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Janus effect of O_2 plasma modification on the electrocatalytic hydrogen evolution reaction of MoS_2

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ABSTRACT

Oxygen incorporation is a promising and effective way for simultaneously engineering the edge and planar sites of MoS_2 to fabricate high-performance HER electrocatalysts. However, the insulating MoO_3 species are inevitably generated during the oxygen incorporation process. Here, controlled plasma exposure time has been designed to explore the influence of MoO_3 species on the HER performance for the O_2 plasma modified MoS_2 catalysts. We find that the MoO_3 species in MoS_2 are not conductive to the HER electrocatalysis. More importantly, the Raman spectrum, X-ray photoelectron spectroscopy, energy-disperse X-ray spectrum and transmission electron microscope analyses demonstrate that these co-generated MoO_3 species are reduced and resolved from the MoS_2 lattice during the electrocatalytic hydrogen evolution, leading to a holey structure in the MoS_2 nanosheets and thus a significant improvement of its hydrogen evolution stability. This work not only helps to understand the electrocatalytic influence of the co-generated MoO_3 species in MoS_2, but also presents a methodological improvement in designing defect-rich, oxygen incorporated and holey MoS_2 nanosheets for highly efficient hydrogen evolution.

1. Introduction

Hydrogen (H_2), with the highest gravimetric energy density among the currently wildly used fuels and zero carbon content leading water as the sole product from its oxidation reaction, has been recognized as the most ideal and clean energy carrier to resolve the growing concern about energy crisis, environmental pollution and global warming, and fulfill our need for the future fuel applications [1–4]. The hydrogen evolution reaction (HER) is the cathodic half reaction of electrocatalytic water splitting and is thus highly desirable to power the "hydrogen-based economy". In electrolysis, noble metals, e.g. platinum (Pt) is still the best catalysts for the HER due to their high electrocatalytic activity. However, the widespread applications of Pt-based noble metal catalysts are hindered by their high cost, scarcity and insufficient stability [5,6]. Therefore, central to the electrocatalysis are efficient and robust electrocatalysts based on nonprecious metals, which are urgently needed for satisfying the hydrogen-based industry.

Earth-abundant MoS_2 has emerged as a promising HER catalyst with high electrocatalytic activity and stability due to its unique physical and chemical properties [7–9]. In the electronic structure of MoS_2, the orbitals of HOMO states are mainly localized at the edged S sites, so that the localized electrons are mainly at the edge of MoS_2 for charge exchange of proton [10]. DFT calculations have elucidated that the MoS_2 plane sites are HER-catalytically inert with the hydrogen adsorption energy (ΔG_H) of is ~1.9 eV, while edge sites especially the [1 0 1 0] Mo edges are HER-catalytically active with a near-optimal ΔG_H as ~0.08 eV, which is even closer to 0 eV than that of the state-of-the-art Pt surfaces (ΔG_H is ~−0.1 eV) [11].

Inspired by this understanding, great efforts have been devoted to developing high-performance MoS_2 nanostructures. On one hand, noteworthy MoS_2 nanostructures including nanoparticle [12], nanosheet [13], amorphous MoS_2 [14], film with ordered double-gyroid network [15], defect-rich nanosheet [16], and vertically aligned stepped edge terminated MoS_2 sheet arrays [10] have been developed to maximizing the active edge sites and illustrated

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to have enhanced HER performance. On the other hand, optimizing the hydrogen adsorption on the inert planar sites by converting the 2H phase to the 1 T phase of MoS_2 layers [17–19], distorting the MoS_2 plane and introducing S-vacancy in the MoS_2 planar sites [20] significantly facilitates the hydrogen binding and thus increases the HER activity. Therefore, simultaneous optimization of both the edge and planar sites of MoS_2 materials is of great importance to fabricate the high-performance HER electrocatalyst.

Xie and co-workers have recently reported a novel oxygen-incorporated MoS_2 ultrathin nanosheet system, in which the oxygen incorporation could effectively reduce the bandgap, increase the intrinsic conductivity of MoS_2 catalyst, and thus enhance its HER performance [21]. In addition, it was believed that such enhancement of HER performance for O-incorporated MoS_2 catalyst could be attributed to not only the enhanced intrinsic conductivity and expanded interlayer spaces, but also the modulated hydrogen binding free energy on the inert planar sites [21–24]. More recently, O_2 plasma was used to engineer the defect-rich and oxygen incorporated structure of MoS_2 to enhance its electrocatalytic activity for HER [25]. Plasma modification is a mild and efficient way to introduce disordered structure and functional foreign atoms on the materials' surface [26–31]. It is believed that there are a variety of reactive species (e.g. electrons, ions and neutral radicals, etc.) generated during the plasma discharge [32,33]. The high-energy electrons in O_2 plasma contribute to the plasma bombardment and ablation, leading to the cracking of the basal planes of MoS_2 and thus defect-rich edge structure. At the same time, the O-species (oxygen ions and oxygen radicals) in O_2 plasma would incorporate into the MoS_2 lattice due to their highly oxidative activity [34]. However, the generation of MoO_3 species is found to be inevitable during the O_2 plasma treatment or other O-incorporation processes [23,25,35]. The influence of these insulating MoO_3 species on the HER activity and stability of MoS_2 and its structure changes after long-term electrocatalytic reaction, which are significant to understand the HER electrocatalysis on the O-incorporated MoS_2 catalysts, however, are still unknown.

Herein, we used the one-step O_2 plasma modification to simultaneously engineer the edge and planar structure of MoS_2 to fabricate the high-performance MoS_2 electrocatalyst with defect-rich edge and oxygen-doped planar structure. As expected, the O_2 plasma modified MoS_2 catalysts possess a smaller HER onset potential and Tafel slope than that of the non-treated MoS_2 catalyst, as well as the excellent long-term durability. To investigate the influence of MoO_3 species on the HER performance, chemical structure and HER performance of the O_2-plasma modified MoS_2 catalysts before and after the long-term durability test were carefully analyzed.

2. Results and discussion

We fabricated the O_2 plasma modified MoS_2 catalysts via a two-step process. The MoS_2 spheres were firstly synthesized by hydrothermal reaction, and then modified by O_2 plasma with different plasma treatment time of 30 s (MoS_2 O_2-plasma 30 s), 60 s (MoS_2 O_2-plasma 60 s) and 120 s (MoS_2 O_2-plasma 120 s). The morphology of the as-synthesized MoS_2 and O_2 plasma treated MoS_2 catalysts was characterized by field-emission scanning electron microscopy (FESEM) shown in Fig. 1. The FESEM images clearly reveal the great difference among various MoS_2 samples. Fig. 1a indicates that the hydrothermal synthesized 3D MoS_2 microsphere is built from large quantities of uniform nanosheets with the edge length of 300–600 nm. Obviously, smaller edge length of the MoS_2 nanosheets can be observed from Fig. 1b–d of the O_2 plasma treated MoS_2 samples, indicating more cracks in the MoS_2 nanosheets comparing to the non-treated MoS_2, and thus more exposed active edge sites on the O_2 plasma treated MoS_2 surface.

The transmission electron microscopy (TEM) images have confirmed the ultrathin nanosheet morphology of as-grown MoS_2 samples. It can be clearly seen from the TEM image in Fig. 2a that the MoS_2 nanosheets were connected to each other through the center to form the 3D microsphere structure. As shown in the high-magnification TEM images, the MoS_2 nanosheets exhibit an interlayer separation of 0.63 nm for both the MoS_2 and MoS_2 O_2-plasma 60 s samples, corresponding to the (0 0 2) facet of 2H-MoS_2 crystal (also see the XRD analysis below). Careful investigation of the TEM image reveals that the crystal fringes along the edge of the MoS_2 O_2-plasma 60 s sample are dislocated and discontinuous (indexed in Fig. 2b), suggesting a defect-rich structure for the plasma treated MoS_2. The dislocated atomic arrangement causes the cracking of the basal planes and thus results in the formation of additional edges [16]. In addition, the corresponding Raman spectra as shown in Fig. 3 for all the MoS_2 samples exhibited two distinct peaks at ~405 cm^{-1} referred to the out-of-plane Mo-S phonon mode (A_{1g}) and at ~379 cm^{-1} corresponded to the in-plane Mo-S phonon mode (E^1_{2g}) of typical MoS_2 layer structure [36]. The relatively high intensity of the A_{1g} mode for the O_2 plasma modified MoS_2 samples confirms more edge-terminated sites generated during plasma treatment process, which is in consistent with the SEM and TEM observations [37].

The energy-dispersive spectroscopy (EDS) spectrum of the as-grown MoS_2 (see Fig. S1) reveals that the ratio of S to Mo is close to 2, confirming the successful synthesis of MoS_2. It is worth noting that after the O_2 plasma modification, O content in MoS_2 samples becomes larger over the plasma processing time (Figs. S2–4), indicating that O_2 plasma modification is an effective way to introduce oxygen species onto the MoS_2 surfaces. To characterize those oxygen species, Raman spectra with large range were recorded for all the MoS_2 samples, shown in Fig. 4a. The spectra of all the MoS_2 samples display two strong vibrational bands at ~379 cm^{-1} and ~405 cm^{-1}, which are attributed to the Mo-S phonon mode of MoS_2. Clearly, the Raman spectra of the MoS_2 O_2-plasma 30 s and non-treated MoS_2 samples are similar, indicating the similar chemical structure between them. However, there are three newly developed bands at 666 cm^{-1}, 820 cm^{-1} and 995 cm^{-1} for MoS_2 O_2-plasma 60 s and MoS_2 O_2-plasma 120 s, not present for MoS_2 O_2-plasma 30 s sample, which are responsible for the layered structure of the α-phase MoO_3. The crystal structure of α-phase MoO_3 contains three nonequivalent oxygen atoms in the MoO_6 octahedral unit, which are edge sharing triply coordinated oxygen (O–Mo_3), doubly coordinated oxygen (Mo—O—Mo), and terminal oxygen (Mo═O). The stretching mode for these three oxygen is located at 666 cm^{-1} for O—Mo_3, 820 cm^{-1} for Mo—O—Mo and 995 cm^{-1} for Mo═O with the relative intensity ratio of 0.2:1:0.5 [38]. Nevertheless, the Raman spectra analysis indicates the formation of MoO_3 species in the MoS_2 O_2-plasma 60 s and MoS_2 O_2-plasma 120 s samples. Moreover, the intensity of these three bands dramatically increased when increasing the plasma processing time from 60 s to 120 s, indicating that much more surface MoO_3 species formed.

The chemical structure of MoS_2 and O_2 plasma modified MoS_2 samples are further studied by X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). As shown in Fig. 4b, the XRD peaks observed at $2\theta = 14.1°$, 32.9°, 39.5° and 58.8° of all the MoS_2 samples can be indexed to (0 0 2), (1 0 0), (1 0 3) and (1 1 0) facets of 2H-MoS_2 crystal, respectively (JCPDS No. 75-1539, JCPDS = Joint Committee on Powder Diffraction Standards). In agreement with the Raman analysis, the XRD patterns further evidence the present of α-phase MoO_3 (marked using star in Fig. 4b) in the MoS_2 O_2-plasma 60 s and MoS_2 O_2-plasma 120 s samples, not present for MoS_2 O_2-plasma 30 s sample, which show peaks