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Chemical blowing strategy synthesis of nitrogen-rich porous graphitized carbon nanosheets: Morphology, pore structure and supercapacitor application

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HIGHLIGHTS

- Chemical blowing synthesized N-doped porous graphitized carbon sheets (N-PGCNS).
- This strategy is cost-efficient, facile and industrial-scale than other synthesis routes.
- N-PGCNS own sheet-like morphology, developed porosity, highly graphitized framework.
- It exhibits a high capacitance of 337.6 F g^{-1} at 0.5 A g^{-1} and superior rate capacity.
- It shows an excellent energy/power density for symmetric cell in 1 M $TEABF_4$/AN.

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ABSTRACT

Herein, we proposed a cost-efficient strategy to prepare nitrogen-doped porous graphitized carbon nanosheets, i.e. urea-assisted chemical blowing via foaming starch into the bubble networks of starch-derived polymers combining catalytic graphitization and subsequent KOH activation. In this synthesis route, starch acts as carbon precursor and foaming agent to build a bubble network of polymer, urea acts as nitrogen source and blowing agent to further blow bubble to form N-doped sheet-like carbons with ultrathin structure, γ-Fe_2O_3 serves as a graphitization catalyst precursor to generate highly graphitized framework. Importantly, the thickness of sheets, the nitrogen content and the graphitization degree can be simply tuned by adjusting the mass ratio of urea/γ-Fe_2O_3/KOH. The optimal sample exhibited uniform sheet-like morphology with a thickness of ~80 nm, a high surface area of 2129.8 m^2 g^{-1}, and a large pore volume of 0.97 cm^3 g^{-1}. Acting as an electrode for supercapacitor in 6 M KOH electrolyte, it presented a high specific capacitance of 337.6 F g^{-1} at 0.5 A g^{-1}. Moreover, the two-electrode symmetric cell was assembled in 1 M $TEABF_4$/AN, and displayed a high energy density of 27.5 Wh kg^{-1} as well as an excellent cycling stability with 87.6% retention after 5000 cycles.

1. Introduction

With the ever-growing demand for sustainability in environment and energy, large amounts of efforts have been contributed to develop new natural resources or design high-performance and environmental-friendly energy storage/conversion devices, such as full cells for efficient energy conversion, batteries as well as electrochemical capacitors for high-efficiency energy storage. Electrochemical capacitors, also called supercapacitors, are considered as the important complementary to batteries for high power density, fast charge-discharge rate, excellent cycling stability and more reliable safety [1,2]. According to energy storage mechanism, supercapacitors can be mainly classified to electric double layer capacitors (EDLCs) and pseudocapacitors. EDLCs store electric energy in an electric double layer formed by physisorption of electrolyte ions on the surface of each porous carbon electrode. Compared to pseudocapacitors, EDLCs feature the high power density and long cycle life, which is favorable for applications in high-power electronic devices, uninterruptable power supplies, electric and hybrid electric vehicles and so on [3–5]. However, the practical

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applications of EDLCs are greatly restricted by their limited energy density (ca. 3–5 Wh kg^{-1}) [6,7].

In general, enhancement of the operational voltage of electrolytes and improvement of the specific capacitance of electrodes are usually employed to achieve a high energy density of supercapacitors [8,9]. Especially, pseudocapacitive materials that store energy by the rapid redox reaction on surface have stimulated numerous research interests because of their large specific capacitance in comparison with EDLCs[10–12]. However, the pseudocapacitive active materials, including oxides, hydroxides, sulfides and conductive polymers, suffer some critical problems, such as low electrical conductivity, poor cycling stability and high cost [13,14]. Currently, introduction of heteroatoms (N, B, P, O and S) into porous carbon framework have provided a promising strategy to obtain the enhanced energy density as well as retain the high power density of EDLCs, where the doped heteroatoms act as the pseudocapacitive active sites [15,16]. Among these doped carbon materials, N-doped carbons have been extensively studied and been demonstrated to possess the improved capacitance and meanwhile not sacrifice the high rate capability and long cycle life [17–19]. Furthermore, N-doping in the carbon skeleton can also modify electronic bands to heighten electrical conductivity and surface wettability [20,21]. Generally, two primary routes are employed to fabricate N-doped carbon materials, namely post-treatment methods by thermal treatment of carbons with N-containing precursors and *in situ* synthesis by direct carbonizing N-containing precursors. Liu et al. adopted the post-treatment way to obtain nitrogen-rich porous carbon material using sugarcane bagasse as carbon precursor, $CaCl_2$ as activating agent and urea as nitrogen source, and it presented superior capacitive performance as well as a high specific capacitance of 323 F g^{-1} at 1 A g^{-1} [22]. Gao et al. synthesized a porous and nitrogen-rich carbon using biomass-derived hydrochar as precursor and melamine as nitrogen source, and it exhibited a high capacitance of 492 F g^{-1} at a current density of 0.1 A g^{-1} in 2 M H_2SO_4 electrolyte [23].

Moreover, the morphology, dimensionality and configurations of carbon materials are also the key topics for the design of supercapacitor electrodes, which can efficiently optimize and adjust the capacitive performance [24,25]. Thus, 3D, 2D and 1D carbon materials with different morphologies have been extensively investigated, such as nanoparticle, nanosphere, nanofiber, nanosheet, nanoflower and so on [26–29]. Among of these carbons, 2D porous carbon nanostructures, especially 2D nanosheets, provide a better alternative as electrode materials for highly capacitive performance of EDLCs, because they can be easily prepared and the ultrathin thickness endows short diffusion distance[30]. Currently, various synthetic methods have been reported to obtain 2D porous sheet-like materials, such as template method, mechanical/chemical exfoliation, chemical vapor deposition, molten-salt route, ball-milling method and so on [31–34]. But, some serious drawbacks are exposed in these synthetic routes, for example fussy and time-consuming operating, high-cost and environmental-harmful, which greatly restrict the industrial scale production [35,36]. Recently, tremendous attentions were focused on the chemical blowing strategy due to its convenience and time-saving [37–39]. Peng et al. synthesized highly crumpled N-doped graphene-like nanosheets with excellent electrochemical performance using urea as a nitrogen source and an expanding agent [40]. Wang et al. synthesized N-doped activated carbon sheets using glucose as carbon precursor via melamine-assisted chemical blowing and the sequent KOH-activation, which exhibited the improved capacitive performance [41]. Whereas, the chemical blowing synthesis of 2D N-doped carbon nanosheets is still a challenge for the poor conductivity of amorphous skeleton and uncontrollable pore structure.

Hence, we reported the synthesis of N-doped carbon nanosheets with a graphitized skeleton and the controllable hierarchical porous texture via the chemical blowing route, where starch was used as carbon source and foaming agent, urea was adopted as blowing agent as well as nitrogen source, KOH was served as activating agent and Fe was employed as a catalyst to graphitize carbon framework. More importantly, the nitrogen content, porous structure and the thickness of sheets were tuned by adjusting the urea/KOH mass ratio. The resultant carbon materials possessed a highly graphitized framework, uniform sheet-like morphology with tunable thickness, a superior porous structure with a high accessible surface area and the tunable nitrogen content. Benefiting the features of morphology and structure, the resulting N-doped graphitized porous carbon nanosheets exhibited a remarkable capacitive property as electrodes for EDLCs in KOH aqueous electrolyte and organic electrolyte, including extremely large specific capacitance, satisfactory rate capacity, enhanced power and energy densities and excellent long-term cycling stability.

2. Experimental section

2.1. Preparation of N-doped graphitized carbon nanosheets

N-doped graphitized carbon nanosheets (N-GCNS) were fabricated *via* a facile urea-blowing route by using starch as a carbon source, urea as a blowing agent and nitrogen source, γ-Fe_2O_3 sphere as a graphitization catalyst precursor. Typically, 4 g of starch was uniformly mixed with fixed mass of γ-Fe_2O_3 (ca. 20 nm in size) and urea by a co-ground method. Subsequently, the process was carried out in a tubular furnace under a N_2 atmosphere by heating the mixture powders at a rate of 3 °C min^{-1} up to 800 °C for 2 h. After cooling to room temperature, the calcined products were washed with hot 3.0 M HCl solution and deionized water to remove the iron species and other metal oxides or salts. Then, the materials were dried at 80 °C for 10 h to obtain the final products of N-GCNS. To study the influences of the additive mass of γ-Fe_2O_3 and urea on the morphology and structure of N-GCNS product, the different dosages of γ-Fe_2O_3 (0.2 and 0.5 g) and urea (0.5, 1 and 2 g) were tuned and investigated.

For comparison, 4 g of the starch was directly carbonized at 800 °C for 2 h, which was denoted C-1. In addition, 4 g of starch mixed with 0.2 g of γ-Fe_2O_3 without urea were carbonized at 800 °C for 2 h, which was named as C-2.

2.2. Preparation of N-doped porous graphitized carbon nanosheets (N-PGCNS)

In a typical activation process, 1 g of the obtained N-GCNS materials was impregnated in 20 mL of KOH aqueous solution with containing various KOH dosages of 1–4 g. After stirred for 6 h, the mixed solution was heated and evaporated at 110 °C for 10 h to obtain KOH-impregnated N-GCNS materials. And then, the activation process was carried out at 800 °C for 1 h in a tubular furnace under flowing N_2 in a ramp rate of 3 °C min^{-1}. After cooling down, the activated samples were thoroughly washed with 2 M HCl solution and deionized water. Finally, the materials were dried at 80 °C for 10 h to obtain the final activated N-PGCNS samples, which were designated as N-PGCNS$_{x\text{-}y\text{-}z}$, where x refers to the additive mass of γ-Fe_2O_3, y represents the dosage of urea and z refers to the concentration of KOH.

2.3. Characterizations

X-ray diffraction (XRD) patterns were monitored by a Bruker D8 diffractometer using Cu Kα radiation (λ = 0.15418 nm) as an X-ray