



Controllable synthesis of 2D amorphous carbon and partially graphitic carbon materials: Large improvement of electrochemical performance by the redox additive of sulfanilic acid azochromotrop in KOH electrolyte



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ABSTRACT

In this work, by simply heating trisodium citrate dihydrate as sole precursor at 800 °C, novel 2D amorphous carbon material (the **SC-blank** sample) occurs, whose high surface area and large pore volume can reach up to 1015.8 m² g⁻¹ and 2.0 cm³ g⁻¹, respectively. Furthermore, we present a synchronous carbonization and graphitization method to produce partially graphitic carbon materials. When heating the mixture of trisodium citrate dihydrate and nickel nitrate hexahydrate as template and graphitization catalyst (the mass ratio of 7:1) at 800 °C, the resulting **SC-7:1** sample's surface area has decreased to be 682.8 m² g⁻¹ due to its improved graphitization degree, together with a lower capacity, but a better rate capability. More importantly, in order to further enhance capacity, certain amount of sulfanilic acid azochromotrop (*abbr.* SAA) serving as redox additive has been introduced into KOH electrolyte. Notably, the **SC-blank** sample incorporated with SAA redox additive (12 mmol L⁻¹) indicates a largely enhanced capacity of 164 mAh g⁻¹ when measured at 3 A g⁻¹, which is much larger than that of the pristine one (20 mAh g⁻¹). To sum up, the SAA is an efficient redox additive for elevating the capacity.

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1. Introduction

In recent years, nanoporous carbon materials with the high surface area, excellent chemical stability, large pore volume, and outstanding electronic conductivity have drawn intense attention owing to their potential applications in many fields, such as catalysts [1], lithium-ion batteries [2], fuel cells [3], and supercapacitors [4]. However, how to realize the purpose of controllable synthesis of nanoporous carbon materials with distinct structural characteristics (sizes and shapes) has not yet comprehensively investigated. As a fascinating research target, 2D amorphous carbon materials have been widely studied due to their high conductivity and hierarchical porous structure [5]. However, up to now, apart from the conventional chemical activation method, the other kind of bottom-top process usually requires various types of templates, such as montmorillonite (a kind of layered material) [6],

metal salts [7], metal oxides [8], etc. Obviously, the synthetic processes of 2D amorphous carbon materials by using the sacrificial templates are complex and time-consuming. In order to solve this problem, one-step carbonization method has been employed to prepare 2D amorphous carbon materials by using various precursors such as potassium citrate [9], eggplant [10] and sodium gluconate [11], etc. However, these 2D carbon materials usually show quite disordered shapes and thick corrugated sheets. As a result, further exploring an alternative precursor for producing 2D amorphous carbon materials is still compulsory and necessary.

The recent studies reveal that nanoporous carbon materials with highly graphitic structures usually possess excellent rate performances due to their outstanding conductive network and efficient electronic conductivity [12,13]. Up to now, how to fulfill the graphitization increase towards nanoporous carbon materials is quite interesting, which can be realized by the following two strategies. Firstly, treating with high temperature (>2500 °C) is usually needed for largely enhancing the graphitization degree, which requires high energy consumption, usually resulting in the

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decline of porosity (surface area and pore volume) [14]. Secondly, incorporating transitional metal catalysts (*i.e.* Fe, Co, Ni) as well as their derivatives, such as FeSO_4 [15], $\text{Co}(\text{NO}_3)_2$ [16], NiCl_2 [17], *etc.*, into carbon precursor has also been widely implemented, which can apparently lower the carbonization temperature not exceeding 1000°C . That is to say, the so-called synchronous carbonization and graphitization method is quite useful for producing partially even highly graphitic carbon materials (also exhibiting nanoporous features) at the mild conditions.

Apart from the method of enhancement of graphitization degree described above, another strategy that introduces redox additives into conventional KOH electrolyte can also largely elevate the electronic conductivities of supercapacitors, accordingly increasing the total capacitances by their pseudo-capacitive contribution. The improved electrochemical performances incurred by redox additives are usually attributed to the quick reversible redox reactions at the electrolyte/electrode interface [18]. To date, many inorganic or organic redox additives have been introduced into H_2SO_4 , Na_2SO_4 or KOH aqueous solution as electrolyte for supercapacitors. For example, Senthilkumar et al. added KI into H_2SO_4 (1 mol L^{-1}) aqueous solution to improve the electrochemical performances of supercapacitors. The redox pairs of $3\text{I}^-/\text{I}_3^-$, $2\text{I}^-/\text{I}_2$, $2\text{I}_3^-/3\text{I}_2$ and $\text{I}_2/2\text{IO}_3^-$ produce reversible redox reactions between electrolyte and electrode, resulting in a markedly elevated capacitance of 912 F g^{-1} , much higher than that of the initial one without KI additive (472 F g^{-1}) [19]. For another example, the supercapacitor measured in the tetraethyl ammonium iodide electrolyte has shown a high capacitance of 270 F g^{-1} at 2 mA cm^{-2} , being about two folds higher than those tested in other electrolytes, in which the enhanced capacitance is mainly derived from the partial charge transfer of iodide ions [20]. In addition, some organic redox additives were also introduced into electrolyte, such as indigo carmine (IC) [21], *m*-phenylenediamine (MPD) [22], hydroquinone (HQ) [23] *etc.* As a typical example, IC is a kind of macromolecular matter with $-\text{NH}$ and $-\text{OH}$ functional groups, which make it possible to give rise to reversibly redox reactions. Markedly, when IC was introduced into the electrolyte, the supercapacitor shows a largely elevated capacitance of 50 F g^{-1} , which are *ca.* 2.9 folds than that of the pristine one (17 F g^{-1}) [21]. On the other hand, an interesting strategy, grafting the organic groups on the electrode materials, has been revealed to effectively improve the capacitance of supercapacitors. Bélanger and co-workers have reported many research works about grafting the organic groups on electrode materials [24–31]. As an excellent example, Bélanger's groups have modified the activated carbon with electroactive anthraquinone groups by a grafting method. Notably, the modified carbonaceous materials show a larger specific capacitance of 195 F g^{-1} , much higher than that of the unmodified activated materials (100 F g^{-1}), which is attributed to the effect of the reversible redox reaction derived from anthraquinone molecules [27]. Therefore, it is still a meaningful work to further explore efficient redox additives containing various kinds of functional groups such as $-\text{NH}_2$, $-\text{NH}$ and $-\text{OH}$ for markedly improving the electrochemical performance of supercapacitors.

In this work, 2D amorphous carbon materials were first synthesized by one-step carbonization method, using trisodium citrate dihydrate as carbon source. Next, we demonstrate a synchronous carbonization and graphitization method to prepare partially graphitic carbon materials, in which nickel nitrate hexahydrate act both as template and catalyst. The electrochemical performances of obtained carbon samples were measured in conventional KOH electrolyte by a three-electrode system. Besides, we introduced a novel redox additive of SAA into KOH electrolyte to improve the supercapacitors' electrochemical performances. There are two functional groups of $-\text{OH}$ consisting in SAA, which

probably produce the reversible redox reactions between electrolyte and electrode to enhance the electrochemical performances. Herein, the influences of SAA concentration on the electrochemical performances of supercapacitors also were studied in details.

2. Experimental

2.1. Synthesis protocol

Herein, 2D amorphous carbon materials named the **SC-blank** sample were produced at 800°C by a simple one-step carbonization method, in which trisodium citrate dihydrate serves as carbon source. Subsequently, trisodium citrate dehydrate ($\text{C}_6\text{H}_5\text{Na}_3\text{O}_7 \cdot 2\text{H}_2\text{O}$) and nickel nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) with the mass ratio of 7:1 were sufficiently mixed by grinding method. Then, the obtained mixtures were carbonized at 800°C to synthesize partially graphitic carbon materials, named as the **SC-7:1** sample. The electrochemical performances of the **SC-blank/7:1** samples were firstly measured in 6 mol L^{-1} KOH electrolyte. On the other hand, a novel redox additive of SAA was added into 6 mol L^{-1} KOH aqueous solution as mixed electrolyte for supercapacitors. The electrochemical performances of the **SC-blank/7:1** samples were further studied in 6 mol L^{-1} KOH electrolyte with different concentrations of SAA (4, 8, 12 and 16 mmol L^{-1}), and the produced samples were marked as **SC-blank-4**, **SC-blank-8**, **SC-blank-12**, **SC-blank-16** and **SC-7:1-4**, **SC-7:1-8**, **SC-7:1-12**, **SC-7:1-16** samples, respectively.

2.2. Synthesis procedure for 2D amorphous carbon materials

Specifically, trisodium citrate dihydrate was carbonized in a tube furnace up to the desired temperature of 800°C with a rate of 4°C min^{-1} under Ar atmosphere and kept at this temperature for 2 h. The obtained black products were then immersed with 1 mol L^{-1} HCl solution, washed with sufficient deionized water, distilled and dried at 110°C for 12 h under the vacuum condition to achieve the **SC-blank** sample.

2.3. Synthesis procedure for partially graphitic carbon materials

Partially graphitic carbon materials were prepared by a simple synchronous carbonization and graphitization method. Typically, trisodium citrate dihydrate and nickel nitrate hexahydrate with the mass ratio of 7:1 were firstly mixed in an agate mortar to obtain uniform mixtures, which was carbonized in a tube furnace up to 800°C with a rate of 4°C min^{-1} , and held at this temperature for 2 h under the Ar flow. Subsequently, the prepared products were immersed with 1 mol L^{-1} HCl solution aqueous to remove soluble/insoluble substances and then washed with abundant deionized water. Finally, the products were dried at 110°C for 12 h to obtain the **SC-7:1** sample.

2.4. Structure characterization

X-ray diffraction (XRD) patterns were obtained on a Rigaku D/MAX2500 V with $\text{Cu K}\alpha$ radiation. Raman spectra were recorded at ambient temperature on a Spex 1403 Raman spectrometer with an argon-ion laser at an excitation wavelength of 514.5 nm . The surface morphologies of the samples were characterized by field emission scanning electron microscopy (FESEM) using a Hitachi S-4800 microscope operated at an acceleration voltage of 10 kV . High-resolution transmission electron microscope (HRTEM) images and selected area electron diffraction (SAED) patterns were performed with a JEM-2100F unit. The samples for HRTEM were prepared by ultrasonic dispersing the powder products in ethanol, which were then deposited and dried on a holey carbon

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