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Feature Article

Three-dimensional N-doped, plasma-etched graphene: Highly active metal-free catalyst for hydrogen evolution reaction

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ABSTRACT

Exploring highly active, durable and low-cost catalysts toward hydrogen evolution reaction (HER) holds a key to clean energy technologies. Heteroatoms-doped graphene-based materials are emerging as the most promising metal-free HER catalysts, but their catalytic activity remains largely unexplored. Herein, by rationally engineering the macroscopic architecture of graphene and its chemical/defective structures, we developed a three-dimensional (3D), N-doped, plasma-etched graphene (3DNG-P) as a highly active metal-free HER catalyst. The obtained 3DNG-P combined the merits of freestanding 3D porous architecture, high-level N-doping and plasma-induced enriched defects, resulting in a highly enhanced HER activity with a low overpotential of 128 mV at 10 mA cm^{-2} in acidic medium. Furthermore, the 3DNG-P displayed a favorable HER activity and stability over a wide pH range. The present study thus provides a new methodology for the design of graphene-based metal-free catalysts with high HER performance.

1. Introduction

Exploring efficient and robust catalysts toward hydrogen evolution reaction (HER) is essential for large-scale hydrogen production from electrocatalytic water splitting [1–3]. Although Pt-based materials are established as the most active HER catalysts, their scarcity and high cost substantially hamper their broad utilization. Several transition-metal-based materials are emerging as the potential replacements for Pt-based catalysts owing to their low cost and high HER activity [4–6]. Nevertheless, these transition-metal-based catalysts have the main drawbacks of low electrical conductivity and corrosion susceptibility to acidic/basic environments [2,7], which considerably restrict them for wide use in hydrogen evolution. To this end, it is highly imperative to develop metal-free HER catalysts with comparable catalytic activity and strong stability.

Carbonaceous materials, especially graphene, have recently attracted considerable attention as the most promising metal-free catalysts for a broad range of electrocatalysis applications owing to their earth abundance, large surface area, excellent electrical conductivity, long-term stability, tailored chemical structures and potentially high catalytic activity [8–12]. Recent progress has revealed that doping of heteroatoms (N, B, S, P, F, Cl, etc.) into carbon frameworks is an efficient approach to substantially promote the catalytic performances of graphene originating from the changed spin density and charge distribution of C atoms adjacent to dopants [2,13]. Currently, heteroatoms-doped graphene (HDG) based materials have been extensively studied as efficient metal-free catalysts or catalyst supports for a wide range of energy-related electrocatalysis applications [14–16]. Most recently, HDG-based metal-free catalysts have been reported to exhibit a pronounced HER activity [2,7]. Ge et al. [17] synthesized a N-rich holey graphene monolith through a supramolecular method. The obtained catalyst exhibited a relatively high HER activity as evidenced by the low overpotential of 337 mV at a current density of 10 mA cm^{-2} (η_{10} = 337 mV). Huang et al. [18] prepared a mesoporous NG by a micelle-template method, and the resulting catalyst presented an apparently improved HER catalytic activity (η_{10} = 240 mV) compared to undoped one. Additionally, the co-doping of N with a second element shows an even higher catalytic activity than single-doped ones due to a synergetic co-doping effect [2]. Zheng et. al [19] reported that the HER performances of N, P co-doped graphene were far better than those of single doped counterparts, which could be attributed to the prominent activation of C atoms nearby

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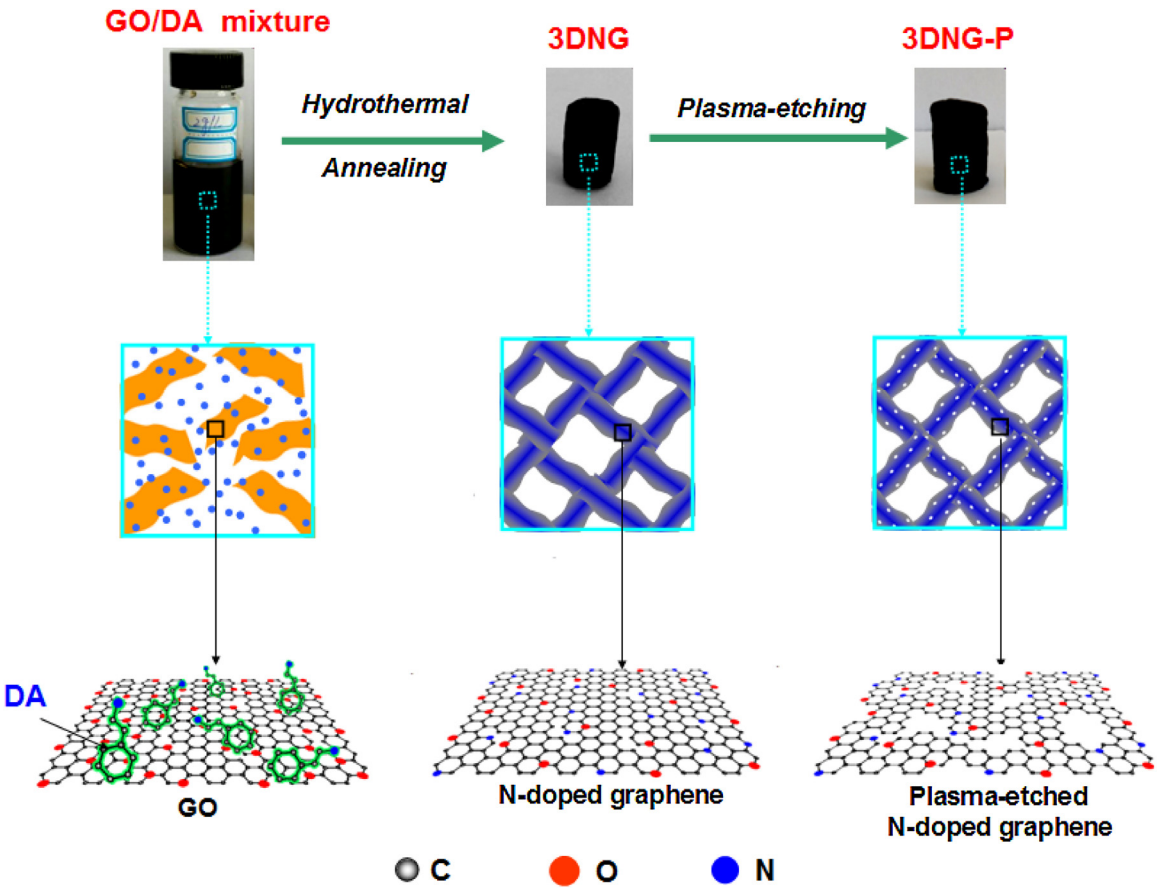

Scheme 1. Schematic illustration of the synthesis process of 3DNG-P.

the N, P dopants, resulting in a synergistically enhanced HER activity. The similar co-doping effect responsible for improved HER has also been reported in other heteroatoms co-doped graphene-based catalysts [20–22].

Despite some efforts in this research, the study of HDG-based metal-free HER catalysts is still in its infant stage and their HER activity is generally lower relative to that of Pt-based and most transition-metal-based catalysts [7], which can be ascribed possibly to the following two aspects. First, nearly all the reported HDG-based metal-free HER catalysts were prepared in the form of fine powders and usually required Nafion as the binder for electrode fabrication, which would cause unavoidable powder agglomerations and reduced charge transfer at electrode/electrolyte interface [15,23,24], leading to the compromised catalytic activity and stability. Thus, the assembly of powdery graphene sheets into three-dimensional (3D) macroscopic architecture directly utilized as the catalyst electrode may be an effective approach to overcome this problem [2,25]. Second, the structural defects and edges on graphene are closely associated with its catalytic activity [26], and generally the exposure of more defects/edges results in a high catalytic activity [27–29]. Accordingly, the heteroatom-doping itself may generate the limited number of active sites on graphene for HER, and the additional defect engineering strategy to create an abundance of defective/active sites may provide the opportunity to considerably enhance the HER activity of HDG.

In this study, we developed a novel 3D N-doped, plasma-etched graphene (denoted as 3DNG-P) that served as a highly active metal-free catalyst for HER. The 3D N-doped graphene (3DNG) was firstly prepared by a self-assembly hydrothermal method followed by annealing [30,31]. The obtained 3DNG was then subjected to Ar plasma treatment to afford additional structural defects to form 3DNG-P (Scheme 1). Plasma treatment is known as a high-efficiency surface modification technique for cleaning and etching owing to its unique characteristics of enhanced catalyst activation, highly active species and short operation time [32]. Previous studies reported that the plasma treatment was capable of creating amounts of defects and improving the catalytic activity of various materials [33–36]. As we demonstrated that the present designed 3DNG-P combined the merits of freestanding 3D porous architecture, high-level N-doping and plasma-induced enriched defects, leading to the significantly enhanced HER activity over a wide pH range.

2. Experimental

2.1. Synthesis of 3DNG-P

Graphene oxide (GO) was prepared from graphite powder (200 μm, 99.9% purity, Qingdao Dongkai Graphite Co., Ltd.) by a modified Hummers method [37]. To synthesize the 3DNG, 20 mg dopamine was dispersed in 20 mL GO dispersion (2 mg mL^{-1}) under ultrasonication for 1 h to form a homogeneous suspension. The mixture was then transferred to a 100 mL Teflon-lined autoclave and heated at 180 °C for 12 h to prepare a cylinderical hydrogel. After cooling down to room temperature, the hydrogel was washed with deionized water and freeze-dried overnight to remove the absorbed water of hydrogel. Subsequently, the as-prepared aerogel was annealed at 800 °C for 3 h under a N_2 atmosphere to obtain the 3DNG aerogel. For comparison, 3D graphene aerogel (3DG) was prepared through the same procedure without the addition of dopamine. The as-prepared aerogels were then subjected to Ar plasma treatment in a commercial AX-1000 plasma system