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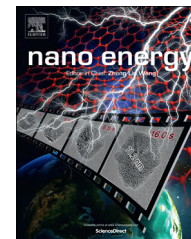
RAPID COMMUNICATION

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Molybdenum sulfide clusters-nitrogen-doped graphene hybrid hydrogel film as an efficient three-dimensional hydrogen evolution electrocatalyst

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Abstract
Nobel metal-free electrocatalysts for hydrogen evolution reaction (HER) with high activity and low cost are essential for hydrogen production. However, the design and fabrication of such catalysts are still highly challenging thus far. In this work, we fabricate a three-dimensional (3D) hybrid electrocatalyst by decorating N-doped graphene hydrogel film (NG) with molecular clusters (MoS_x). This material has successfully combined the desired merits for electrocatalysis, such as highly active MoS_x sites for HER, excellent mechanical properties for strong catalyst durability, highly hydrated framework for sufficient active site exposure as well as 3D conductive networks for fast charge transport. The 3D electrode shows a remarkable catalytic activity toward HER (140.6 mV at 10 mA cm^{-2}), which outperforms most graphene and/or MoS_x-based electrocatalysts reported in the literature. Also, the catalyst electrode demonstrates favorable reaction kinetics (Tafel slope, 105 mV dec^{-1}) and strong durability (seldom performance degradation after 12 h or 1000 cycles). Further mechanism study reveals that Volmer reaction is the dominant process on the 3D electrode and the dual active sites are highly probable during electrocatalytic process, that is, pyridinic/pyrrolic structures of N-doped graphene and defects/edges of MoS_x are both active centers.
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Introduction

The design of highly active and cost-effective catalysts is extremely desirable for a number of energy-related electrochemical reactions such as hydrogen evolution reaction (HER), oxygen evolution reaction (OER), and oxygen reduction reaction (ORR) [1-6]. Precious metal materials (platinum, ruthenium, iridium, etc.) show high catalytic performance toward these reactions [3,7-9]; however, their scarcity and prohibitive cost limit large-scale applications. As a consequence, extensive efforts have been devoted to the fabrication of non-precious metal and metal-free electrocatalysts. Completely metal-free catalysts are mainly constituted by various heteroatoms (N [1], S [10], O [11], P [12], and B [13]) doped carbons where their activities originate from the charge separation of carbon backbones during doping. However, their catalytic activities are still low as compared to precious metal catalysts. To improve their performances, numerous metal-based species have been intentionally introduced as catalytic centers. Recently, there is great interest in the catalyst design of interfacing metal-free materials with molecular clusters, for example, CNTs anchored with polyoxometalate clusters [14] and graphene with polyoxotungstates [15]. This kind of hybrid electrocatalysts have generally exhibited high activity due to the excellent structural features such as highly active metal centers, conductive carbon frameworks, as well as strong synergistic effects between the components. Despite great progress in this research field, the activity and stability of these electrocatalysts could be further improved by optimizing electrode architectures, wettability as well as mechanical properties.

Hydrogen evolution is a fundamental reaction of many state-of-the-art devices such as water electrolysis and photoelectrochemical water splitting cells, which usually takes place on platinum (Pt)-based electrocatalysts [16]. Because of the high price of Pt, various low cost alternatives have been developed. Recently, a few studies have been published on metal-free HER electrocatalysts, for example, boron (B)-doped graphene [13], nitrogen (N), phosphorus (P)-dual doped graphene [12], N-doped graphene-C_3N_4 hybrid [3] and activated carbon nanotubes (CNTs) [17]. However, the activities of these metal-free electrocatalysts are still poor, requiring high overpotentials (> 200 mV vs. RHE) to achieve the current density of 10 mA cm^{-2}. To enhance their performance, various molecular clusters such as MoS_x [7] and $C_{60}(OH)_8$ complexes [18] can be added into their matrix. In particular, MoS_x clusters are extensively studied as inexpensive HER electrocatalysts, with their edges and defective sites being identified as active centers [19-21]. The blending of MoS_x clusters with these metal-free materials such as N-doped graphene may form a class of efficient yet low cost electrocatalysts for HER.

Our recent studies reveal that a number of parameters other than the chemical components can significantly influence the activity, durability, and reaction kinetics of electrocatalysts, such as electrode architectures, mechanical properties, and wettability [22,23]. For example, most catalyst electrodes are prepared by decorating active species on various substrates such as glassy carbon [11], indium tin oxide (ITO) [2], and nickel foam [24] by the techniques of dip coating [11] and solution casting [25], where the active species may tend to peel off from substrates during operation, resulting in the loss of catalytic activity and shelf life. In contrast, a new category of substrate-free electrocatalysts can be fabricated on the basis of various self-supported materials, such as hydrogels, aerogels, and free-standing films [22], which may have good mechanical properties and can directly act as working electrodes, assuring strong catalyst durability. In particular, three-dimensional (3D) hydrogel-based materials with highly hydrophilic frameworks can greatly increase wettability of electrodes, facilitate the access to electrolytes, and consequently enhance the activity and reaction kinetics [23]. In this respect, the fabrication of hybrid catalysts of N-doped graphene-MoS_x clusters in the form of self-supported hydrogels may become an attractive target for achieving enhanced catalytic performance, but such kind of electrocatalysts are rarely reported.

Herein, we report a hybrid electrocatalyst of free-standing N-doped graphene (NG) hydrogel films decorated with MoS_x clusters (denoted as NG-Mo). The material combines a number of excellent structural properties for electrocatalysis, such as highly active MoS_x species, good mechanical properties, highly hydrated framework as well as 3D conductive networks. The catalyst can work as a substrate-free electrode with high activity, favorable kinetics and strong durability toward HER. The enhanced performance is correlated with the dual-active-sites mechanisms originated from the synergistic effects of N-doped graphene and MoS_x, as well as the remarkable structural features that facilitate the process of water dissociation.

Experimental section

Synthesis

Graphite flakes (99%), sulfuric acid (H_2SO_4, 95-98%), potassium permanganate ($KMnO_4$, 99%), phosphorus pentoxide (P_2O_5, 98%), potassium persulfate ($K_2S_2O_8$, 99%), hydrogen peroxide (H_2O_2, 35 wt%), ethanol (EtOH, absolute), hydrochloric acid (HCl, 38 wt%), hydrazine hydrate ($N_2H_4 \cdot H_2O$, 80 wt%), ammonia ($NH_3 \cdot H_2O$, 35 wt%), platinum/carbon (Pt/C, 99%), ammonium tetrathiomolybdate (($NH_4)_2MoS_4$, 99%), and potassium chloride (KCl, 95%) were purchased from Sigma-Aldrich and directly used without further treatment or purification.

The synthesis of NG-Mo is shown in **Scheme 1**, which includes three steps, that is, preparation of graphene hydrogel film, N-doping of graphene, and hybridization of graphene with MoS_x clusters. In the first step, graphene hydrogel film was prepared by the vacuum-assisted filtration of its dispersion. Specifically, graphene oxide (GO) was prepared by the oxidation of graphite through Hummer's method [26], and then converted to graphene dispersion by using hydrazine hydrate (35 wt% in water) at 95 °C [27]. Next, the graphene dispersion (50 mL, 0.2 mg mL^{-1}) was filtered through a mixed cellulose ester filter membrane (0.2 μm pore size) [28]. When the entire graphene solution was drained out, the vacuum suction was stopped. The resultant filtration cake was immediately transferred to a Petri dish for further experiments.

In the second step, the as-obtained graphene hydrogel film was doped with nitrogen atoms by adding $NH_3 \cdot H_2O$ (20 mL, ~35 wt%) and then heating at 150 °C for 12 h. The as-obtained N-doped graphene hydrogel film (denoted as NG) was dialyzed against DI-water.

Thirdly, MoS_x clusters were electrodeposited onto NG film. The deposition was carried out through cathodic reduction of ($NH_4)_2MoS_4$ (20 mL, 5 mM) in KCl electrolyte (20 mL, 0.1 M).