

Microwave Pyrolysis and Electrochemical Supercapacitor of S-doped g-C₃N₄ Nanoparticles^①

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ABSTRACT In this study, S-doped g-C₃N₄ nanoparticles were successfully prepared by one-step solid-state microwave synthesis. The detailed characterizations through XRD, FT-IR, SEM and XPS were studied. In addition, the electrochemical properties as supercapacitor of the sample were tested by cyclic voltammetry (CV), galvanostatic charge-discharge (GCD) and electrochemical impedance spectroscopy (EIS) techniques. The results showed a high specific capacitance of 691 F/g at current density of 4 A/g in 2 M KOH + 0.15 M K₃[Fe(CN)₆] electrolyte. This study shows that the microwave synthesis is a promising way to design carbon-based electrodes for supercapacitor.

Keywords: S-doped g-C₃N₄ nanoparticles, microwave pyrolysis, supercapacitor;

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1 INTRODUCTION

With the rapid development of social economy and the exhaustion of fossil energy, environmental deterioration is especially attracting global concerns. Research and development of new energy-saving environmental protection materials have become a top priority^[1]. The shortcomings of traditional capacitors and other rechargeable batteries are gradually exposed in the used process, so the development of a new, efficient and green capacitor has become the focus of a majority of researchers. Supercapacitors have attracted more and more attention owing to their higher power density, faster charge and discharge rate, better cycle stability, environmental, etc, which are different from the traditional capacitors^[2].

Two-dimensional graphitic-like carbon nitride (g-C₃N₄), which has received considerable interest in the field of supercapacitor electrode materials owing to its suitable band

gap, physicochemical features, and cadenced carbon-to-nitrogen framework, provides more active reaction sites for electron donor/acceptors that facilitates large additional pseudo-capacitance behavior, and an easy synthesis process^[3, 4]. By doping g-C₃N₄ with nonmetallic elements, its electronic structure can be effectively regulated and its electrochemical activity can be improved^[5]. It has been reported that the non-metallic elements used to dope g-C₃N₄ are mainly composed of oxygen, nitrogen, boron, phosphorus and sulfur atoms^[5-8]. There are many reports on non-metal-doped g-C₃N₄ composite nanomaterials in the field of sensing and photocatalysis, but there are few reports on supercapacitor electrode materials^[9, 10]. It is of great scientific significance to prepare non-metal doped g-C₃N₄ as electrical storage materials by a simple green method.

To the best of our knowledge, high temperature calcination is mostly used to synthesize g-C₃N₄, which has some defects, such as high energy consumption, long reaction time and

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difficult control of the morphology of the product^[11]. The study of simple green method to synthesize g-C₃N₄ is of great significance for the development of new domestic materials. Compared with the conventional calcination method, the solid-phase microwave method has the advantages of mild reaction conditions and short reaction time, which meets the technical requirements of green synthesis^[12].

In this study, S-doped g-C₃N₄ nanoparticles, S@g-C₃N₄, have been prepared through simple one-pot microwave pyrolysis, in which melamine was used as carbon source and nitrogen source, and thiourea as sulfur source in the raw materials. The microstructure and composition of the prepared sample were characterized by XRD, FT-IR, SEM and XPS, and their electrochemical properties as supercapacitor electrode were tested by cyclic voltammetry (CV), galvanostatic charge-discharge (GCD) and electrochemical impedance spectroscopy (EIS) techniques. The specific capacitance of S@g-C₃N₄ was up to 691 F/g at current density of 4 A/g in a 2 M KOH + 0.15 M K₃[Fe(CN)₆] electrolyte, and has good cyclic stability after 2500 cycles. This work provides a new synthesis method for practical energy storage application.

2 EXPERIMENTAL

2.1 Materials and methods

All reagents were obtained from commercial sources and used without further purification. X-ray diffraction studies (XRD) was carried out on a Bruker D8 Advance diffractometer with CuK α radiation (scanned range: 5~80°, scan rate: 8°/min). Fourier transform infrared spectroscopy (FT-IR) was recorded on a Nicolet 6700 FTIR spectrometer using KBr pellets. Scanning electron microscopy (SEM) was conducted with a Quanta-achrome NOVA 4000-E microscope. X-ray photo-electron spectroscopy (XPS) was performed on a Thermo ESCALAB 250Xi spectrometer with AlK α radiation (Analyser Mode: CAE, full-spectrum: 150 eV, narrow-spectrum: 30 eV, Spot Size: 500 μ m).

2.2 Synthesis of S@g-C₃N₄

The S@g-C₃N₄ was prepared by a facile green microwave pyrolysis as follows: First, melamine (0.252 g, 2 mmol) and thiourea (0.304 g, 4 mmol) were mixed and grounded for 5 min at room temperature. Then, the mixture was packed in a dry beaker and heated in a household microwave oven

(P70D20TL-D4, Guangdong Galanz, China) under medium and high fire for 15 minutes. Subsequently, the mixture was pyrolyzed in the microwave power. Finally, the mixture was cooled to room temperature and the yellow target product was obtained by grinding.

2.3 Electrochemical experiment

Electrochemical properties of the samples were evaluated using a potentiostat (CS350, Wuhan Kesite, China) based on a conventional three-electrode system consisted of the working electrode, a platinum wire as the counter electrode, and a saturated calomel electrode as the reference electrode in a 2 M KOH + 0.15 M K₃[Fe(CN)₆] electrolyte. For the working electrode, a mixture containing 80 wt% active material, 10 wt% acetylene black, and 10 wt% poly (tetrafluoroethylene) binder was mixed well. Then, the mixture with several drops of ethanol was coated onto a piece of nickel foam (1.0cm \times 1.0cm) using a spatula. Finally, the fabricated electrode was pressed at 2 MPa to a thin foil and then dried under vacuum at 80 °C for 10 h. The mass loading of the sample was about \sim 5 mg. The EIS data were collected with an AC voltage of 5 mV amplitude in the frequency range from 0.01 Hz to 100 kHz at open-circuit potential.

3 RESULTS AND DISCUSSION

3.1 Synthesis and characterization

The S@g-C₃N₄ can be prepared by melamine and thiourea in 75% yield. The S@g-C₃N₄ is an air-stable faint yellow solid, which has been characterized by XRD, FT-IR, SEM and XPS. The X-ray diffraction patterns of the as-prepared S@g-C₃N₄ are recorded as shown in Fig. 1(a). There are corresponding diffraction peaks at around $2\theta = 13.1^\circ$ and 27.4° , which correspond to (100) and (002) crystal surfaces of g-C₃N₄. The FT-IR spectrum of the as-prepared S@g-C₃N₄ sample is shown in Fig. 1(b). The absorption peak at 811 cm⁻¹ is the triazine ring vibration diffraction peak of g-C₃N₄, while the absorption diffraction peaks at 1200 and 1700 cm⁻¹ are generated by the heterocycle vibration of g-C₃N₄^[13]. The absorption peaks at 2900 and 3500 cm⁻¹ are the stretching vibration peaks of N-H and O-H, which is caused by the incomplete condensation of the mixed materials of melamine and thiourea and the adsorbed water molecules on the surface of the materials^[14].

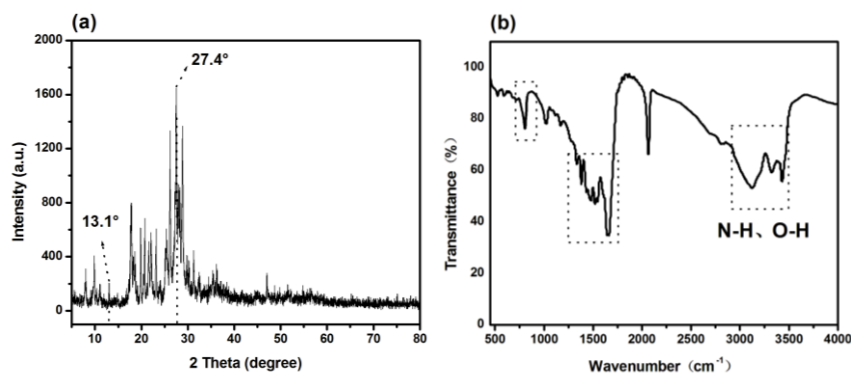


Fig. 1. (a) XRD patterns, and (b) FTIR spectrum of the as-prepared S@g-C₃N₄ sample

As shown in Fig. 2(a), the morphology of the as-prepared S@g-C₃N₄ sample is mostly nanoparticles, and the size is between 20 and 70 nm. In order to better characterize the surface chemical composition and chemical states of

S@g-C₃N₄, XPS measurements were performed as shown in Fig. 2(b). The survey scan XPS spectra provided S, C, N and O peaks for S@g-C₃N₄ nanowires, which once again indicates the successful doping of sulfur elements.

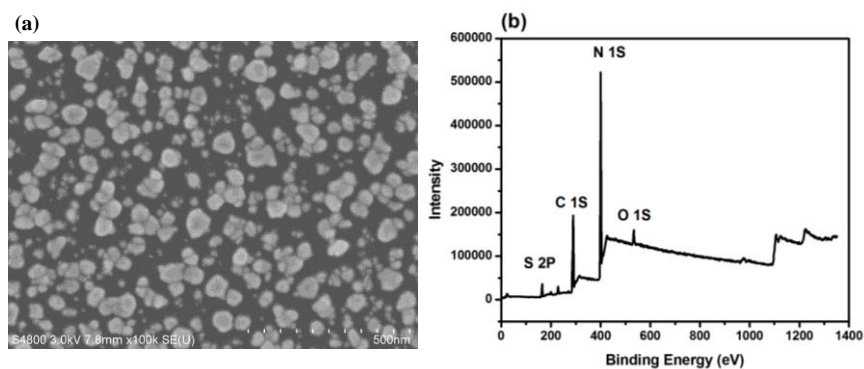


Fig. 2. (a) Image of SEM, and (b) XPS survey spectrum of the as-prepared S@g-C₃N₄ sample

3.2 Electrochemistry properties

The CV curves of the S@g-C₃N₄ electrode at different scan rates (5, 10, 20, 50 and 100 mV/s) are depicted in Fig. 3(a). A pair of strong redox peaks is observed in the CV curve, indicating that the pseudo capacitive behaviour is mainly based on redox reactions. At the scan rates of 5, 10, 20, 50 and 100 mV/s, the corresponding specific capacitances of

S@g-C₃N₄ are 680, 569, 438, 284 and 193 F/g, respectively. It can be seen from Fig. 3(b) that with increasing the scanning rate, the specific capacitance gradually decreases. This may be that the proton diffusion in the electrode is limited and cannot spread to a part of the electrode surface at a high charge and discharge rate, which leads to the incomplete redox^[15].

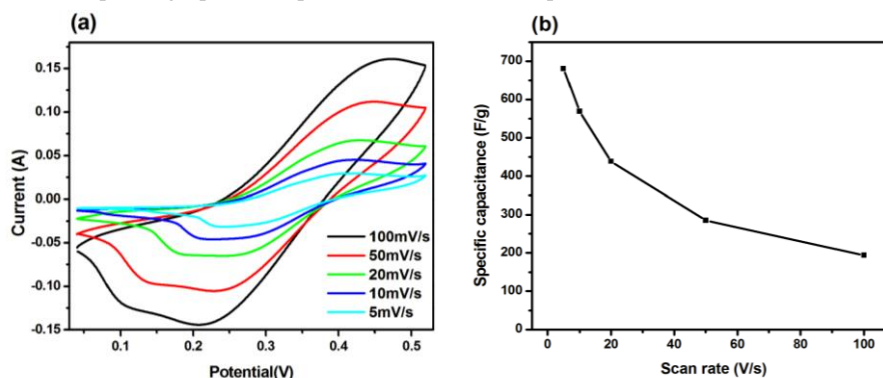


Fig. 3. (a) CV curves at different scan rates of 5, 10, 20, 50 and 100 mV/s, (b) Cs versus scan rates plot

The charge discharge curves of S@g-C₃N₄ at various current densities are plotted in Fig. 4(a). The electrode exhibited gravimetric specific capacitances of 1850, 691, 480, 362 and 278 F/g at current densities of 2, 4, 6, 8 and 10 A/g,

respectively. Such high specific capacitances and symmetric electrochemical characteristics proved the outstanding advantages of the S@g-C₃N₄ electrode.

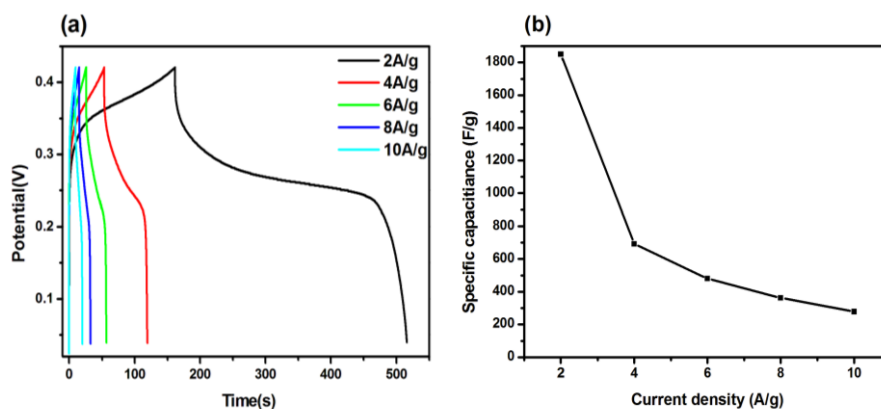


Fig. 4. (a) GCD curve, and (b) C_m versus current density plot of the as-prepared S@g-C₃N₄ electrode

Fig. 5(a) shows the electrochemical impedance spectroscopy (EIS) of the as-prepared S@g-C₃N₄ sample is recorded in the frequency range from 0.01 Hz to 100 kHz at open circuit potential with an Ac amplitude of 5 mV. In the high frequency region, they have relatively low inner resistance obtained from the point of intersecting with the x -axis, that is 0.54 Ω . This resistance basically includes the internal resistance of the electrode material itself, the internal resistance of electrolyte ions and the internal resistance between the electrode and electrolyte interface. Obviously, it can be observed that the resistance of the sample is small, revealing a high electronic conductivity and electrochemical

stability of the sample.

The electrochemical stability is likewise a very important factor for determining the capacitive properties of pseudocapacitors. The long-term stability of the supercapacitor was evaluated by cycling the as-prepared S@g-C₃N₄ supercapacitor in 2 M KOH + 0.15 M K₃[Fe(CN)₆] electrolyte at a current density of 4 A/g for more than 2500 times. As demonstrated in Fig. 5(b), we can see that the specific capacitance of as-prepared sample decreased slightly before 250 cycle, remained unchanged at 2000 cycle, and increased slightly after 2500 cycle, which was the result of activation of electrode material in electrolyte.

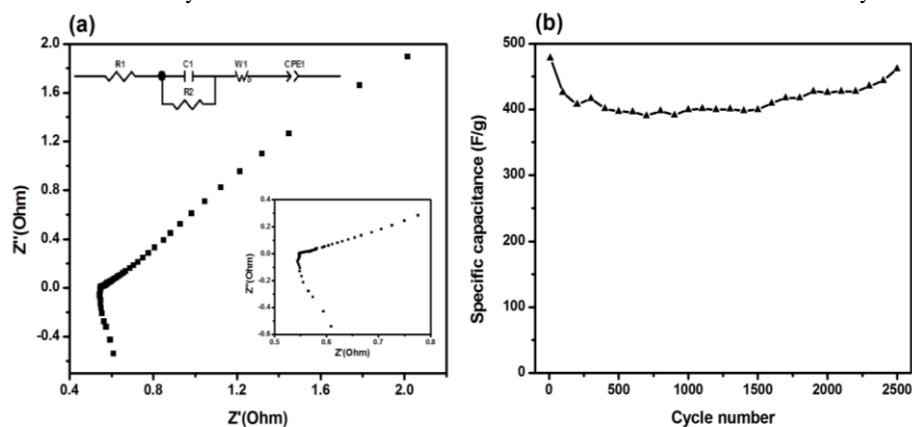


Fig. 5. (a) EIS spectra, and (b) cycling performance at a current density of 4 A/g of the as-prepared S@g-C₃N₄ sample

4 CONCLUSIONS

In summary, S-doped g-C₃N₄ nanoparticles were successfully prepared by one-step solid-state microwave synthesis.

The detailed characterizations through XRD, FT-IR, SEM and XPS were also studied. The morphology of the as-prepared S@g-C₃N₄ sample mostly shows a layered morphology, and the size is between 20 and 70 nm. The

electrochemical properties as supercapacitor of the sample were recorded by cyclic voltammetry, galvanostatic charge-discharge and electrochemical impedance spectroscopy techniques. The results show a high specific capacitance of 691 F/g at current density of 4 A/g in 2 M

KOH + 0.15 M K₃[Fe(CN)₆] electrolyte, and it has good cyclic stability after 2500 cycles. This study shows that the microwave solid-state synthesis is a promising way to design carbon-based electrodes of supercapacitor.

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