



Chemically grafting graphene oxide to B,N co-doped graphene via ionic liquid and their superior performance for triiodide reduction

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ABSTRACT

The fast reduction and regeneration of triiodide/iodide (I_3^-/I^-) redox couple is one of the key issues for low cost dye-sensitized solar cells (DSSCs). Compared with traditional and expensive Pt counter electrodes (CEs) that act as the catalyst for reduction and regeneration of I_3^-/I^- , the low-cost and high-efficiency CEs are highly sought after for Pt replacement. Here, we report an efficient strategy for synthesis of B and N co-doped graphene (B,N-G) samples via chemically grafting ionic liquid (IL), followed by thermal annealing. The corresponding photovoltaic and electrochemical performances were investigated in detail. It was found that chemically grafting via IL is an efficient strategy for inhibiting and avoiding the agglomeration and restacking of graphene oxide (GO) sheets to a great degree in comparison to that of physically mixed IL and GO, further leading to efficient doping. When evaluated as CEs for DSSCs, an annealing temperature-dependent electrochemical behavior is demonstrated in B,N-G samples. The B,N-G-1200 annealed at 1200 °C derived from IL-grafted GO as CE has demonstrated the best electrochemical performance, yielding a power conversion efficiency of 8.08% the synergetic effects of co-doped B and N, which is superior to 6.34% of Pt CE. The present work will provide a simple and efficient method for configuring the heteroatom-doped graphene or carbon-related electrode materials with high electrocatalytic activity for high-performance and low-cost energy storage and conversion devices.

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1. Introduction

Graphene with high crystallinity and electrical conductivity has been widely investigated as an eco-friendly replacement of noble metals for electrocatalytic applications [1,2], especially demonstrated a high catalytic activity towards the reduction of I_3^-/I^- redox couple that is one of the extremely key points to maintain a steady power output for low-cost dye-sensitized solar cells (DSSCs) [3–7]. Nevertheless, high electrocatalytic activity requires graphene containing large amount of defects, which will contribute to low conductivity and further lead to slow electron transfer and low efficiency. In this case, the enhancement of activity for graphene without decreasing conductivity remains a major challenge and urgently needs to be considered in future [8–10].

Incorporating heteroatoms (e.g. B, N, S, and/or P) into graphene carbon backbone can tailor electrocatalytically active sites with a minimized change of the conjugation length and an increase of

conductivity to some degree [11–13]. It has also been revealed that the π electrons of carbon can be activated by lone-pair electrons from doped N atoms, thus having a potential superiority towards the reduction of I_3^-/I^- redox couple [6,14–15]. Recently, our work has demonstrated that doping graphene with electron-deficient atoms such as B represents an alternative strategy that can efficiently reduce and regenerate I_3^-/I^- redox couple [16]. It was pointed out that the dopants of electron-rich N or electron-deficient B can also activate π electrons of carbon atoms to enhance catalytic and conductive properties of single atom-doped (B or N) graphene by breaking the electroneutrality of sp^2 carbon to create charged sites [17]. In particular, codoping with two elements, one with higher and one with lower electro-negativity than that of C ($c=2.55$), for example, B ($c=2.04$) and N ($c=3.04$), can create a unique electronic structure with a synergistic coupling effect between heteroatoms, producing much more catalytically active sites than singly atom doped graphene catalyst [1]. Thus, dual-doped graphene with N and B will be a promising option to further tailor chemical and physical properties of graphene and enhance its electrocatalytic activity for DSSCs that takes advantage of the additionally created defect sites and increased conductivity.

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Despite the existence of B and N co-doped graphene, how to develop a facile strategy that can efficiently dope the carbon network remains a great challenge. It was found that a feasible synthesis can be achieved using eco-friendly ionic liquids (IL) by controlling the incorporation of a certain amount of heteroatoms due to the existence of more heteroatoms and long-term survival thermal stability of IL in comparison to that traditional volatile agents [18]. Dai et al. described novel protocols for the synthesis of boron and nitrogen-rich porous carbon using IL as the carbon source [19]. Lee et al. reported a N-doped reduced graphene oxide (GO) FET by using IL-NH₂, in which the high boiling point of IL leads to the simultaneous thermal reduction of GO and reaction of IL anchoring group with the GO oxygen functional groups to form a partially-reduced nitrogen-containing intermediate [20]. And it is also interesting to note that the IL can be grafted to carbon nanomaterials such as carbon nanotube and graphene to enhance the processability of the carbon materials into films, gels, and papers, demonstrating the enhanced electrochemical performances to a great degree due to specific interaction between the imidazolium ion component and the p-electronic carbon surface [21,22].

With this information in mind, herein, we report an efficient strategy for synthesis of B and N co-doped graphene (B,N-G) samples via chemically grafting IL to GO, followed by thermal annealing. The used IL has dual roles: dopants for heteroatom doping, and dispersing media for inhibiting and avoiding the agglomeration and restacking of GO sheets via covalently grafting. The photovoltaic and electrochemical performances of a series of B,N-G samples were investigated in detail. It is very interesting that covalently bonding or chemically grafting GO with IL is a key process and responsible for high-performance CE for reduction of I₃⁻ to I⁻. The electrochemical performances of B,N-G samples demonstrate an annealing temperature-dependence behavior. The B,N-G-1200 annealed at 1200 °C derived from IL-grafted GO as CE can deliver a power conversion efficiency (PCE) of 8.08% due to synergetic effects of co-doped B and N species, being superior to that of Pt CE (6.34%). This will provide a simple and efficient method for configuring the heteroatom-doped graphene or carbon-related electrode materials with high electrochemically catalytic activity.

2. Materials and methods

2.1. Preparation of B,N-G

GO was prepared via a modified Hummers method [23], as reported in our previous work. Ionic liquid-grafted GO was synthesized following the literature [24,25]. For a typical run, the GO (100 mg) was dispersed in 200 mL of N,N-dimethylformamide (DMF) solution, then, 300 mg of 1-aminopropyl-3-methylimidazolium tetrafluoroborate (IL-NH₂(BF₄⁻)), and 200 mg of N,N'-Dicyclo-hexylcarbodiimide (DCC) was slowly added to the DMF solution including GO under strongly stirring conditions under N₂ atmosphere. The reaction mixture was heated at 50 °C for 24 h. Finally, the product was filtered through membrane filter paper (0.2 μm) and washed with DMF, water and ethanol for several times to remove the excess reagents. Then it was dried under vacuum for 12 h, yielding the IL-grafted GO (IL-GO). After that, the IL-GO was treated in a tube-like reactor in flowing Argon of 50 mL min⁻¹. The reactor was ramped at 2 °C min⁻¹ as follows: from RT to 300 °C in 1 h and kept at 300 °C for 2 h; then from 300 °C to carbonization temperature (T) at 5 °C min⁻¹ and kept at this temperature for 1 h. After being cooled back to room temperature naturally, the dark powders B,N-G samples were obtained. The B,N-G prepared at different temperatures were

designated as B,N-G-T, where T refers to the annealing temperature. For comparison, the corresponding GO and the mixture of IL and GO was also treated in a tube-like reactor, yielding G and B,N-G-M. Moreover, single atom doped-G samples (B-doped G and N-doped G) were also synthesized using B₂O₃ as boron source and polyaniline as nitrogen source, respectively.

2.2. CE preparation

30 mg sample and 0.5 mL binder containing ethyl cellulose, ethanol, and terpineol (mass ratio of 1:9:8) were grinded for 30 min, yielding the counter electrode paste. The obtained paste was coated on FTO glass, yielding CE loading of ca. 200 μg cm⁻², and then sintered in a tube furnace in Ar atmosphere at 500 °C for 30 min. Pt electrode was purchased from Dalian Heptachroma Solar Tech Co., Ltd.

2.3. Device fabrication

The dye-coated TiO₂ photoanodes were prepared by immersing TiO₂ film (Ti-Nanoxide D, Solaronix SA, Aubonne, Switzerland) in a 0.5 mM N719 dye (Solaronix) ethanol solution for 20 h, and then assembled with the G, B,N-G or Pt counter electrodes. The electrodes were separated by a 45 μm thick hot melt ring (Surlyn, Yingkou OPV Tech New Energy Co., Ltd.) and sealed up by heating. The cell internal space was filled with OPV-AN-I type electrolytes (Yingkou OPV Tech New Energy Co., Ltd.).

2.4. Characterization

The microscopic observations were performed on a field emission scanning electron microscopy (FESEM, FEI, NOVA Nano-SEM 450) and a transmission electron microscopy (TEM, FEI, TF30) respectively. The Raman spectra were recorded on a DXR Raman Microscope (Thermo Scientific) with excitation wavelength of 532 nm. The X-ray diffraction (XRD) patterns of samples were recorded on a Rigaku D/Max2400 diffractometer. The X-ray photoelectron spectroscopy (XPS) was recorded on ESCALABMK II X-ray photoelectron spectrometer. The FT-IR spectra of the B,N-G samples were recorded using JASCO FT/IR-430 spectrometer with a resolution of 4 cm⁻¹ (KBr pellet, carbon loading of ca. 0.5 wt%). The conductivity of a series of samples was evaluated by linear sweep voltammetry through electrochemical workstation (Chenhua, CHI 760e, China).

2.5. Electrochemical testing

The cyclic voltammograms (CVs) were carried out in a conventional three-electrode electrochemical cell by using B,N-G as the working electrode, Pt as a counter electrode and Ag/Ag⁺ as a reference electrode in an acetonitrile solution containing 0.1 M LiClO₄, 10 mM LiI, and 1 mM I₂ at a scan rate of 10 mV s⁻¹ using an electrochemical analyzer (CHI660D, Chenhua, Shanghai). The electrochemical impedance spectroscopic (EIS) experiments were conducted in the dark with dummy cells using a computer-controlled potentiostat (Zenium Zahner, Kronach, Germany). The measured frequency ranged from 100 mHz to 1 MHz at 0.8 V bias voltage, and the amplitude of the alternating current was set at 10 mV. Tafel-polarization measurements were carried out with an electrochemical workstation system at a scan rate of 10 mV s⁻¹ (CHI660D, Chenhua, Shanghai) in a symmetrical dummy cell. Photocurrent-voltage performance of the DSSCs was conducted in simulated AM 1.5 illumination (I = 100 mW cm⁻², 94032A, Newport, USA) with a Keithley digital source meter (Keithley 2400, Cleveland, OH).

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