Co doped MoS$_2$ as Bifunctional Electrocatalyst for Hydrogen Evolution and Oxygen Reduction Reactions

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Received: 25 May 2019 / Accepted: 1 August 2019 / Published: 30 August 2019

Pure MoS$_2$ and MoS$_2$ compounds were doped with Co using a hydrothermal method. XRD results indicate that two of the five diffraction peak results at 9.2$^\circ$ and 18.2$^\circ$ may be attributed to low crystallinity of MoS$_2$. The (002) diffraction peaks for the Co-doped MoS$_2$ shifted to smaller angle, which may be due to the Mo$^{4+}$ ions ($r = 0.65$ Å) having been replaced by larger Co$^{2+}$ ions ($r = 0.74$ Å). Raman results show that the intensity of the A$_{1g}$ mode was greater than that of the E$_{1g}$ mode for our samples; this indicates that the samples have edge-terminated structures and possess more electrocatalytic active sites. The results of XPS also confirm that the cobalt ions substituted molybdenum atoms into the lattice of MoS$_2$. Results from the electrocatalytic test confirms that cobalt doping reduces the charge transfer resistance and increases the electrocatalytic active sites, which are conducive to improving its electrocatalytic performance.

**Keywords:** Co-MoS$_2$; electrocatalysts; hydrogen evolution reaction; oxygen evolution reaction

1. INTRODUCTION

Many of our current environmental problems are a results of fossil fuel emission, which seriously affect human survival and development. Hydrogen production from water splitting has been regarded as a promising technology capable of meeting the needs of development and overcome the current environmental issues we face [1]. However, it is well known that hydrogen evolution reaction
(HER) requires an efficient catalyst to be effective. The noble metal palladium and other Pt-based materials possess high catalytic activity for HER [2-4], but large-scale applications have been limited by their high cost and scarcity of supply. In the past few years, significant amounts of research have been devoted to develop new and non-noble metal electrocatalysts for HER [5-7]. Various non-noble metal-based electrocatalysts such as carbides, selenide, nitrides, and transition metal sulphides have been adopted as alternative materials for HER, with the transition metal sulphides as the most promising alternative materials. MoS$_2$, a transition metal sulphide with a two-dimensional layered structure, has a unique graphene-like structure, providing MoS$_2$ good electrocatalytic performance and mechanical strength. It is well known that the electrocatalytic active sites in MoS$_2$ catalysts are seated at the exposed Mo and the unsaturated S atoms on the edges of the molecule [8]. However, electrocatalytic performance of bulk MoS$_2$ has been hindered due to poor intrinsic conductivity and the fewer electrocatalytic activity edge sites [9]. In order to promote the electrocatalytic performance of MoS$_2$, a layered structure of MoS$_2$ was designed and constructed by doping and coupling with other two-dimensional structural materials, which can enhance the conductivity and electrocatalytic activity edge sites of MoS$_2$ [10-12]. MoS$_2$ nanosheets were successfully grown on multiwall CNTs using a simple method for enhanced HER performance [13]. The effect of film thicknesses on the HER activity was also investigated using prepared porous 2D MoS$_2$ films [10]. While the layered structure MoS$_2$-based nanomaterial is a typical HER electrocatalyst, it is but a good oxygen evolution reaction (OER) electrocatalyst, which is not conducive overall as an applied MoS$_2$-based electrocatalyst in the general field of water splitting. Bifunctional Co-MoS$_2$ catalysts involving the HER and OER have seldom been reported in literature [14].

This research report on the results of Co doping for MoS$_2$ catalysts, which were prepared using a one-step hydrothermal method. The microstructure and morphology were also investigated by means of X-ray diffractometer, Raman spectrometer, and scanning electron microscope, and the chemical compositions and the element valence states of MoS$_2$ and Co-3-MoS$_2$ composite were tested using X-ray photoelectron spectroscopy. Finally these results report on the effects of Co doping on the catalytic performance in both acidic and alkaline media with HER and OER reactivity.

2. EXPERIMENTAL

Using a standard preparation process, 4.567g thiourea (CH$_4$N$_2$S), and 17.302g hexaammonium heptamolybdate tetrahydrate ( (NH$_4$)$_6$Mo$_7$O$_{24}$$\cdot$4H$_2$O) were added to 80 mL deionized water. Then 0.058g, 0.174g, 0.291g, and 0.407g cobalt nitrate (Co(NO$_3$)$_2$) were dissolved into the mixed solution. The homogeneous solution was obtained by use of magnetic stirring at room temperature. Then the solution was transferred into a 100 mL Teflon-lined autoclave and kept at 220 °C for 24 h in an oven. The autoclave was cooled to room temperature after the reaction. The derived powders were first cleaned ultrasonically several times in absolute ethanol and deionized water, and then dried at 60 °C in a vacuum atmosphere. The Co-MoS$_2$ prepared from 0.058g, 0.174g, 0.291g, and 0.407g cobalt nitrate were named as Co-1-MoS$_2$, Co-2-MoS$_2$, Co-3-MoS$_2$, and Co-4-MoS$_2$, respectively. Un-doped molybdenum disulfide was also prepared without nickel nitrate (Ni(NO$_3$)$_2$) under the same conditions for comparative purposes.
The microstructure of the Co-MoS$_2$ was investigated by X-ray diffraction analysis (XRD, TD-3500) and Raman spectroscopy (inVia-Reflex, Renishaw). Surface topography of the samples was measured by field emission scanning electron microscopy (FE-SEM, Hitachi S-4800). X-ray photoelectron spectrometer (XPS, Thermo, ESCALAB 250) was used to survey the elemental composition and valence states of the Co-MoS$_2$ composite. The electrocatalytic performance of the Co-MoS$_2$ composites were characterized by linear sweep voltammetry (LSV), electrochemical impedance spectroscopy (EIS), and cyclic voltammetry (CV), which were carried out using a CHI 660E electrochemical workstation. Homogeneous catalyst ink was obtained by ultrasonically dispersing 10mg Co-MoS$_2$ composites in a mixed solution isopropanol alcohol (400 μL) and Nafion solution (5.0%, 25 μL) for 1h. Then, the ink was dripped onto carbon paper (1.0×1.0 cm$^2$), which was dried at 60 °C for 10 h so as to obtain the working electrode. A pure MoS$_2$ working electrode was also made using the same process. A carbon cloth and Ag/AgCl (3 M KCl) acted as the counter and reference electrode, respectively.

3. RESULTS AND DISCUSSION

The crystal structures of MoS$_2$, Co-1-MoS$_2$, Co-2-MoS$_2$, Co-3-MoS$_2$ and Co-4-MoS$_2$ were characterized using the XRD technique, and the XRD patterns of each sample are shown in Fig.1. It could be seen from the XRD patterns that the diffraction peaks located at 2$\theta$ = 14.3°, 33.5°, and 58.3° correspond to the (002), (101), and (110) crystal face of 2H-MoS$_2$ with a space group of P63/mmc (JCPDS37-1492). The other two diffraction peaks at 9.2° and 18.2° correspond to the d spacings at 9.50 Å and 4.75 Å, which might be attributed to low crystallinity of MoS$_2$ [15, 16]. The results indicated that a new layered structure with interlayer spacing of 9.5 Å in the sample was greater than that of 6.15 Å in 2H-MoS$_2$. The strong diffraction peaks at 9.2° clearly demonstrated that the content of layered structure with interlayer spacing of 9.5 Å in the sample was more robust than that of 2H-MoS$_2$. Compared with the pure MoS$_2$, the (002) diffraction peaks for the Co-doped MoS$_2$ were shifted at a smaller angle (2$\theta$ = 13.82°). These results might be due to the substitution doping of Mo$^{4+}$ ions ($r =0.65$ Å) by Co$^{2+}$ ions ($r =0.74$ Å), which have a larger ionic radius [17].

![Figure 1. XRD pattern of the Co-doped MoS$_2$ and pure MoS$_2$.](image-url)
Fig. 2 presents the Raman spectra of the samples, which could be used to characterize their microstructure. Two Raman characteristic peaks were located at about 378 and 405 cm$^{-1}$, which may be indexed to the $E_{2g}^1$ and $A_{1g}$ corresponding. These correspond to the in-plane vibration phonon mode of two S atoms with opposite orientation to Mo atom and the out-of-plane vibration phonon mode of S atoms, respectively [18]. It was reported that the intensity of $E_{2g}^1$ vibration phonon mode and $A_{1g}$ vibration phonon mode were indexed to the edge-terminated and terrace-terminated structures, also respectively [19]. Results showed that the intensity of the $A_{1g}$ mode was greater than that of the $E_{2g}^1$ mode for our samples, indicating that all of the samples present the edge-terminated structures [16, 19], which would offer more edge sites and further improve the activity of electrocatalytic hydrogen production.

![Figure 2. Raman spectra of the Co-doped MoS$_2$ and pure MoS$_2$.](image)

Fig. 3 visualized the typical FE-SEM images of the pure MoS$_2$ and Co-MoS$_2$ nanostructure. A small amount of perpendicularly oriented MoS$_2$ nanosheets were observed in the pure MoS$_2$ (in Fig. 3a). Topical flower-like MoS$_2$ nanosheets were observed in the Co-1-MoS$_2$ (Fig. 3b). The size of flower shaped MoS$_2$ nanosheets increases gradually with the increasing amount of Co doping content. The Co-2-MoS$_2$ and Co-3-MoS$_2$ exhibit dispersed and homogeneous flower-like nanostructures and have more edge-terminated structures, which might also provide more active for electrocatalytic reactions. However, Co-4-MoS$_2$ began to lose the perpendicularly oriented feature of MoS$_2$ nanosheets as the cobalt nitrate increased to 0.407g.
Figure 3. FE-SEM images of (a) pure MoS$_2$, (b) Co-1-MoS$_2$, (c) Co-2-MoS$_2$, (d)Co-3-MoS$_2$ and (e) Co-4-MoS$_2$.

XPS has been used to characterize the chemical compositions and the element valence states in the pure MoS$_2$ and Co-3-MoS$_2$ composite. The XPS survey spectrum (Fig. 4a) showed that the predominant elements were Mo, S, Co, O, and C. The Mo, S and Co elements originated from the Co-3-MoS$_2$ composite and the C and O elements are most likely present due to the surface adsorption of O$_2$, H$_2$O, and CO$_2$ [20]. The high resolution XPS spectrum of S$_2$p has been presented in the Fig. 4b. The S$_2$p peaks for the Co-3-MoS$_2$ composite could be divided into five peaks; two peaks were located at ~161.5 and ~162.8 eV were indexed to the S$_2$p$_{3/2}$ and S$_2$p$_{1/2}$ orbits from the -2 oxidation state of
the S element, and three peaks were situated at ~164.2 and ~168.8 eV and ~170.1 eV from the C-S and S-O bonds, respectively[21]. The intensity of the three peaks might be improved by the incorporation of Co atoms since it is considered to be an important factor for enhancing the HER activity [22, 23]. Fig. 4c shows the high resolution XPS spectrum of Mo3d. Two strong peaks were located at 228.9 and 231.9 eV and assigned to Mo 3d5/2 and Mo 3d3/2 of Mo(IV), suggesting that Mo(IV) was predominant in the samples. In addition, two weak peaks were seen from Mo 3d5/2 and Mo 3d3/2 of Mo(VI) located at 233.4 and 236.7 eV, indicating that a small amount of the Mo element existed in the form of Mo(VI) compounds. The XPS results indicated that there were Mo(VI) compounds in the Co-3-MoS2 than in the pure MoS2. Fig. 4d shows that the Co2p XPS spectrum of Co-3-MoS2 composite, where the characteristic peaks located at 781.5 eV and 797.7 eV correspond to 2p3/2 and 2p1/2 orbits of Co2+, respectively. The results indicated that the cobalt ions substituted for the molybdenum atoms into the lattice of MoS2.

Figure 4. XPS (a) survey spectrum, (b) S 2p, (c) Mo 3d and (d) Co 2p for Co-doped MoS2 and MoS2.

In order to study the effects of the Co molecule on the HER activities of the Co-MoS2 composite electrodes, polarization curves of Co-MoS2 composite electrodes were tested in 0.5M H2SO4 solution with a three-electrode system (Fig. 5a). For comparison, the pure MoS2 and Pt electrodes were also measured using the same method. It can be seen that the Co-3-MoS2 has the
lowest overpotential of 220 mV (vs. RHE) at 10 mA cm\(^{-2}\), indicating that the Co-3-MoS\(_2\) electrode displays the optimum electrocatalytic activity for HER. The Tafel slope, which is another important parameter for investigating the dynamic process of HER activity, was also used for analysis of the polarization curves. The Tafel curves of pure MoS\(_2\) and Co-MoS\(_2\) composite electrodes, which originated from the LSV polarization curves in the low cathodic overpotential range [24], are displayed in Fig. 5b. The Tafel slope can be calculated by fitting the linear portions of the Tafel curve using the Tafel equation [8, 15]:

\[ \eta = a + b \log |j| \]  

(1)

where \( \eta \) is the overpotential, \( b \) is the Tafel slope, and \( j \) is the current density. The apparent exchange current density (\( j_0 \)) can be calculated as follows [8]:

\[ j_0 = 10^{-a/b} \]  

(2)

The obtained Tafel slopes (\( b \)) and exchange current density (\( j_0 \)) of the samples are listed in Table 1. It can be seen that the Tafel slopes of Co-MoS\(_2\) composite electrodes can be reduced by Co doping. The Co-3-MoS\(_2\) composite electrode presents the smallest Tafel slope of 141 mV dec\(^{-1}\), and when compared to other electrodes, the Co-3-MoS\(_2\) composite electrode also has the largest exchange current density of \( j_0 \). The smaller Tafel slope implies that the reaction rate increases as the overpotential increases [24, 25]. The results indicate that Co doping is an effective method for enhancing HER activity.

The electrochemical impedance spectroscopy (EIS) results were used to characterize the electrode kinetics for HER. The impedance spectra of the samples are shown in Fig. 5c and fit using an equivalent circuit model (inset of Fig. 5c). \( R_s \) and \( R_{ct} \) represent the solution resistance and charge transfer resistance, respectively, where the smaller \( R_{ct} \) value reflects the higher HER activity. The fitting \( R_{ct} \) values of the samples are listed in Table 1. It can be seen that the Co-3-MoS\(_2\) composite electrode has the smallest semicircle radius in the Nyquist plots, and the \( R_{ct} \) of Co-3-MoS\(_2\) composite electrode (~169 \( \Omega \)) is much smaller than the pure MoS\(_2\) electrode (~6108 \( \Omega \)). These results indicate that electron transfers are more easily completed in the interface between electrolyte and Co-3-MoS\(_2\) composite electrode [26].

Another important parameter that was explored for the practical application was the durability of catalysts. In order to evaluate the stability of Co-3-MoS\(_2\) composite electrode, polarization curves before and after 1000 cycles were measured; results showed measurements of 0.2 to -0.4 V (vs. RHE) with a scan rate of 10 mV s\(^{-1}\) (Fig. 5d). It can be seen that the polarization curves after 1000 cycle has a slightly different initial polarization curve in the region of low current density. In addition, the chronoamperometric curve at 248 mV (vs RHE) is present in the inset of Fig. 5d. This result shows that current density of Co-3-MoS\(_2\) composite catalyst decreases slightly, and the Co-3-MoS\(_2\) composite catalyst has steady HER activity for 5 h [27].
Figure 5. (a) HER polarization curves, (b) corresponding Tafel curves, (c) electrochemical impedance spectroscopy of pure MoS$_2$ and Co-doped MoS$_2$ in 0.5 M H$_2$SO$_4$ (d) HER durability tests for the Co-3-MoS$_2$.

Table 1. List of the HER catalytic properties of the pure MoS$_2$ and Co-doped MoS$_2$ in 0.5 M H$_2$SO$_4$

<table>
<thead>
<tr>
<th>Sample</th>
<th>Potential for 10mA cm$^{-2}$ (mV)</th>
<th>Tafel slope (mV/dec)</th>
<th>$j_0$ (mA cm$^{-2}$)</th>
<th>$R_{ct}$ (Ω)</th>
<th>Refs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>MoS$_2$</td>
<td>343</td>
<td>163.3</td>
<td>0.07965</td>
<td>6108</td>
<td>this work</td>
</tr>
<tr>
<td>Co-1-MoS$_2$</td>
<td>286</td>
<td>160.2</td>
<td>0.17282</td>
<td>2701</td>
<td>this work</td>
</tr>
<tr>
<td>Co-2- MoS$_2$</td>
<td>277</td>
<td>149.8</td>
<td>0.14389</td>
<td>1296</td>
<td>this work</td>
</tr>
<tr>
<td>Co-3- MoS$_2$</td>
<td>220</td>
<td>141.1</td>
<td>0.27655</td>
<td>169</td>
<td>this work</td>
</tr>
<tr>
<td>Co-4- MoS$_2$</td>
<td>286</td>
<td>156.4</td>
<td>0.1567</td>
<td>1308</td>
<td>this work</td>
</tr>
<tr>
<td>MoS$_2$</td>
<td>270</td>
<td>135.0</td>
<td>0.0138</td>
<td>70</td>
<td>22</td>
</tr>
<tr>
<td>Ni-MoS$_2$/Ni</td>
<td>207</td>
<td>65</td>
<td>-</td>
<td>-</td>
<td>26</td>
</tr>
<tr>
<td>foam</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MoS$_2$@Fe$_3$O$_4$</td>
<td>110</td>
<td>52</td>
<td>-</td>
<td>357</td>
<td>28</td>
</tr>
</tbody>
</table>

In this paper, the OER activities of the samples have been measured in the KOH solutions with a concentration of 1.0 M. Fig. 6a shows the LSV plots of MoS$_2$ and Co-MoS$_2$ composite electrodes. It can be seen that the Co-2-MoS$_2$ exhibits the lowest overpotential at 10 mA cm$^{-2}$ of 390 mV (vs. RHE), indicating that the Co-2-MoS$_2$ electrode has the best OER activity. The results indicate that OER activity of the MoS$_2$ electrode could be enhanced by moderate Co doping, which could regulate the
The electronic structure of MoS$_2$. The Tafel curves from the LSV curves of the electrode show that the Tafel slope value of the Co-2-MoS$_2$ electrode is 177 mV dec$^{-1}$ (Fig. 6b), which indicates that it has the optimum OER reaction kinetics [8].

**Figure 6.** (a) OER polarization curves and (b) Corresponding Tafel curves of pure MoS$_2$ and Co-doped MoS$_2$ in 1 M KOH.

**4. CONCLUSION**

In summary, HER and OER performance of MoS$_2$-based electrocatalysts have been measured in both acidic and alkaline solutions, respectively. The results show that Co doping could increase the edge-terminated structures and electrocatalytic active sites, as well as reduce the charge transfer resistance, which can affect electrocatalytic performance. The Co-3-MoS$_2$ electrocatalyst exhibits the lowest applied potential for HER, the smallest Tafel slope, and good stability. The lowest applied potential for OER and smallest Tafel slope have been observed in the Co-2-MoS$_2$ electrocatalyst. This study reports a bifunctional Co doped MoS$_2$ electrocatalyst for HER and OER, which might be a very promising candidate for overall water splitting applications.

**ACKNOWLEDGEMENTS**

This work was supported by National Natural Science Foundation of China (Nos. 51701001, 61804039), Academic funding projects for Top Talents in Subjects ( Majors) of Universities (No. gxbjZD31), Natural Science Foundation of Anhui Higher Education Institution of China (KJ2019A0734, KJ2019A0736, KJ2017A924, KJ2017A002), Natural Science Foundation of Anhui Province (No. 1808085QE126), Doctor Scientific Research Fund of Anhui University (No. J01001927), Youth Core Teacher Fund of Anhui University (No. J01005111) and Foundation of Cooperative Innovation Research Center for Weak Signal-Detecting Materials and Devices Integration Anhui University (No. Y01008411, WRXH201703).

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