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NS codoped carbon nanorods as anode materials for high-performance lithium and sodium ion batteries

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ABSTRACT

NS codoped carbon nanorods (NS-CNRs) were prepared using crab shell as template and polyphenylene sulfide (PPS) as both the C and S precursor, followed by carbonization in NH_3. The as-obtained NS-CNRs had a diameter of ~50 nm, length of several micrometers, and N and S contents of 12.5 at.% and 3.7 at.%, respectively, which can serve as anodes for both lithium-ion batteries (LIBs) and sodium ion batteries (SIBs). When serving as an anode of LIB, the NS-CNRs delivered gravimetric capacities of 2154 mAh g^{-1} at current densities of 0.1 A g^{-1} and 625 mAh g^{-1} at current densities of 5.0 A g^{-1} for 1000 cycles. When serving as an anode of SIB, the NS-CNRs delivered gravimetric capacities of 303 mAh g^{-1} at current densities of 0.1 A g^{-1} and 230 mAh g^{-1} at current densities of 1.0 A g^{-1} for 3000 cycles. The excellent electrochemical performance of NS-CNRs could be ascribed to the one-dimensional nanometer structure and high level of heteroatom doping. We expect that the obtained NS-CNRs would benefit for the future development of the doped carbon materials for lithium ion batteries and other extended applications such as supercapacitor, catalyst and hydrogen storage.

Lithium ion batteries (LIBs) have been extensively applied in portable electronic devices and electric vehicles owing to their high energy density and long cycle life [1–5]. Very recently, sodium ion batteries (SIBs) have attracted remarkable research interest and are considered as a promising power source in large-scale sustainable energy storage system because of the low cost and wide distribution of sodium [6,7]. Graphite, the commercialized anode material in LIBs, has a low gravimetric capacity of 372 mAh g^{-1}, which is unsuitable for the demands from growing LIB markets [8]. And the low interlayer distance of 0.34 nm for graphite is unsuitable for accommodating Na^+ because of the larger ion radius (~0.106 nm for Na^+ and ~0.076 nm for Li^+) [9]. It is important to develop anode materials with high electrochemical performance and low cost for LIBs and SIBs. Recent research indicated that carbon-based nanostructures such as carbon nanotubes [10], graphene [11], nanofibers (NFs) [12], hollow nano-spheres [13], porous carbon [14] and their hybrids possess promising electrochemical performances for Li^+/Na^+ storage. And the heteroatom dopants in carbon lattices (such as N [10], S [15], B [16] and P [17,18]) are critical factors for the improved electrochemical performance [19]. These heteroatoms with a proper doping configuration in carbon matrices can provide active sites for anchoring Li^+/Na^+ due to the difference in electronegativity between heteroatoms and C [20,21]. Especially, the electronegativity of these three elements are in the order of N (3.04) > S (2.58) > C (2.55). The coexistence of binary-heteroatom doping can lead to improved electrochemical activity for Li^+ and Na^+ storage. Crab shells are sustainable biological templates, as the $CaCO_3$ framework contains hollow channels with inner diameter of ~50 nm and length of several micrometers. The framework can be removed by hydrochloric acid (HCl) [22]. In addition, $CaCO_3$ generates CO_2 gas during thermal annealing, which is a pore-forming agent for activating carbon materials to yield microporous structure. Such heteroatom doped carbon nanostructure with microporous structure is expected for Li^+ and Na^+ storage.

In this work, we obtained NS codoped carbon nanorods (NS-CNRs) by carbonization of polyphenylene sulfide (PPS) in NH_3 with crab shell as a template. PPS with a high S content of 14.3 at.% is the precursor for both the C and S. NH_3 generates N dopants in C matric. And crab shell provides nanometer wide channels to yield NS codoped carbon nanorods. As the anode of LIB, the NS-CNRs delivered gravimetric capacities of 2154 mAh g^{-1} at current densities of 0.1 A g^{-1} and 625 mAh g^{-1} at current densities of 5.0 A g^{-1} for 1000 cycles. As the anode of SIB, the NS-CNRs delivered gravimetric capacities of 303 mAh g^{-1} at current densities of 0.1 A g^{-1} and 230 mAh g^{-1} at current densities of 1.0 A g^{-1} for 3000 cycles.

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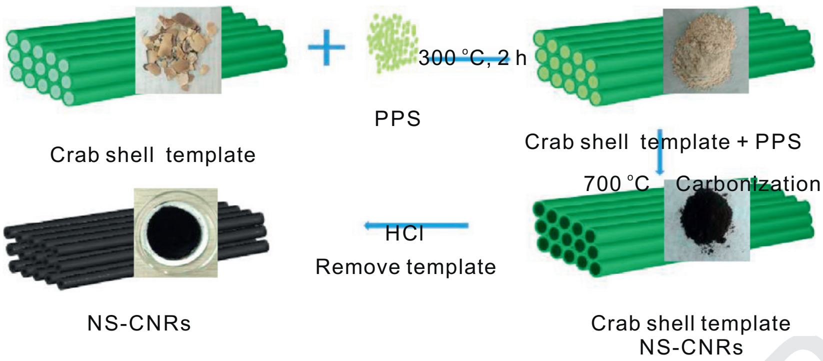

Scheme 1. Schematic presentation of the procedures to prepare the structure-controlled NS-CNRs precursor.

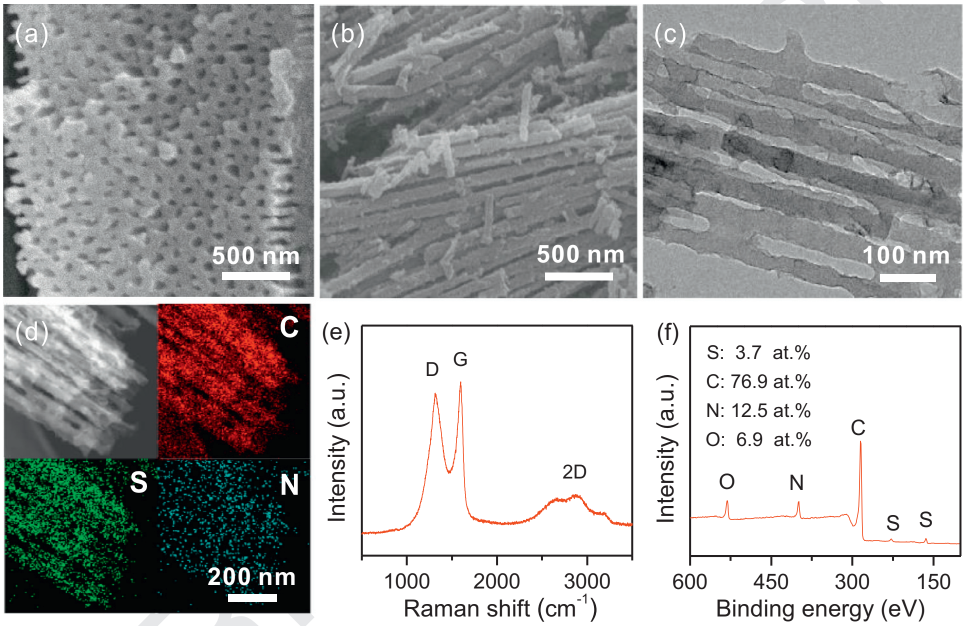

Fig. 1. (a) Cross sectional SEM images of crab shell template. (b) SEM and (c) TEM images of the NS-CNRs-700. (d) Dark field image and corresponding EDX mapping of C, S, and N elements acquired at the same position, showing a uniform distribution of the N and S. (e) Raman spectrum and (f) XPS survey spectrum of the NS-CNRs-700.

As shown in Scheme 1, the crab shell was calcinated first and grinded to obtain the structure template for filling PPS that was performed by mixing the template with PPS (2:1 w:w) by mortar grinding for 20 min. The PPS fills in the channels of crab shell template at 300 °C, and the mixture was further carbonized at 700 °C for 2 h in a mixture of Ar and NH_3. Finally, the crab shell was removed by 1 M HCl aqueous solution to yield NS-CNRs-700. The PPS filled crab shell was also carbonized at the temperatures of 600, 800 and 900 °C, which are named as NS-CNRs-600, NS-CNRs-800, and NS-CNRs-900, respectively, to study the effect of dopant contents on the electrochemical performance.

The crab template is composed of $CaCO_3$ with parallel channels as shown in the scanning electron microscopy (SEM) images (Figs. 1(a) and S1). The NS-CNRs show a diameter of $\sim$50 nm and a length of several micrometers (Figs. 1(b), (c) and S2) and which is independent on the carbonization temperature. The energy-dispersive X-ray (EDX) mapping of C, S, and N elements matching well with the morphology (Fig. 1(d)) acquired by transmission electron microscopy (TEM), indicating a uniform distribution of the chemical compositions in the NS-CNRs. The Raman spectrum shows a broad 2D band (2500–3200 cm^{-1}), and the intensity ratio of the G band over D band (I_G/I_D) is 1.06 (Figs. 1(e) and S3a). The XRD patterns show diffraction peak (Fig. S3b) at around 23° [23,24]. These results indicate a moderate graphitization level. The quantity of N and S dopants were measured by X-ray photoelectron spectroscopy (XPS, Fig. 1(f)), which are 12.5 and 3.7 at.%, respectively. The presence of O 1*s* can be attributed to the reaction between CO_2 and carbon that leaves oxygen contained function groups in carbon. The $CaCO_3$ decompose to form CO_2 at the carbonization temperature, and CO_2 is a widely used agent to form microporous structure in carbon. The N_2 adsorption–desorption isotherms (Fig. S4) presents type-IV hysteresis loops with a steep climbing increase at low relative pressure ($P/P_0 < 0.1$), indicating the existence of microspores and mesoporous structure. The calculated S_{BET} of NS-CNRs-700 is 686 m^2 g^{-1} with an average pore width of 5.7 Å (Table S1).

The electrochemical properties of NS-CNRs-700 for Li^+ and Na^+ storage were investigated in a half cell. Fig. 2(a) and (b) presents the galvanostatic charge–discharge profiles and rate capability, respectively, of NS-CNRs-700 for Li^+ storage. The NS-CNRs-700 demonstrates gravimetric capacities of 2071, 1485, 1304, 1066, 828, 616, and 412 mAh g^{-1} at the current densities of 0.1 to 0.2, 0.4, 0.8, 1.6, 3.2, and 5.0 A g^{-1}, respectively, which is considerably higher than most of the NS codoped carbon-based anode materials (Fig. S5a) [32–36]. Besides, the NS-CNRs-700 shows a reversible capacity of 625 mAh g^{-1} after 1000 cycles with coulombic efficiency of 99.8% (Fig. 2(c)), indicating a stable cycling stability and reversibility. According to previous reports [25], porous carbon

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