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Full Length Article

Controllable desulfurization in single layer MoS_2 by cationic current treatment in hydrogen evolution reaction

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ABSTRACT

The sulfur vacancy (Sv) generation in the MoS_2 basal plane is an efficient strategy for improving the hydrogen evolution reaction (HER). By using cationic current treatment, the Sv density can be controlled by modifying the setting voltage ranges and treatment time. The Sv generation mechanism was clearly defined using Raman mapping. From the Raman mapping characterizations, for the first time, we experimentally found that Sv tends to be generated next to existing Sv by appearing around cracked/damaged areas or group formations. The S: Mo atomic ratio reduced from 2.02:1 to 1.86:1 after treatment. As a result, the current density at −0.3 V vs RHE sharply increases up to 27-fold in comparison to that with untreated MoS_2, and the overpotential of treated MoS_2 reaches 222 mV at 10 mA/cm^2 with a Tafel slope of 96 mV/decade. Hence, the controllable Sv generation in monolayer MoS2 using a cationic current method can be considered as a fast, simple, and effective process to improve HER performance in large-scale production.

1. Introduction

The extensive use of fossil fuels is known to be one of the leading causes of air pollution; there has been a strong focus on investigating the potential of clean, renewable energy to replace them. With the advantages of having the highest mass-energy density, zero-emission pollution, and renewable sources, the production of hydrogen using electrochemical water splitting is an excellent approach to be employed in synthesizing an environment-friendly, carbon-neutral fuel.

Two-dimensional (2D) semiconductors, such as transitional metal dichalcogenides (TMDCs), have been paid much attendance for wide applications in electronic, optoelectronic, and catalysis [1–6]. MoS_2, one of the TMDCs, has been recently considered as a promising cathode material in hydrogen evolution reaction (HER) based on its structure stability, great electrochemical activities, and earth abundance [7–10]. Also, the DFT Gibb-free energy calculation reported that MoS_2 has a free energy level is close to 0, and a high ex-change current density which is comparable with Pt and other metal [11]. That demonstrates a great potential for MoS_2 to be an alternative to platinum, which is the most efficient but too scarce and expensive for industrial applications [7,10–12]. Although the Mo (1 0 1 0) edge site has been known to be an excellent active site, the Mo (0 0 0 1) basal plane is inert to electrochemical activities [13–15]. Thus, treating the basal plane to expose the Mo (1 0 1 0) edge is an essential step in enhancing the HER performance of MoS_2. Recently, many studies have been published in surficial and electrical engineering on MoS_2 such as plasma treatment, hydrogen annealing, phase transition, and metal doping [9,16–19]. However, another simple method has been largely overlooked, namely, electrochemically treated MoS_2 that can be employed while characterizing HER performance.

In this work, an electrochemical treatment method was employed on monolayer MoS_2 by performing a linear sweep scan on a cationic current with different voltage ranges, namely cationic current treatment, to investigate the structural modification of MoS_2 to improve HER performance. The continuous monolayer MoS_2 film was synthesized using a two-zone thermal chemical vapor deposition (CVD). The morphologies, elemental bonding, and optical properties were characterized using spherical aberration-corrected scanning transmission electron microscopy(Cs-corrected STEM), X-ray photoelectron spectroscopy (XPS), and Raman spectroscopy, respectively, to confirm the sample quality before applying it to HER performance. The cationic current treatment-induced S vacancy (Sv) generation was demonstrated using a calculated double-layer capacitance value from cyclic voltammetry, Raman mapping, and XPS characterizations.

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