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Conversion of uniform graphene oxide/polypyrrole composites into functionalized 3D carbon nanosheet frameworks with superior supercapacitive and sodium-ion storage properties

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HIGHLIGHTS

- 2D graphene oxide/polypyrrole (GO/PPy) is derived from *in-situ* polymerization.
- N-doped carbon nanosheet frameworks is obtained by one-step activation of GO/PPy.
- Highly porous carbon layer is tightly connected with conductive graphene sheets.
- High supercapacitive performances (quasi-rectangular CV curve at 3000 mV s^{-1}).
- High sodium-ion storage properties (144 mAh g^{-1} after 500 cycles at 500 mA g^{-1}).

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ABSTRACT

Two-dimensional (2D) graphene oxide/polypyrrole (GO/PPy) hybrid materials derived from *in-situ* polymerization are used as precursors for constructing functionalized three-dimensional (3D) porous nitrogen-doped carbon nanosheet frameworks (FT-PNCNFs) through a one-step activation strategy. In the formation process of FT-PNCNFs, PPY is directly converted into hierarchical porous nitrogen-doped carbon layers, while GO is simultaneously reduced to become electrically conductive. The complementary functions of individual components endow the FT-PNCNFs with excellent properties for both supercapacitors (SCs) and sodium ion batteries (SIBs) applications. When tested in symmetrical SC, the FT-PNCNFs demonstrate superior energy storage behaviour. At an extremely high scan rate of 3000 mV s^{-1}, the cyclic voltammetry (CV) curve retains an inspiring quasi-rectangle shape in KOH solution. Meanwhile, high capacitances (~247 F g^{-1} at 10 mV s^{-1}; ~146 F g^{-1} at 3000 mV s^{-1}) and good cycling stability (~95% retention after 8000 cycles) are achieved. In addition, an attractive SIB anode performance could be achieved. The FT-PNCNFs electrode delivers a reversible capacity of 187 mAh g^{-1} during 160th cycle at 100 mA g^{-1}. Its reversible capacity retains 144 mAh g^{-1} after extending the number of cycles to 500 at 500 mA g^{-1}.

1. Introduction

There has been an urgent demand for clean and efficient energy-storage devices, due to ever-increasing concerns about limited global energy supply, environmental issues and climate change [1,2]. Recently, electrical double-layer supercapacitors (EDLCs) and sodium ion batteries (SIBs) have attracted tremendous interest in the field of energy storage owing to their individual charge storage characteristics.

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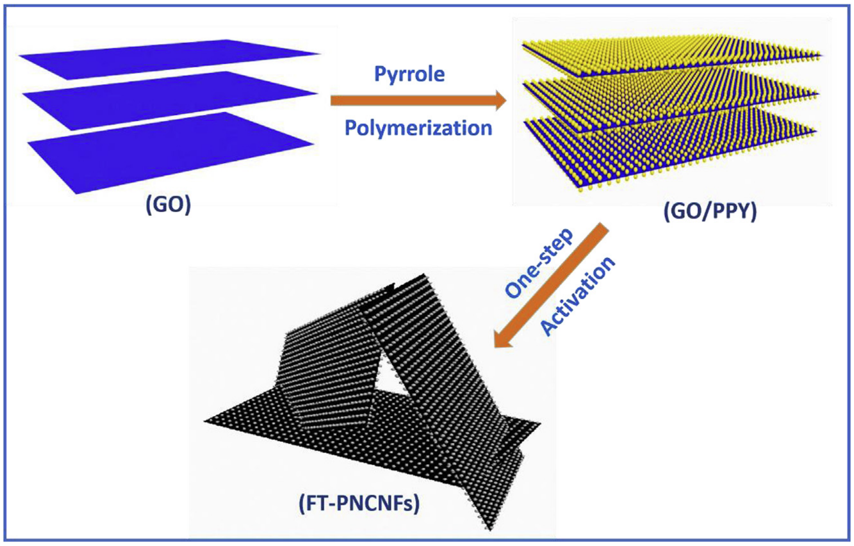

Fig. 1. The formation process of FT-PNCNFs.

In the exploration of promising EDLCs electrode materials, carbonaceous materials have always been regarded as viable candidates because of their high specific surface area, excellent chemical stability and electrical conductivity [3–5]. To date, the family of EDLC materials have already been expanded from activated carbon [6], biomass-derived carbon [7], mesoporous carbon [8], carbon nanotubes/fibers [9,10], carbide-derived carbon [11], to the most recent graphene (or reduced graphene oxide (GO)) [12]. Although much progress has been achieved in the development of nanostructured carbon materials and understanding of their charge storage mechanisms, most of the carbon electrodes (especial for powder samples) reported in literature still exhibit poor high-rate performance *i.e.* at scan rates over 1000 mV^{-1}. In this regard, design and development of carbon materials with efficient ionic and electronic transport are highly desirable for EDLCs.

For SIBs, progress is hindered due to lack of appropriate active materials for both cathodes and anodes. Recently, much work has been performed on the investigation of cathode materials for SIBs, such as $NaCrO_2$ [13], $NaTi_2(PO_4)_3$ [14], $Na_{0.6}[Cr_{0.6}Ti_{0.4}]O_2$ [15], $Na_3V_2O_2(PO_4)_2F$ [16]. On the other hand, research on the anode materials is still in its infancy. Although some alloy/de-alloy (such as Sn, Ge, Sb, Bi, P) materials show high capacities, large volumetric expansion during sodiation and the intrinsic low conductivity have restricted their application in SIBs. Recently, a lot of attention has been directed towards hard carbons due to their disordered structure and large interlayer distance that allow facile sodium-ion insertion–extraction [17-19]. As the first study reported by Doeff et al., the electrochemical insertion of sodium ions into carbon (*e.g.* petroleum-coke) provided a reversible capacity of ~85 mAh g^{-1} [20]. Following this work, other kinds of carbonaceous materials have been investigated in SIBs, such as carbon black [21], hollow carbon nanospheres [22], mesocarbon microbeads [23], carbon fibres [24], and carbon nanowires [25]. The high reversible capacity of 300 mAh g^{-1} (with sodium plating) at C/80 (35 μA cm^{-2}) was achieved for carbons derived from ball-milled glucose [26]. Wenzel et al. demonstrated that hierarchically porous carbon monoliths could deliver a capacity of ~100 mAh g^{-1} at 1.86 A g^{-1} [27], and very recently, double-shelled hollow carbon spheres exhibit high reversible capacity of 120 mAh g^{-1} at a current rate of 0.2 A g^{-1} after 100 cycles [28]. From these results, it can be seen that the cyclability and rate capability of these materials are far from meeting market expectation. From the viewpoint of process–structure–property relationship, it is very essential to construct multifunctional carbon networks with sufficient sodium-ion storage channels and highly conductive nature.

Based on the above considerations, we report a successful preparation of a functionalized 3D carbon framework by facile activation of uniform graphene oxide (GO)/polypyrrole (PPy) nanocomposites. This carbon material possesses several structural characteristics: (1) highly porous carbon layer is tightly connected with conductive graphene sheets; (2) 3D interconnected nanosheet networks; (3) ultrahigh specific surface area (~2274 m^2 g^{-1}) and short ion diffusion path; (4) heteroatom (N, O) doping, and (5) hierarchical porosity structure. As a result of having these structural merits, the as-synthesized functionalized 3D porous nitrogen-doped carbon nanosheet frameworks (FT-PNCNFs) show promising application in EDLCs and SIBs applications. When used in EDLCs, the FT-PNCNFs electrode shows high gravimetric (~247 F g^{-1} at 10 mV s^{-1}; ~146 F g^{-1} at 3000 mV s^{-1}; ~229 F g^{-1} at 20 A g^{-1}) and volumetric (~154 F cm^{-3} at 10 mV s^{-1}; ~91 F cm^{-3} at 3000 mV s^{-1}; ~143 F cm^{-3} at 20 A g^{-1}) performances. When used as anodes of SIBs, the FT-PNCNFs electrode presents reversible capacities of 187 mAh g^{-1} at 160th cycle at 100 mA g^{-1}, 144 mAh g^{-1} at 500 mA g^{-1} after extending 500 cycles, and 63 mAh g^{-1} at 5 A g^{-1}.

2. Experimental

2.1. Synthesis of graphene oxide/PPy precursors

Graphene oxide (GO) was firstly synthesized using a modified Hummers method [29,30]. Pyrrole was distilled under reduced pressure before use. 100 mg of GO was firstly dispersed in 100 mL of distilled water by ultrasonication. Then, pyrrole (1 mL) was dispersed in above solution and sonicated for 1 h to facilitate homogeneous adsorption of pyrrole onto the surface of GO. Upon stirring, 1 M HCl solution (20 mL) containing ammonium persulfate (APS) (10 mmol) was slowly added to the above mixture, and the mixture was kept at 0–5 °C for the polymerization of pyrrole. After that, the stirring was continued for 12 h. The resulting powder was filtered and washed successively with 1 M HCl, water and ethanol until the filtrate became colourless, and then the powder was dried at 60 °C under vacuum overnight.