Phosphorus-assisted solid-phase approach to three-dimensional highly porous graphene sheets and their capacitance properties

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ABSTRACT

Although graphene has emerged as a promising candidate for constructing a high-performance supercapacitor electrode, its electrochemical performance has been restricted by the irreversible layer-restacking or aggregation. Here we report that a simple solid-phase pyrolysis approach to fabricate 3D highly porous and self-supporting graphene sheets under the assistance of thermal sensitive amidinourea phosphate served as the inserting and sacrificing template. The as-synthesized 3D graphene architecture features with ultralight, fire-resistant, heteroatoms incorporated and hierarchically porous characteristics as well as other specific properties, being a very promising metal-free material for various applications. Employing as an electrode material in supercapacitor, the 3D architecture combines wrinkled graphene layers, hierarchical interlayer pores, and defects or vacancies in graphene sheets, are very beneficial to resist layer stacking, minimize ions diffusion resistance and enhance intrinsic capacitance. By introducing phosphorus sacrificing template, the product delivered an approximate 2.7 folds higher specific capacitance with faster ionic and electronic transport than that of the counterpart synthesized without phosphorus participation.

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1. Introduction

With the increasing demand for energy along with the rapid economy development, advanced energy storage and management systems should be improved significantly for a wide variety of applications such as hybrid-electric vehicles, personal electronics, smart grid, *etc*. Supercapacitors have attracted extensive attentions owing to their great energy storage potentiality with high power density, fast charging rate and excellent cycling stability. The most commonly used electrode materials for supercapacitors are carbon-based materials because of the huge carbon reserves, commercial availability and versatile existing forms. However, few inexpensive or conventional carbon materials simultaneously exhibit high specific surface area (SSA) as well superior bulk conductivity to meet the intrinsic demands. Generally, crystalline sp^2 carbons possess considerable electrical conductivity but rather limited SSA, while the amorphous carbon materials have high SSA but inferior conductivity [1].

Graphene, a rising-star two-dimensional sp^2-hybridized carbon sheets in combination with extensive theoretical SSA and high carrier mobility [2] as well as electrochemical stability, has been considered as an excellent electrode material for advanced supercapacitors. Numerous graphene-based materials have shown outstanding energy storage performance and life-cycle stability. However, all the reported specific capacitances (C_s) of graphene-based materials without additive polymer or metal are still far below the theoretical value of 550 F g^{-1} calculated for the graphene monolayer [3]. This is often attributed to the irreversible aggregation or restacking of graphene layers due to the strong π-π stacking and van der Waals interactions, leading to a seriously reduction in SSA and consequential C_s. Recently, post-assembly of curved graphene sheets [4] or direct synthesis of porous graphene architectures [5,6] has been demonstrated as effective strategies to prevent restacking and thus to enhance the performance of graphene-based capacitors in terms of C_s and charge/discharge durability. It should be noted that the post-assembly route on the basis of the chemically modified graphene precursors including graphene oxide and reduced graphene oxide with abundant structural defects usually results in a relatively poor conductivity and stability, limiting the use at a high current density. In comparison to the post-treatment methods, the

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direct synthesis approach of graphene sheets has distinct advantages in creating a self-supporting, structurally intact and highly conductive architecture with sufficient pores. The reported sacrificing template technique, one of the numerous direct routes developed by Antonietti [7], was succeeded in *in situ* fabricating monolayer-patched graphene sheets by removal of the interlayer spacer at an elevated temperature. The produced free-standing graphene sheets featured with a shrinking characteristic and displayed good performance in electrochemical catalytic reaction [7,8]. Nevertheless, their SSAs are too modest (representative below $1000 \, m^2 \, g^{-1}$) for supercapacitor application due to the underdeveloped micropores and mesopores. Chemical activation as a common way of generating pores in carbon materials was employed to activate microwave exfoliated graphite oxide (MEGO) and thermally exfoliated graphite oxide (TEGO) by using KOH as a pore forming reagent [9]. Other chemicals like NaOH, CO_2 and H_3PO_4 are also able to tailor the microstructures of carbon materials, especially the micropore size distribution and effective surface area, to enhance the energy storage performance of the supercapacitors.

Herein, we report a simple one-step pyrolysis approach to fabricate 3D highly porous graphene sheets (HPGS) via a phosphorus-assisted sacrificing template method. *In situ* generated amidinourea phosphate (AUP) as a thermally sensitive compound was used as inserting and sacrificing templates, while glucose acted as a carbonizing agent to generate hexatomic carbon network. In brief, as illustrated in Fig. 1, Dicyandiamide (DCDA) was dissolved into dilute H_3PO_4 solution and reacted with H_3PO_4 and H_2O to form AUP, which is an excellent fire retardant. A small amount of glucose was added into the above system to obtain a solid mixture after evaporation. The final graphene sheets were produced by calcining the as-synthesized precursor in inert atmosphere at a high temperature. The as-synthesized 3D architecture features wrinkled graphene layers, hierarchical interlayer pores and universal surface compatibility, being beneficial to resist layer stacking, minimize ion diffusion resistance and enhance electric-double-layer capacitance (EDLC), respectively [10].

2. Experimental section

2.1. Materials preparation

In a quintessential preparation of HPGS, 80 g DCDA was dissolved into 600 mL dilute H_3PO_4 solution (1 wt%) and stirred at 80 °C. Afterwards, 2 g glucose was slowly added into the system. Then a solid mixture obtained as a precursor by evaporating the suspension. The final HPGS was produced by thermal pyrolysising the as-synthesized precursor in high purity N_2 atmosphere at 1000 °C after a series of heating processes reported before [8]. The referential sample was synthesized using the same procedure just without H_3PO_4 in precursor (noted as NGS). In addition, NGS was further activated by appropriate H_3PO_4 and KOH respectively, noted as NGS + H_3PO_4 and NGS + KOH (detailed in the Supporting Information).

2.2. Characterization

The morphologies of samples were taken on a HITACHI S-4800 scanning electron microscope and high resolution JEOL 2100 transmission electron microscope. The textural properties were performed using a Micromeritics ASAP 2020 instrument. The oxidative stability was tested by a thermogravimetric analyzer (Netzsch 449 F3). Surface chemistry of samples was recorded on an Kratos AXIS ULTRA[DLD] instrument. The degree of graphitization was determined by a Renishaw inVia-Reflex Raman spectroscopy. The lattice structure was analyzed on a Bruker D8 DISCOVER X-ray diffractometer. The domains size and stack thickness of graphene sheets were checked using a Bruker Dimension 3100 atomic force microscope. The contact angle measurement was carried out on Data Physics OCA20 system. The conductivity was studied by a ST2258A four-point probe electrical measurement.

2.3. Electrochemical measurements

The electrochemical performance was characterized by cyclic voltammetry (CV), galvanostatic charge/discharge (GCD) and electrochemical impedance spectroscopy (EIS) in a three-electrode system with 6 M KOH solution as electrolyte. A slurry of HPGS mixing with 10 μL 5 wt% polytetrafluoroethylene (PTFE) and 490 μL ethanol was spread onto a $1 \, cm^2$ nickel-foam and then compressed with 10 MPa to form working electrode (WE). The mass load of active material on WE was ~3 mg cm^{-2}. The counter electrode (CE), a 2×2 cm titanium foil plated with iridium-tantalum alloy, was aparted from the WE with 1 cm to form a parallel electric field, while a saturated calomel electrode (SCE) dipped in a capillary KCl-
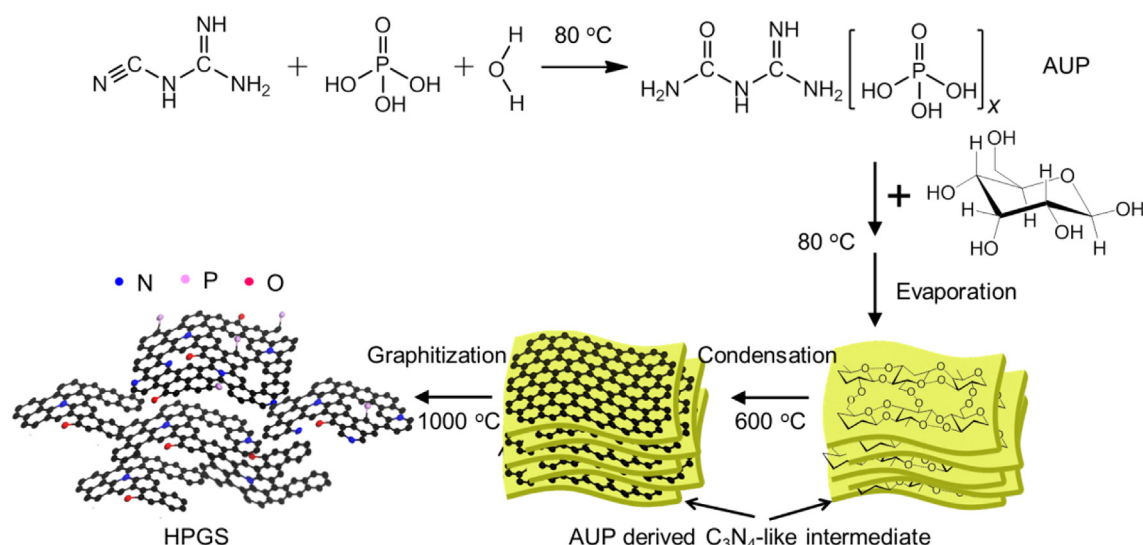

Fig. 1. Schematic illustration for preparing HPGS. (A colour version of this figure can be viewed online.)