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Water-soluble triphenylphosphine-derived microgel as the template towards in-situ nitrogen, phosphorus co-doped mesoporous graphene framework for supercapacitor and electrocatalytic oxygen reduction

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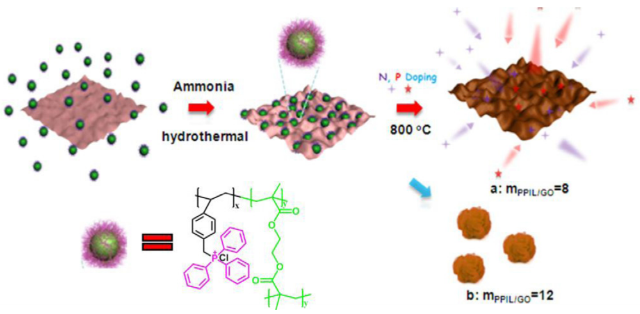
HIGHLIGHTS

- Water-soluble PIL microgel was used as a soft template and phosphorus dopant.
- Nitrogen, phosphorus co-doped mesoporous graphene framework was obtained.
- Its specific area and pore structure could be adjusted with microgel content.
- High capacitance and excellent ORR catalytic activity were achieved.

GRAPHICAL ABSTRACT



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ABSTRACT

In this work, we endowed the hydrophobic triphenylphosphine (TPP) with vinyl group as a new copolymerization monomer to synthesize water-soluble microgels, in which the hydrophilic and positively charged TPP-derived chain segments are mainly located at the surface. These synthesized microgel is simultaneously used as a soft template and phosphorus dopant to fabricate nitrogen, phosphorus co-doped mesoporous graphene framework (NP-PG) via a facile hydrothermal process containing graphene oxide and ammonia. Self-assembly of graphene oxide sheets and microgels induced by their electrostatic interaction enable a tight contact between them, which would confine the phosphorus doping mostly in the pore walls. The obtained NP-PG, as a metal-free electrocatalyst for oxygen reduction, shows a comparable electrocatalytic activity to commercial Pt/C catalyst with a peak potential of −0.18 V (vs. Ag/AgCl) and long-term durability. Additionally, it can also be used as a supercapacitor electrode to achieve a high specific capacitance of 245 F g^{-1} at 0.5 A g^{-1} and 95% of capacitance retention even after 3000 cycles at 5 A g^{-1}.

1. Introduction

Graphene, as an attractive ultrathin two-dimensional (2D) material with exceptional physical and chemical properties, has attracted massive interest for the applications in various fields, such as catalysis [1], separation [2], and energy conversion and storage [3–5]. However, pristine graphene nanosheets are easy to restack irreversibly because of the π-π stacking interactions and hydrophobic affinities between them, resulting in the severe decrease of its specific surface area [5–7]. In order to prevent the self-aggregation of graphene, various three-dimensional (3D) porous architectures have been developed by controlling their assembly [7–11]. Template-directed method is one of the most facile

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strategies to prepare porous graphene materials by assembling graphene oxide (GO) with many template materials, such as inorganic particles (metal oxide [12], silicon dioxide [11], calcium carbonate [13] and ice [7]), polymer microspheres (polystyrene (PS) [14–16], poly(methyl methacrylate) (PMMA) [17]) and supramolecular micelles [8]. Nevertheless, inorganic particles employed as sacrificial templates finally need to be removed through an additional harsh and time consuming step, which make this method infeasible for large scale production of 3D porous graphene materials [18–20]. When PS and PMMA microspheres are used as the templates, they would provide a limited contribution to the surface area, and the obtained porous graphene usually has a macroporous structure accompanied with thick pore wall and unstable architecture [16]. Moreover, using supramolecular micelles as the soft template can also conveniently incorporate mesopores into the graphene architectures. More importantly, the introduced soft template is easy to remove *via* a high-temperature annealing which is a commonly-used processing technique for carbon materials [21,22]. For example, Huang et al. prepared a graphene mesoporous framework with well-defined pore structures using the triblock copolymer F127 as the soft template [8]. However, to our knowledge, water-soluble polymer microgel as the soft-template to prepare the mesoporous graphene materials has rarely been reported.

On the other hand, incorporation of heteroatom into graphite lattices, such as N, B, S and P, is widely-used method to regulate the electronic structure of carbon materials for enhanced electrochemical performance [23–27]. Because heteroatom doping can create more electrochemical active sites by modulating the charge and spin densities of carbon atom around the doped atom, which are favorable for oxygen adsorption and reduction as an ORR catalyst as well as electrochemical energy storage by the additional pseudo-capacitance as a supercapacitor electrode [28–30]. For an instance, nitrogen has a higher electronegativity than that of carbon. Thus it can provide n-type doping and then induce the charge redistribution of carbon to create positively charged site (C^+), contributing to the enhanced electrical conductivity of carbon materials [29,31–33]. Compared to single nitrogen doping, several pioneering works have confirmed that co-doping nitrogen with another lower electronegativity heteroatom than carbon (P and B) can demonstrate much higher catalytic activity due to the synergistic coupling effect between them [26,34–37]. Phosphorus, another high-ability electron-donator, lies in the third period with large covalent radius and favors the sp^3-hybrid orbital with pyramidal-like configuration. Therefore, P doping would drag the adjacent C atoms together protruding out of the carbon lattice plane, giving rise to a highly distorted and wrinkled morphology with many open edge sites, which has a positive effect on the ORR activity [33,38–41]. Intriguingly, even a small P doping amount could largely improve the catalytic activity of the N single-doped carbon materials [42–44]. However, the widely-used P precursor, triphenylphosphine (TPP), is insoluble in water but benzene and acetone, which limits its application in heteroatom doping based on graphene oxide. According to conventional strategy, TPP is commonly mixed with the objective carbon material to achieve the P doping after high-temperature calcination, by which the P doping is always inhomogeneous in the carbon lattice plane [23,44–46]. The excess P doping is believed to cause the morphology alteration and decrease electrical conductivity [42,47]. Therefore, it is very necessary to develop a new TPP-based phosphorus dopant that takes into account of the water-solubility and homogeneous doping.

Inspired by Xiong's work [48], herein, a versatile microgel with good water-solubility was synthesized by a one-step copolymerization of TPP-derived monomer and crosslinking monomer. In this case, the positively charged TPP-derived chain segments tend to locate at the outer shell of the microgel. This as-prepared microgel was simultaneously utilized as a sacrificial template as well as a phosphorus dopant to assemble with graphene oxide nanosheets and then fabricate the nitrogen, phosphorus co-doped mesoporous graphene framework. TPP-derived microgel as a soft template can integrate the following fascinating advantages: 1) continuously mesoporous structure with thin pore walls and large surface area for the resultant graphene materials; 2) homogeneous dispersion in water and no additional procedure needed to remove them; 3) more importantly, the tight wrapping of graphene oxide nanosheets on the microgel surface due to the strong electrostatic interactions between them would confine the P doping mostly on the pore wall after high-temperature pyrolysis. The as-prepared N, P dual-doping mesoporous graphene frameworks show a comparable electrochemical performance for supercapacitor and electrocatalytic oxygen reduction.

2. Materials and methods

2.1. Materials

All chemicals were of analytical grade and used without further purification. Azobisisobutyronitrile (AIBN) and triphenylphosphine were purchased from Aladdin (shanghai) Co., Ltd. Ethylene dimethacrylate (EDMA) (98%) was purchased from TCI (shanghai) Development Co., Ltd. Graphite powder and 4-vinylbenzyl chloride were brought from Sigma-Aldrich. Other reagents, such as acetone, methanol and diethyl ether were A.R. grade. All the reagents above were used as received. Deionized water was used in all experiments.

2.2. Synthesis of the phosphorus ionic liquid (PIL) monomer

4-Vinyl benzyl chloride (8.4 g, 55 mmol), triphenylphosphine (14.9 g, 57 mmol) and acetone (50 ml) were introduced into a dried flask with a magnetic stirrer. The mixture was stirred at 45 °C under N_2 for 24 h. Then, PIL monomer was obtained by filtration and washed with acetone. The product was dried overnight under vacuum at room temperature to give a white power. The structure of PIL was characterized by ^1H NMR using D_2O as solvent (see Fig. S1 in ESI file).

2.3. Synthesis of the polyphosphorus ionic liquid microgel (PPIL)

The PPIL was prepared via a modified dispersion polymerization method [48]. EDMA (3 g, 15 mmol), PIL (2.074 g, 5 mmol) and AIBN (0.04 g, 0.24 mmol) were dissolved in methanol (130 ml), and the mixture was stirred at 70 °C for 3 h. Then, the solution was poured into a dialysis bag and then dialyzed in deionized water for 3 days, obtaining the PPIL/H_2O dispersion (26 mg/ml).

2.4. Preparation of N, P co-doped mesoporous graphene framework (NP-PG)

Graphene oxide (GO) sheets were synthesized by a modified Hummers method [49]. The details are provided in ESI file. 32 mg (NP-PG-1), 128 mg (NP-PG-4), 256 mg (NP-PG-8) or 384 mg (NP-PG-12) of PPIL microgel was dispersed in 64 ml of water by ultrasound, followed by adding 16 ml of GO dispersion (2 mg/ml) dropwise under agitation, respectively. After stirring for 15 min, ammonia (3 ml) was added and hydrothermally treated at 180 °C for 12 h. Then the autoclave was cooled to room temperature and the product was washed with distilled water and dried in vacuum at 50 °C for 12 h. After that, the resultant samples were put into a horizontal tube furnace, heated to 800 °C at 5 °C/min and