Co Doping and 1T Phase Jointly Enhanced HER Activity for Co-1T/2H MoS$_2$

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Abstract. Earth-abundant MoS$_2$ is viewed as a promising HER electrocatalyst, but its HER activity is still restricted due to the low fraction of edge sites and poor electronic conductivity. In this work, we combined the Co doping and 1T strategies to promote the HER activity of Co-1T/2H MoS$_2$. Our experimental results demonstrated that Co doping could bring more active sites while the 1T phase benefical fast electron transfer. As a consequence, Co-1T/2H MoS$_2$ displayed markedly improved activity, which only required an overpotential of 178 mV to deliver a current density of 10 mA cm$^{-2}$ in 1.0 M KOH aqueous solution. And our work also provided an effective strategy for improving the catalytic activity towards other two-dimensional (2D) materials.

1. Introduction

Electrocatalytic water splitting is a sustainable and ecofriendly way to obtain hydrogen energy, which has been viewed to alleviate the crisis of traditional fossil fuel[1]. However, the electricity input is still relatively high in water splitting reaction. Therefore, excellent catalysts are required to low down the overpotential as much as possible. To date, platinum has been viewed as an outstanding hydrogen evolution reaction (HER) catalysts because of its moderate $\Delta G_{\text{H}}$ value of bonding hydrogen atoms[2]. Nevertheless, the scalable application of Pt-based catalysts has been greatly hindered by the scarcity and high cost. Therefore, exploring the earth-abundant catalysts with active performance is very attractive[1].

MoS$_2$, a new rising 2D material, not only possessing unique physical and chemical properties, but also an earth-abundant material with low price. Recent years, MoS$_2$ have been extensively studied in HER, and theoretical calculations and experimental results identified that the active sites for 2H MoS$_2$ lies in the edge position[3], while the big majority of basal planes exhibit inert activity. Therefore, exploiting the inert basal plane become more active would be a promising way to improve HER performance. Recently, element doping MoS$_2$ has been identified to enhance the catalytic activity[2]. It was believed that element doping not only exploited the inert basal plane, but also modulating the electronic density[4], thus greatly improving the hydrogen evolution performance. In another aspect, 2H MoS$_2$ is a semiconducting material with poor electron transfer ability. Studies showed 1T phase MoS$_2$ capable of higher electron transfer ability than 2H MoS$_2$[5]. Therefore, introducing 1T phase into 2H MoS$_2$ structure is also an effective strategy to obtain high efficient MoS$_2$-based catalysts.

In this work, we conducted a simple hydrothermal method to construct the Co-1T/2H-MoS$_2$ catalyst, which combining Co doping and 1T phase MoS$_2$. And we expect that Co doping could increase the active sites while 1T phase enhance the electronic conductivity, therefore, the Co-1T/2H-MoS$_2$ catalyst can behave as an excellent catalyst in hydrogen evolution.
2. Experimental

2.1 Synthesis of electrocatalysts

The Co-1T/2H MoS$_2$ was synthesized via a simple hydrothermal method. Firstly, 0.241 g Na$_2$MoO$_4$$\cdot$2H$_2$O and 0.228 g CS(NH$_2$)$_2$ were added into a beaker with 15 mL of deionized water and 5 mL of propionic acid. The beaker was conducted sonicating for 10 min to obtain homogeneous solution, then dropped 1 mL CoCl$_2$ (0.1 mM) into the beaker and sonicated for another 10 min. Following, the whole solution was transferred into a 50 mL Teflon-lined autoclave and heated at 180 °C for 6 h. After the autoclave cooling down naturally, the black precipitate was collected via centrifugation. Finally, the collected products (Co-1T/2H MoS$_2$) were dried at 60 °C under vacuum condition. At the same condition, however, by changing the propionic acid into deionized water or not adding CoCl$_2$, we obtained the control samples Co-2H MoS$_2$ and 1T/2H MoS$_2$, respectively. And if the propionic acid were substituted for deionized water, meanwhile the CoCl$_2$ was not adding, the final product were 2H MoS$_2$.

2.2 Electrochemical Measurements

Linear sweep voltammetry (LSV) test were conducted under the potential range from 0 to -0.5 V (vs. RHE) with the scan rate of 2 mV s$^{-1}$. Tafel slopes were obtained by fitting the LSV polarization curve with the Tafel equation $\eta = a + b \log j$ ($b$ and $j$ represented Tafel slope and current density, respectively). The double-layer capacitance ($C_{dl}$) were obtained through cyclic voltammetry (CV) measurements under none-faraday region 0.1 to 0.3 V (vs. RHE) with the scan rate of 20, 40, 60, 80, 100, 120 mV s$^{-1}$, respectively. And Nyquist plots were performed under an overpotential of 170 mV with frequencies ranging from 100 kHz to 0.01 Hz.

3. Results and Disscussion

X-ray diffraction (XRD) measurements were conducted to investigate the crystal structural information of synthesized products. Co-1T/2H MoS$_2$ showed peaks at 14.2°, 32.9°, 33.6°, 58.7° (Figure 1a), which should be indexed to (002), (100), (010) and (110) planes of 2H-phase MoS$_2$ (PDF# 75-1539). And Raman characterization was further used to study the structure information (Figure 1b). As for Co-1T/2H MoS$_2$, the characteristic peaks appearing at 146, 235, 281 and 334 cm$^{-1}$ are associated with the J$_1$, J$_2$, E$_{1g}$ and J$_3$ vibration mode of 1T phase MoS$_2$, respectively, which implies that the 1T phase was successfully introduced into the Co-1T/2H MoS$_2$ structure[6]. In addition, another two distinct peaks appeared at 377 and 402 cm$^{-1}$, which are the E$_{1g}^1$ and A$_{1g}$ mode of 2H phase MoS$_2$[7]. Surprisingly, the E$_{1g}^1$ and A$_{1g}$ characteristic peaks in Co-1T/2H MoS$_2$ shifted to a lower wavenumber as compared with 2H MoS$_2$ sample. This phenomenon is probably induced by Co doped effect. Therefore, the above Raman results strongly demonstrated that 1T phase was introduced into the Co-1T/2H MoS$_2$ structure.

![Figure 1](image-url) (a) XRD patterns and (b) Raman spectra of Co-1T/2H MoS$_2$ and 2H MoS$_2$.

The SEM and TEM characterization techniques were used to study the surface morphology and
inner structure. As depicted in Figure 2a and Figure 2b, Co-1T/2H MoS$_2$ exhibited merely flower-like structure, while no other particle phase associated with CoS$_x$ could be observed, implying that Co probably doped into the structure of MoS$_2$. Additionally, STEM-EDS elemental mapping images (Figure 2c) showed Mo, Co, and S element evenly distribution in the Co-1T/2H MoS$_2$ structure. Therefore, the above results strongly validated that Co element successfully doped into the Co-1T/2H MoS$_2$ structure.

Figure 2. (a) SEM and (b) TEM images of Co-1T/2H MoS$_2$ and (c) STEM-EDS elemental mapping of Mo, Co, and S in the Co-1T/2H MoS$_2$.

We evaluated the HER activity through a typical three electrodes system in 1.0 M KOH. As shown in Figure 3a, 2H MoS$_2$ showed inert HER activity, which required an overpotential of 450 mV to drive a current density of 10 mA cm$^{-2}$. Suprisingly, compared with 2H MoS$_2$, both Co-2H MoS$_2$ and 1T/2H MoS$_2$ catalysts exhibited promoted HER activity, which required 285 mV and 327 mV to deliver 10 mA cm$^{-2}$, respectively. Those results indicated that Co doping or 1T phase could effectively boost HER performance. More importantly, Co-1T/2H MoS$_2$ displayed even better performance than both Co-2H MoS$_2$ and 1T/2H MoS$_2$. To produce a current density of 10 mA cm$^{-2}$, Co-1T/2H MoS$_2$ required an overpotential of 178 mV, which is 107 mV and 149 mV lower than that of Co-2H MoS$_2$ and 1T/2H MoS$_2$, respectively, implied that Co doped effect and 1T phase could jointly promoted HER activity for Co-1T/2H MoS$_2$. In order to understand the hydrogen evolution machanism, we analysed Tafel slopes of various samples. As displayed in Figure 3b, Co-1T/2H MoS$_2$ showed a small Tafel slope of 59 mV dec$^{-1}$, which is at the range of 40-120 mV dec$^{-1}$, implying the catalyst followed Volume-Heyrovsky machanism in HER process.

Figure 3. (a) LSV polarization curves and (b) Tafel slopes for various catalysts.

The electrochemically active surface area (ECSA) is also an important ingredient to affect HER performance. As ECSA is generally proportional to the double-layer capacitance (C$_{dl}$), thus we can assess the ECSA value by calculating the C$_{dl}$ through cyclic voltammogram (CV) measurements. As shown in Figure 4a, the C$_{dl}$ value of Co-1T/2H MoS$_2$, Co-2H MoS$_2$, 1T/2H MoS$_2$, 2H MoS$_2$ are 9.1 mF cm$^{-2}$, 9.0 mF cm$^{-2}$, 6.2 mF cm$^{-2}$, 5.9 mF cm$^{-2}$, respectively. And it can observed that the value of 2H MoS$_2$ and 1T/2H MoS$_2$ are very close, suggesting that 1T phase did not bring more active sites. However, it is worth noting that the C$_{dl}$ value of Co-1T/2H MoS$_2$ is 1.5 times of Co-2H MoS$_2$. 

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therefore we can affirm that Co doping would bring more active sites [4], which caused catalysts exhibited markedly improved activity. In addition, the electrochemical impedance spectroscopy (EIS) was further to investigate the charge transfer resistance ($R_{ct}$) in the electrochemical reaction process. Nyquist plots (Figure 4b) shows that $R_{ct}$ of Co-1T/2H MoS$_2$ is 90 $\Omega$, much smaller than the Co-2H MoS$_2$ (460 $\Omega$) and 2H MoS$_2$ (1100 $\Omega$), suggesting the 1T phase made Co-1T/2H MoS$_2$ possess higher electrochemical electron transfer ability.

Figure 4. (a)The $C_{dl}$ obtained at 0.2 V versus RHE and (b) Nyquist plots of Co-1T/2H MoS$_2$, Co-2H MoS$_2$, 1T/2H MoS$_2$, 2H MoS$_2$.

4. Conclusion
In conclusion, we successfully proved that Co-1T/2H MoS$_2$ is an efficient HER catalyst. Experimental results showed that Co doping could bring more active sites while the 1T phase beneficial fast electron transfer. Therefore, the Co doping and 1T phase jointly promoting the HER performance for Co-1T/2H MoS$_2$ catalysts. Consequently, the Co-1T/2H MoS$_2$ electrocatalyst only required a low overpotential of 178 mV to deliver a current density of 10 mA cm$^{-2}$ in 1.0 M KOH aqueous solution. And our work also provided a promising method for constructing other active HER electrocatalysts.

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References
[1] Jiao, Y., Zheng, Y., Jaroniec, M., Qiao, S. Z. (2015) Design of electrocatalysts for oxygen- and hydrogen-involving energy conversion reactions. Chemical Society reviews, 44: 2060-2086.
[2] Zhang, J., Wang, T., Liu, P., Liu, S., Dong, R., Zhuang, X., Chen, M., Feng, X. (2016) Engineering water dissociation sites in MoS$_2$ nanosheets for accelerated electrocatalytic hydrogen production. Energy Environ. Sci., 9: 2789-2793.
[3] Jaramillo, T. F., Jørgensen, K. P., Bonde, J., Nielsen, J. H., Horch, S., Chorkendorff, I. (2007) Identification of Active Edge Sites for Electrochemical H$_2$ Evolution from MoS$_2$ Nanocatalysts. Science, 317: 100.
[4] Xiong, Q., Wang, Y., Liu, P. F., Zheng, L. R., Wang, G., Yang, H. G., Wong, P. K., Zhang, H., Zhao, H. (2018) Cobalt Covalent Doping in MoS$_2$ to Induce Bifunctionality of Overall Water Splitting. Advanced materials, e1801450.
[5] Liu, Z., Gao, Z., Liu, Y., Xia, M., Wang, R., Li, N. (2017) Heterogeneous Nanostructure Based on 1T-Phase MoS$_2$ for Enhanced Electrocatalytic Hydrogen Evolution. ACS applied materials & interfaces, 9: 25291-25297.
[6] Wei, W., Sun, K., Hu, Y. H. (2016) An efficient counter electrode material for dye-sensitized solar cells—flower-structured 1T metallic phase MoS$_2$. Journal of Materials Chemistry A, 4:
12398-12401.

[7] Kong, D., Wang, H., Cha, J. J., Pasta, M., Koski, K. J., Yao, J., Cui, Y. (2013) Synthesis of MoS$_2$ and MoSe$_2$ Films with Vertically Aligned Layers. Nano letters, 13: 1341-1347.