the soluble starch and needle-like nano-sized $Mg(OH)_2$ particles. The resultant materials possess high surface areas more than 1000 $m^2 g^{-1}$ and large pore volumes in a range from 2.39 to 3.51 $cm^3 g^{-1}$ [10].

On the other hand, nitrogen doping also has been confirmed as an efficient method to further improve the electrochemical properties of carbon materials [11]. The incorporation of nitrogen into carbon materials can not only enhance the interfacial wettability between the electrode and electrolyte and but also induce pseudocapacitive behavior [12]. From the angle of nitrogen sources, there are two methods to synthesize carbon materials doped with nitrogen [13]. One is through the carbonization of nitrogen-containing precursor like polypyrrole [14], diaminobenzene [15] and melamine resin [16], etc. Another is to use dopant such as urea [17], melamine [18] and ammonia [19], etc. Some

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researchers also attempt to integrate the use of two methods. For example, Young et al. successfully prepared nitrogen-doped hierarchically porous carbon nanofibers, with nitrogen contents of up to 9.1%, by using polyacrylonitrile as a nitrogen-containing precursor and melamine as additional dopant. The N-HPCNFs displays a specific energy of 113 Wh kg^{-1} and a specific power of 105 kW kg^{-1}, both are higher than that of sample whose nitrogen source is only the precursor [20]. The combination of template carbonization method with nitrogen doping toward carbon matrix is thus expected to deliver higher nitrogen content and better electrochemical performance.

In this work, we present a template carbonization method to prepare nitrogen-doped porous carbons, using phenidone as carbon/nitrogen sources and $Mg(OH)_2$ as hard template. The reason we chose phenidone as precursor is basically illustrated as follows: it contains a benzene ring to guarantee favourable carbon yield, while two nitrogen atoms can be *in-situ* doped into the carbon materials. More importantly, azobisformamide was introduced into the process of carbonization, which can largely improve the nitrogen content of carbon materials, consequently resulting in better electrochemical performance. The crystallinities, compositions and pore structures of as-obtained carbon samples were characterized by many scientific techniques. The resultant electrochemical behaviors were investigated by a three-electrode system, using 6 mol L^{-1} KOH as electrolyte.

2. Experimental

2.1. Typical template carbonization method for the synthesis of the carbon-1:1 and carbon-1:1:1 samples

In present work, several contrast experiments were carried out to produce N-doped nanoporous carbon. First, certain amount of phenidone and $Mg(OH)_2$ (the mass ratio of 1:1) were used as raw materials, which were converted into N-doped carbons via a template-carbonization method at 800 °C, obtaining the **carbon-1:1** sample; on the other hand, carbonizing the mixture of phenidone, $Mg(OH)_2$ and azobisformamide (the mass ratio of 1:1:1) under the same synthesis conditions can also achieve N-doped carbons, named as the **carbon-1:1:1** sample. The corresponding schematic illustration is displayed in Fig. 1a, and the unit structures of phenidone and azobisformamide are depicted in Fig. 1b, and c.

In a typical synthesis procedure, phenidone and $Mg(OH)_2$ were ground with the mass ratio of 1:1, and then transferred to a horizontal tube furnace. The furnace was heated to 800 °C and maintained at this temperature for 2 h under nitrogen flow. The obtained product was immersed with 1 mol L^{-1} HCl solution to remove inorganic components, subsequently washed with adequate deionized water until pH = 7.0. Finally, the sample was dried under vacuum at 120 °C for 12 h to achieve the **carbon-1:1** sample.

Regarding the synthesis procedure for the **carbon-1:1:1** sample, it is similar to that of the **carbon-1:1** sample detailedly depicted above expect that the initial raw materials are of phenidone, $Mg(OH)_2$ and azobisformamide with a mass ratio of 1:1:1.

2.2. Structure characterization

X-ray diffraction (XRD) patterns were measured on a Rigaku D/MAX2500 V with Cu Kα radiation. (Copper Kα line was used as a radiation source with λ=0.15406 nm.) Raman spectra were performed on a Spex 1403 Raman spectrometer with a 514.5 nm argon-ion laser excitation at ambient temperature. X-ray photoelectron spectra (XPS) analysis was performed on a VG ESCALAB MK II X-ray photoelectron spectrometer with Mg Kα (1253.6 eV) as the exciting source. Field emission scanning electron microscopy (FESEM) was carried out with a Hitachi S-4800 scanning electron microscope. High-resolution transmission electron microscope (HRTEM) images and selected area electron diffraction (SAED)

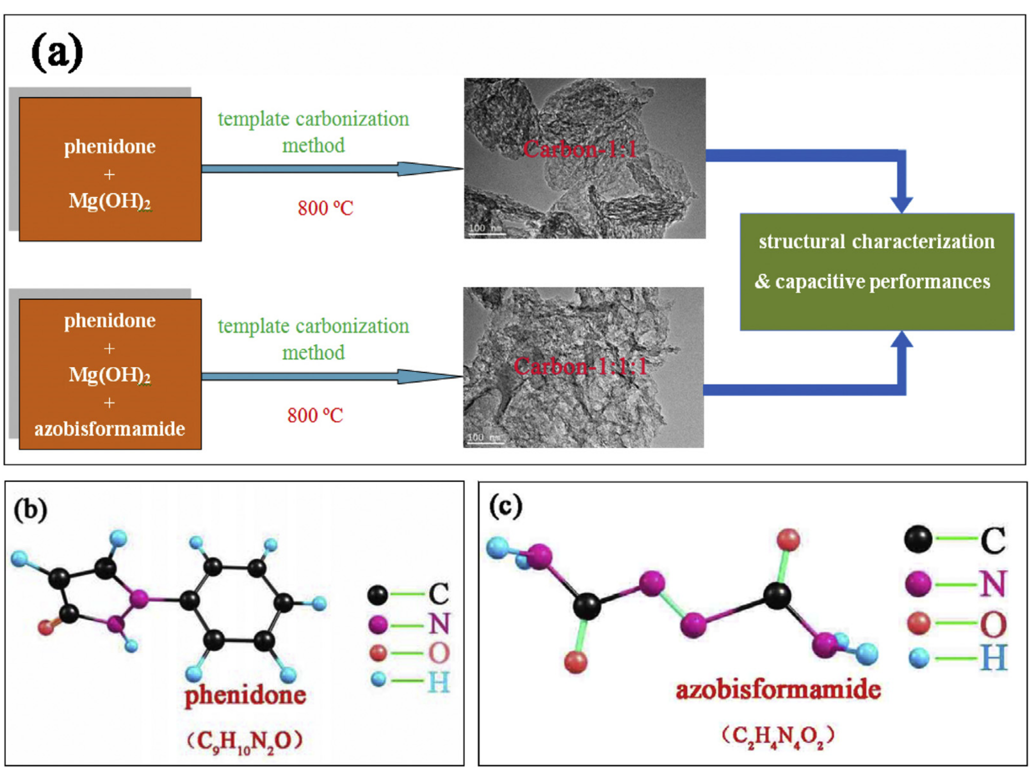

Fig. 1. (a) Schematic illustration of the formation of N-doped nanoporous carbon materials in the present work; (b) ball-and-stick model of phenidone; (c) ball-and-stick model of azobisformamide.

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