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Ionic liquid-assisted synthesis of dual-doped graphene as efficient electrocatalysts for oxygen reduction

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ABSTRACT

Dual-doped graphene is synthesized by a facile solvothermal method with the assistance of ionic liquids containing both N and X (X = B, P or S) atoms. All three types of co-doped graphene present excellent catalytic activity, demonstrating preferred four-electron selectivity and low peroxide yields toward oxygen reduction reaction in alkaline solution. Particularly, N, P-graphene exhibits superior catalytic activity to its counterparts in terms of half-wave potential ($\Delta E_{1/2} = -70$ mV relative to commercial Pt/C), methanol tolerance and long-term stability. This could be attributed to the unique porous nanostructure, change of charge density and high distortion of carbon structures originating from the combination of large electronegativity of N element and big covalent radius of P atoms.

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1. Introduction

Efficient and stable electrocatalysts for oxygen reduction reaction (ORR) as close to the reversible conditions as possible are critical for fuel cells. The intrinsically sluggish kinetics of ORR on the cathode remains a technological bottleneck for the mass production of fuel cells [1]. Pt-based materials are the most efficient catalysts for ORR, which possess near-zero overpotential and desirable four electron transfer in the ORR process [2–4]. However, the scarcity accompanying high cost and poor stability limit their widespread application. As a result, exploring non-noble metal catalysts including nanocarbons, metal oxides/carbides/nitrides and their composites to replace precious and nondurable Pt-based catalysts attracts much attention in the past years [5–9]. Graphene, as a new member of carbon allotropes, demonstrates the potential application as either catalyst support or metal-free catalyst itself owing to its intrinsic advantages, such as large specific surface area, high electrical conductivity and ease of modification [10,11]. The large specific surface area increases the interaction between catalysts and electrolyte, while the high electrical conductivity is beneficial for the electron transport in the ORR process. Furthermore, modification of graphene with heteroatoms or functional groups has been extensively demonstrated to be a competitive alternative to noble-metal catalysts toward ORR [12,13]. The incorporation of foreign atoms is believed to create abundant charged sites favourable for O_2 adsorption and reduction by altering the electroneutrality of adjacent C atoms [14,15]. Moreover, dual-doping process endows graphene with unique electronic property and further enhances the chemical reactivity due to the synergistic coupling effect of two kinds of heteroatoms [16–20]. For examples, Qiao's group suggests that N has the role of an electron-withdrawing group to indirectly activate B and thus makes the latter an active site to enhance the ORR activity of N, B-graphene, while the dual doping of S and N introduces asymmetrical spin and charge density into graphene [16,20].

Given the pronounced electrocatalytic activity of dual-doped graphene, the heteroatoms doping is normally realized by chemical vapour deposition (CVD), thermal reaction between reduced graphene oxide (rGO) and guest gas (e.g. H_2S or NH_3) [19] or solid

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precursors (e.g. melamine and benzyl disulfide) [20]. The toxicity of heteroatom precursors at high temperature or the rigorous multiple steps limit the mass production and practical application of doped graphene [21]. Moreover, achieving doped graphene with porous architecture will become more difficult and complex. For example, utilization and etching of template are usually involved to create porosity in doped graphene in the synthetic process [20,22]. Therefore, the design and synthesis of various dual-doped graphene (e.g. N, B or N, P) with porous structure by a facile method becomes imperative and attractive.

Herein, we report a versatile routine to synthesize N, X (X = B, P, S) dual-doped graphene (named as NBG, NPG, and NSG respectively) by introducing ionic liquids into a Wurtz-type reductive coupling (WRC) reaction. The WRC reaction involves a bottom-up process for the rapid preparation of high-quality pristine graphene by utilizing CCl_4 and metal K as precursors [23,24]. During this process, ionic liquids (ILs), which are easily soluble in solvent [25–28], play a dual role in the fabrication process. On one hand, the ILs containing an organic, nitrogen-containing cation and a bulky inorganic anion can provide two or more doping elements with target materials [25,29]. On the other hand, the released gas caused by the decomposition of ILs will act as porogenic agent, giving rise some pores in the resultant doped graphene. Furthermore, ILs possess unique properties, such as low inflammability, wide liquid temperature range, large electrochemical window, and environmental friendliness, which make the synthesis safe, facile, and feasible [30,31]. Though there were several reports about Wurtz-type reaction for producing graphene or about ILs as precursors for carbon materials or dopants as mentioned above, the combination of them to produce heteroatom-doped graphene has been rarely reported. The as-prepared N, X co-doped graphene exhibits improved electrocatalysts toward ORR compared with pristine graphene, which could be ascribed to the synergistic effect of N and X atoms together with the porous structures.

2. Experimental

2.1. Synthesis of N, X (X = B, P, S) dual-doped graphene

In a typical synthesis of N, B-doped graphene nanosheets, 5 mL of tetrachloromethane (CCl_4) and 112 μL of ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate (Bmim[BF_4]) as nitrogen and boron source were placed into a 100 mL Teflon-lined stainless steel autoclave. Then, 1.0 g of metallic potassium (K) was rapidly added to the autoclave in a plastic glove box purged with Ar gas. The autoclave sealed in the glove box was heated at 200 °C in an oven for 6 h, and then naturally cooled down to room temperature. The resultant product was dispersed in a mixed solution of ethanol and distilled water (1:1 vol.%) under magnetic stirring for 2 h to remove the residual CCl_4. After it was filtered and washed several times with ethanol and water, the product was dried in a vacuum oven at 80 °C for 12 h. The N, P-doped graphene and N, S-doped graphene were prepared by replacing Bmim[BF_4] with 1-butyl-3-methylimidazolium hexafluorophosphate (Bmim[PF_6]) and 1-butylsulfonate-3-methylimidazolium bisulfate ([BSO_3Hmim][HSO_4]), respectively. For comparison, pristine graphene was also prepared following the procedure mentioned above, except that no heteroatom source was added. All the samples were annealed at 600 °C for 2 h under Ar atmosphere.

2.2. Physical characterization

The samples were characterized by X-ray powder diffraction (XRD) on a Rigaku D/MAX-2250 V diffractometer with Cu K_α radiation. Transmission electron microscopy (TEM) images were observed using a JEOL 2010F electron microscope operating at 200 kV. The as-prepared powders were glued onto indium (In) metal particles for X-ray photoelectron spectroscopy (XPS) measurements with an ESCALAB 250 X-ray photoelectron spectrometer with Al K_α ($h\upsilon$ = 1486.6 eV) radiation. All spectra were calibrated using 284.5 eV as the line position of adventitious carbon. Nitrogen sorption isotherms were measured using a Micromeritics ASAP 2010 surface area and pore size analyser at liquid nitrogen temperature (−196 °C). Prior to measurement, the powders were dehydrated under vacuum at 120 °C overnight. The specific surface areas were calculated by the Brunauer–Emmett–Teller (BET) method. The pore size distribution curves were calculated based on the analysis of the desorption branch of the isotherm using the Barrett–Joyner–Halenda (BJH) model. Raman spectra were recorded on a DXR Raman Microscope (Thermal Scientific Co., USA) with 532 nm excitation length.

2.3. Electrochemical characterization

The N, X co-doped graphene (5 mg) was dispersed in the mixture of water (0.5 mL) and ethanol (0.5 mL), and 25 μL Nafion solution as binder (5 wt.%) under ultrasonic irradiation for *ca.* 2 h until a homogeneous ink was formed. Then, 20 μL of ink containing 62.5 μg of catalyst was transferred onto the glassy carbon electrode with a diameter of 5 mm, yielding a catalyst level of 0.32 mg cm^{-2}. The electrode with the catalyst was dried at 50 °C in an oven, which was used as the working electrode for further electrochemical measurements. For 20 wt.% Pt/C commercial catalyst (Johnson Matthey), the electrode was prepared following the same procedure.

An aqueous solution of 0.1 M KOH was used as the electrolyte for the electrochemical studies. Electrochemical activity of the working electrode was studied by cyclic voltammetry (CV), rotating disk electrode (RDE), and rotating ring disk electrode (RRDE) measurements using a standard three-electrode cell with a Pt plate as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode in 0.1 M KOH solution. The electrochemical cell was controlled by a bipotentiostat (Pine Instrument Co.). Prior to measurement, the electrolyte was saturated by bubbling O_2 (or N_2) for 20 min. The working electrode was cycled at least fifty times before the CV data were recorded at a scan rate of 50 mV s^{-1}. The RDE measurements were performed at different rotating rates varying from 400 to 2025 rpm with a scan rate of 10 mV s^{-1}. The number of transferred electrons (n) is calculated based on the Koutecky–Levich equation as follows:

$$J^{-1} = J_k^{-1} + \left(B\omega^{1/2}\right)^{-1}$$

$$B = 0.2nFD_{O_2}^{2/3}\upsilon^{-1/6}C_{O_2}$$

where J and J_k are the measured current density and kinetic-limiting current density, respectively, n is the electron transfer number, F is the Faraday constant (96485 F g^{-1}), υ is the viscosity of the electrolyte (0.01 cm^2 S^{-1}), C_{O2} is the concentration of O_2 (1.2×10^{-6} mol cm^{-3} in 0.1 M O_2-saturated KOH solution), and D_{O2} is the diffusion coefficient (1.9×10^{-5} cm^2 s^{-1} in 0.1 M O_2-saturated KOH solution). The coefficient 0.2 is adopted when the rotating speed is expressed in rpm.

In the case of RRDE measurement, ring current (I_R) and disk current (I_D) were collected using a Pt ring-disk electrode in O_2-saturated 0.1 M KOH solution at a rotating speed of 1600 rpm with a

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