

MoS₂ nanostructure electrodeposited on Ni-P coating: an efficient and durable hybrid cathode catalyst in alkaline water electrolyses

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Abstract. In this work we report a simple electrodeposition method to synthesize novel MoS₂/Ni-P hybrid electrocatalyst for the first time. Compared with pure MoS₂ and Ni-P, the hybrid MoS₂/Ni-P exhibits the better electrocatalytic activity for HER in alkaline media and a excellent stability of MoS₂/Ni-P can be obtained. The enhancement of HER performances may be owing to the excellent conductivity of Ni-P and the synergistic effect between Ni-P and MoS₂. The simple synthesizing hybrid materials through electrodeposition process provide an efficient approach for MoS₂-based electrocatalysts for HER in large-scale industrial alkaline water electrolyzers.

1. Introduction

Hydrogen (H₂) as clean energy provides a promising solution to new energy vehicles fuels as well as to large-scale energy storage. Presently, more than 95% of H₂ comes from fossil fuel feedstock. Electrocatalytic production of H₂ with precious metals as catalyst in alkaline water is broadly considered to be sustainable strategy [1-4]. However the employment of precious metals is largely restricted due to their high price and low reservation [5-7]. Since years nickel alloys were broadly employed as cathode material for alkaline water electrolysis. Among nickel-metal alloys, NiMo alloys are thought to have additional mechanisms for hydrogen evolution reaction (HER) catalysis [8-11]. As metal-nonmetallic alloy Ni-S was widely studied, especially their preparation methods as well as their influences on the HER activity [12-14]. Catalytic activities and alloy structures (amorphous, crystal or their composition) influenced by P content in nickel alloys were reported in several studies [15-17]. In recent years, MoS₂ as one of the most fascinating transitional chalcogenides has been studied in various fields [18-20]. To enhance the HER properties, phase transformation from 2H-MoS₂ to the metallic 1T-MoS₂ [21], gentle oxidation [22], functional structural design [23], and stabilizing the edge layers with organic molecules [21] have been extensively attempted. Promoters such as gold [24], core-shell MoO₃ [25], macroporous and mesoporous carbon materials [20, 26], grapheme [27], and graphene oxide [28] have been employed as electrical conduction supports to increase the intrinsic activity.

In spite of numerous studies on the HER activities of Ni-P alloy and MoS₂ nanostructures in alkaline water electrolyses, the composition of the advantages of these two materials were seldom studied. Inspired by this, we are interested in a hybrid cathode catalyst from both materials through composited electrodeposition. There are three reasons. First, Ni-P alloy has excellent corrosion



resistance and mechanical stability, also at an operating temperature 330 - 380 K. This could fulfill the operating requirements in industrial alkaline water electrolysis application. Second, MoS₂ nanostructure is an effective catalyst for HER since it owns much large specific surface area and more activity sites. Third, electrodeposition is an economical and reliable method for large-scale cathode production. Herein, we report a stepwise electrodeposition strategy to synthesize hybrid cathode for alkaline water electrolyses. By using stepwise strategy, firstly Ni-P coating was deposited on nickel basis. The P amount, coating layer structure and coating thickness can be controlled. In second step, MoS₂ prepared by a simple facile hydrothermal method was installed on the Ni-P coating. The hybrid surface structure obtained via stepwise deposition is favorable to alkaline water electrolysis by assisting both mass and charge transportation. This work is therefore a valuable solution reference to industrial water electrolyses practice.

2. Experiments

2.1. Preparation of Cathode

Cathode was prepared with nickel foam (500 g/m², Changle new power Co., Ltd., China) which was firstly polished mechanically to mirror finish, cleaned with ethanol and distilled water successively. Then, they were immersed into 3 mol/L of HCl solution at room temperature for 3 min, followed by cleaning with distilled water for the preparation of Ni-P coating. Ni-P coating was prepared by stepwise pulsed electrodeposition. The solution contained 300 g/L NiSO₄ 6H₂O as nickel salt, 50 g/L NiCl₂ 6H₂O, 40 g/L H₃BO₃ 6H₂O, 20 g/L NaH₂PO₂ H₂O, 0.25 g/L sodium dodecyl sulfate as buffer agent. Ammonium hydroxide was used to adjust the solution pH within 4.0 - 5.0 during deposition process. Deposition temperature 40 °C, current 25 mA/cm², pulse frequency 500 Hz, duty ration 1:10, deposition time 15 min.

2.2. Preparation of Amorphous MoS₂

1.5 g (NH₄)₆Mo₇O₂₄·4H₂O was dissolved in 20 ml of distilled water, and then 15 ml of N₂H₄·H₂O (85%, wt%) as reducing agent was injected. The mixture solution was stirred for 0.5 h, and then 5.0 g Na₂S·9H₂O dissolved in 20 ml of distilled water and 20 ml of hydrochloric acid was injected and stirred for another 10 min. The final solution was transferred into a 200 ml Teflon-lined stainless steel autoclave and heated at 230 °C for 12 h. After filtering, black powders were collected, dried at 60 °C for 5 h and then retained for use.

2.3. Preparation of Cathode Catalyst

MoS₂ nanoflowers on Ni-P coating was prepared by pulsed electrodeposition. The solution contained 300 g/L NiSO₄ 6H₂O as nickel salt, 45 g/L NiCl₂ 6H₂O, 40 g/L H₃BO₃ 6H₂O, 15 g/L NaH₂PO₂ H₂O, 0.25 g/L sodium dodecyl sulfate as buffer agent, 3 g/L MoS₂ nanoparticles. Ammonium hydroxide was used to adjust the solution pH within 4.0 - 5.0 during deposition process. Deposition temperature 40 °C, current 35 mA /cm², pulse frequency 500 Hz, duty ration 1:10, deposition time 1 h.

3. Results and Discussions

3.1. Structure Characterization

X-ray powder diffraction (XRD) patterns for samples prepared with MoS₂ nanostructure, Ni-P and MoS₂/Ni-P as hybrid structure were recorded via D/max-2500 system (Rigaku, Japan) using Cu K radiation ($\lambda = 0.154$ nm). The XRD patterns present low diffraction peaks of (002) compared to commercial bulk MoS₂ [18], which indicates a poor crystallinity in MoS₂ nanostructures. However, the slight (100) and (110) diffraction peaks still can demonstrate the existence of MoS₂ on the hybrid structure. It is noteworthy that all the peaks are significantly broadened than the pristine 2H-MoS₂ (JCPDS Card No.73-1508) due to the worse crystallinity and smaller particle size. High HER activity can be expected because of the absence of (002).

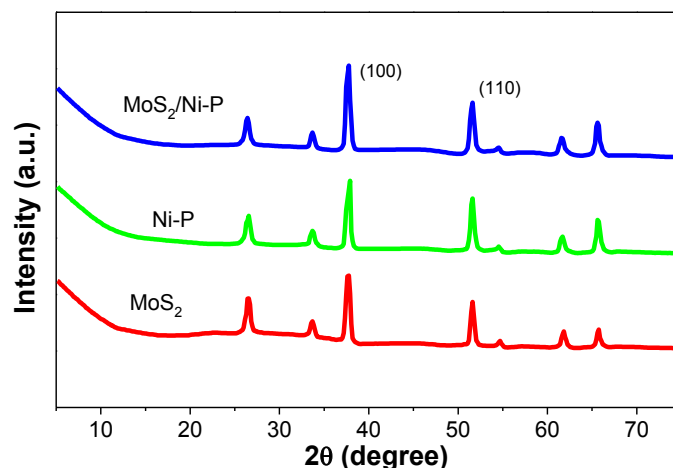


Figure 1. XRD of the MoS_2 , Ni-P and hybrid $\text{MoS}_2/\text{Ni-P}$

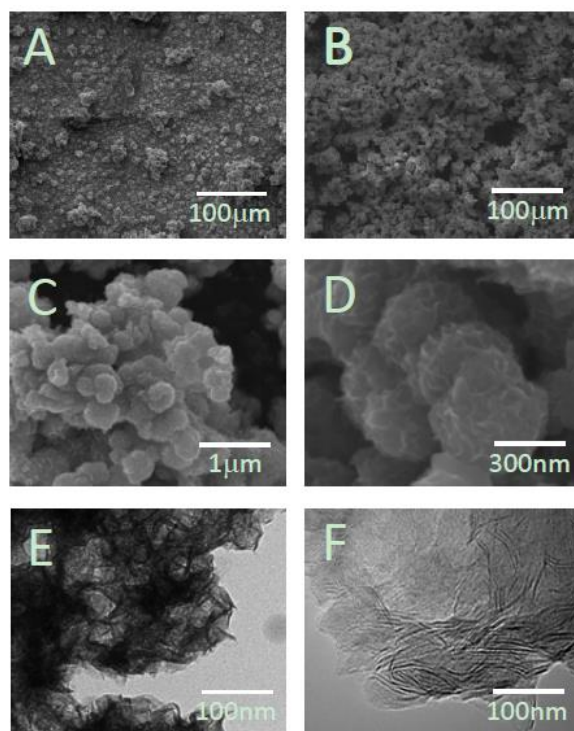


Figure 2. SEM of Ni-P (A) and $\text{MoS}_2/\text{Ni-P}$ (B, C, D), and TEM images of MoS_2 (E, F).

Microstructures were observed by scanning electron microscopy (SEM) Nova NanoSEM 230 (FEI, USA) and transmission electron microscopy (TEM) JEM-2010F (JEOL, Japan). The Ni-P and $\text{MoS}_2/\text{Ni-P}$ hybrid structure were selected to represent the typical morphologies and structures. As shown in Fig. 2A, Ni-P film deposited on the nickel surface are composed of many isolated small bulk nanoflowers with different diameter ranging from 100 nm to 300 nm. The morphology of the electrodeposited hybrid $\text{MoS}_2/\text{Ni-P}$ is shown in Fig. 2B. It can be seen that Ni-P as the substrate contributes to the good dispersion of MoS_2 , exhibiting smaller nanoparticles. In addition, the electrodeposited Ni-P does not cover up the edges of MoS_2 . Therefore, the hybrid $\text{MoS}_2/\text{Ni-P}$ takes the advantages of both MoS_2 and Ni-P, which ensures better HER activity. The SEM images provide a general view, and show that the catalysts are nanoflowers with a diameter of 100 - 500 nm, assembled

by lamellar nanosheets (Fig. 2C and D). It can be observed by TEM that these nanosheets are about 100 nm in length and 10 nm in thickness, respectively, as shown in Fig. 2E.

More information is obtained in Fig. 2F with a higher magnification. It can be observed that the MoS₂ nanosheets are short with low stacking height, presenting an expanded interlayer distance of 0.75 nm, larger than the standard value of 0.6 nm, indicating a lattice expansion. There are many defects in the stacking structures, which increase the interlayer resistance and will lead to a remarkable decrease of the final HER activity. Although the previous XRD and Raman analysis demonstrate the absence of (002) peaks and layer stacking along c-axis, there are still stacking structures observed with expanded interlayers. This abnormal phenomenon should be attributed to the existence of rich defects, which greatly deteriorate the crystallinity, leading to the missing of related XRD and Raman signals.

Raman spectroscopy was recorded using the instrument LabRAM HR-800 (Hoirba, France). Raman spectroscopy was employed to further confirm the MoS₂ phase, where the appearance of two peaks at 265 and 360 cm⁻¹ corresponds to the E_{1g} and E_{2g}^1 vibration models of hexagonal MoS₂, respectively, Fig. 3.

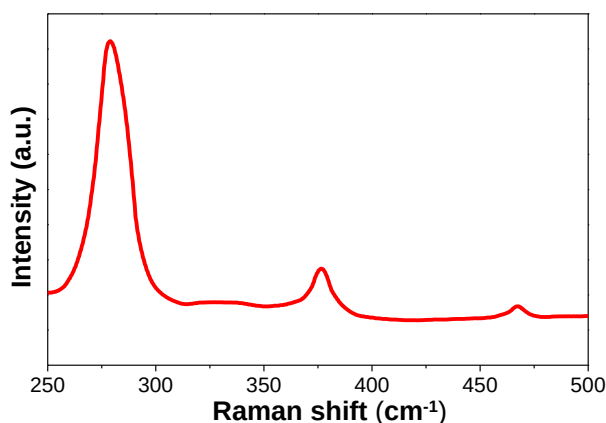


Figure 3. Raman spectra of various MoS₂ samples.

It is known that the E_{1g} and E_{2g}^1 correlate with the relative vibration mode along the layer of the bond between Mo and S. And the E_{2g}^1 peak presents the in-layer displacements of Mo and S atoms [29, 30]. The relatively larger E_{2g}^1 peak width and the weaker intensity suggest that the crystal structure of MoS₂ may contain substantial defect sites [31]. However, it must be noted that the Raman peak corresponding to the out-of plane Mo-S phonon mode (A_g , 408 cm⁻¹) is absent, indicating that the relative vibration along the direction of vertical layer of the bond between Mo and S is not significant, which is also coincident with the absence of (002) peak in Fig. 1.

3.2. Electrocatalytic Activity

The electrochemical measurements were carried out on a three-electrode setup. The electrocatalytic activities of CB-MoS₂, Ni-P and hybrid MoS₂/Ni-P was examined through linear sweep voltammetry (LSV) with a scan rate of 1 mV s⁻¹ on an IM6ex (Zahner, Germany) in 1.0 M KOH at room temperature. Before the electrochemical measurements, the electrolyte solution was purged with N₂ for 1 h to remove completely the oxygen, and stable polarization curves were recorded after 20 cycles. An Ag/AgCl electrode was employed as the reference electrode and a Pt foil as the counter electrode. Electrode potentials were recorded vs. reference electrode, which was calibrated with respect to reversible hydrogen electrode (RHE). The overpotentials of CB-MoS₂, Ni-P and hybrid MoS₂/Ni-P samples reach 265 mV, 180 mV and 125 mV by $j = 10 \text{ mA cm}^{-2}$ respectively, Fig. 4. The Tafel slope of the hybrid MoS₂/Ni-P samples was 51 mV dec⁻¹ for HER in alkaline media, which is consistent with the most positive onset potential of -125 mV. It is much smaller than that of the CB-MoS₂ (185 mV

dec^{-1}) and Ni-P (105 mV dec^{-1}). The smaller Tafel slope demonstrates that the hybrid $\text{MoS}_2/\text{Ni-P}$ catalysts possess a superior catalytic performance.

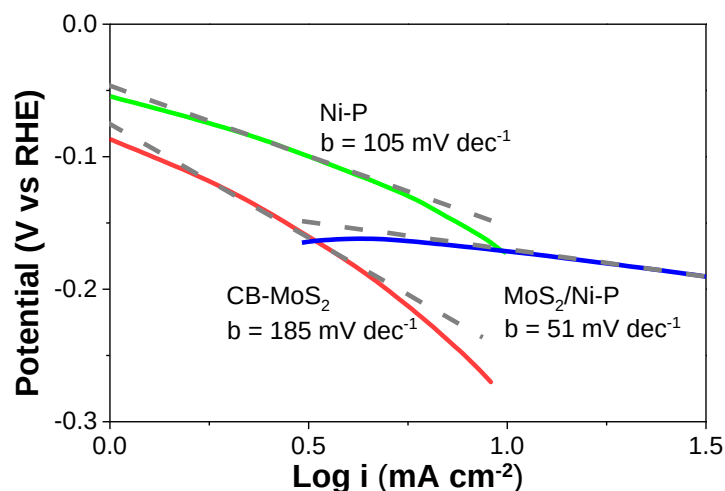


Figure 4. The Tafel plots of the MoS_2 catalysts derived from the polarization curves.

To get a direct site-to-site comparison, the rough estimation of TOFs following Jaramillo's method, makes it possible to compare the activity of hybrid $\text{MoS}_2/\text{Ni-P}$ with other catalysts. The so-called TOF here was actually defined as the peratom exchange rate of Mo, where the active sites were probably located. The hybrid $\text{MoS}_2/\text{Ni-P}$ catalysts possess much higher TOF value of 0.04 s^{-1} , compared to CB-MoS_2 (0.007 s^{-1} [18]), indicating an excellent intrinsic HER activity.

4. Durability Tests

Besides the HER activity, the stability is another important criterion to evaluate the HER electrocatalyst. The performance of a real operating electrolyser system highly depends on operating temperature, catalyst surface structure, absorption of hydrogen within the catalyst structure, adsorption of organics onto the catalyst surface or deposition of less active metals from impurities or component corrosion. To study the cathode stability in acidic environment, long-term potential cycling stability of $\text{MoS}_2/\text{Ni-P}$ and typical industrial Ni-S-Mo electrodes were conducted in an alkaline electrolyses cell from Beijing Wenli Technology Co., Ltd. The operating temperature was $80 \pm 5 \text{ }^\circ\text{C}$, pressure 0.006 MPa , electrolyte 30% KOH, H_2 production $0.3 \text{ m}^3/\text{h}$, current density 1500 A m^{-2} .

The industrial Ni-S-Mo electrode was prepared by Beijing Wenli Technology Co., Ltd using a stepwise electrodeposition which is an established process at the company for years. The long-term stability test was carried out on the prepared $\text{MoS}_2/\text{Ni-P}$ electrode and the industrial Ni-S-Mo electrode. Cathode using the electrode, the anode using pre-treated foam nickel, cathode and anode sandwiched between the industrial diaphragm (2 mm thickness). The stability of the electrode during the electrolysis process was analyzed by measuring the change in the cell voltage with time. As can be seen from Fig. 5, the starting cell voltage of the $\text{MoS}_2/\text{Ni-P}$ electrode is lower than that of the industrial Ni-S-Mo electrode and Ni-P electrode. And there is a decrease in the cell voltage of the electrode at the electrode initial stage, which may be due to the fact that the precipitation of the electrode surface S or the falling of the particles exposes more active sites of the electrode so that the activity of the electrode has been briefly raised [32]. The $\text{MoS}_2/\text{Ni-P}$ electrode remained relatively stable after a brief decrease in the cell voltage, while the electrolytic cell voltage using the industrial Ni-S-Mo electrode increased rapidly. Due to the deposition of four layers at industrial Ni-S-Mo electrode, the internal stress is high; the coating stability is affected, and falls off easily during the electrolysis. With incorporation of particles, a certain internal stress in the coating at the stepwise electrodeposition of $\text{MoS}_2/\text{Ni-P}$ electrode was released, so the stability is higher. The coating peeling off at Ni-S-Mo electrode is more serious after 500 h electrolysis, than the $\text{MoS}_2/\text{Ni-P}$ electrode, Fig. 6.

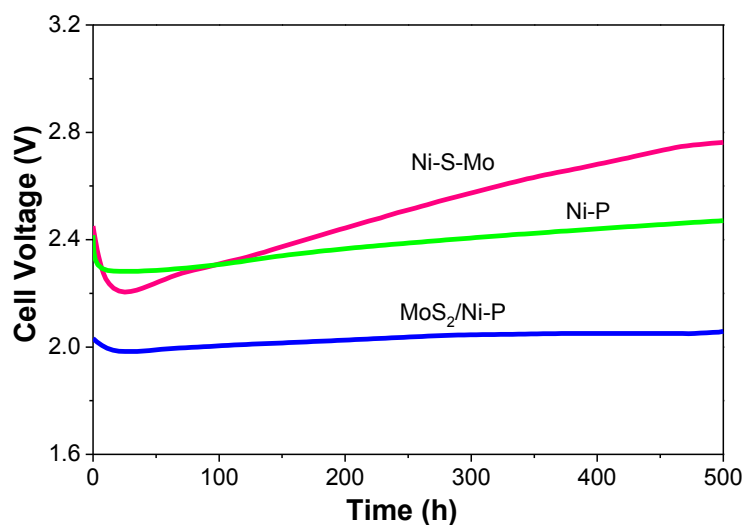


Figure 5. Cell voltage as a function of cell operating time.

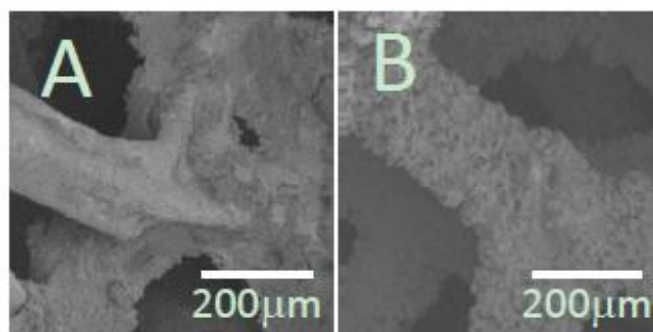


Figure 6. Industrial Ni-S-Mo electrode and MoS₂/Ni-P electrode after 500 h stability tests in alkaline water electrolyses cell.

Compared with the above-mentioned supports, the hybrid MoS₂/Ni-P cathode exhibits the advantages of facile fabrication, anticorrosion, prominently electrical conductivity, and the promisingly electrocatalytic activity of HER.

5. Conclusions

In summary, a simple electrodeposition method has been used to synthesize novel MoS₂/Ni-P hybrid electrocatalyst for the first time. Compared with pure MoS₂ and Ni-P, the hybrid MoS₂/Ni-P exhibits the better electrocatalytic activity for HER in alkaline media. Moreover, the excellent stability of MoS₂/Ni-P can be obtained. The enhancement of HER performances may be owing to the excellent conductivity of Ni-P and the synergistic effect between Ni-P and MoS₂. Thus, synthesizing hybrid materials through electrodeposition process can provide an efficient approach for MoS₂-based electrocatalysts for HER in large-scale industrial alkaline water electrolyzers.

References

- [1] S.U. Khan, M. Al-Shahry, W.B. Ingler, *Science* 297 (2002) 2243 – 2245.
- [2] T. Bak, J. Nowotny, M. Rekas, C. Sorrell, *Int. J. Hydrogen Energy* 27 (2002) 991 – 1022.
- [3] Y. Jiao, Y. Zheng, M. Jaroniec, S.Z. Qiao, *Chem. Soc. Rev.* 44 (2015) 2060 – 2086.
- [4] M. Zeng, Y. Li, *J. Mater. Chem. A* 3 (2015) 14942 – 14962.
- [5] Grigoriev SA, Porembskii VI, Fateev VN. Pure hydrogen production by PEM electrolysis for hydrogen energy. *Int J Hydrogen Energy* 2006, 31:171- 5.

- [6] Hamann CH, Ropke T, Schmittinger P. Electrowinning of other inorganic compounds. In: MacDonald DD, Schmuki P, editors. Encyclopedia of electrochemistry, vol. 5. Wiley; 2007. p. 299-304.
- [7] Zoulas E, Varkaraki E, Lymberopoulos N. Hydrogen-based uninterruptible power supply. *Int J Hydrogen Energy* 2007, 32:1589 - 96.
- [8] Trasatti S. Progress in cathode activation. In: Gerischer H, Tobias CW, editors. Advances in electrochemical science and engineering, vol. 2. VCH; 1992. p. 1- 85.
- [9] Appleby AJ, Crepy G, Jacquelin J. High-efficiency water electrolysis in alkaline solution. *Int J Hydrogen Energy* 1978, 3: 21- 37.
- [10] Brown DE, Fogarty PO, Mahmood MN, Turner AK. The development of low overvoltage cathodes. In: Jackson C, editor. Modern chlor-alkali technology, vol. 2. SCI/Horwood; 1983. p. 233-45.
- [11] Brown DE, Mahmood MN, Man MCM, Turner AK. Preparation and characterisation of low overvoltage transition-metal alloy electrocatalysts for hydrogen evolution in alkaline solutions. *Electrochim Acta* 1984, 29: 1551 - 6.
- [12] Vandenborre H, Vermeiren Ph, Leysen R. Hydrogen evolution at nickel sulphide cathodes in alkaline medium. *Electrochimica Acta*, 1983, 29 (3): 297 - 301.
- [13] Paseka I. Sorption of hydrogen and kinetics of hydrogen evolution on amorphous Ni-Sx electrodes. *Electrochimica Acta*, 1993, 38(16): 2449 - 2454.
- [14] Shan ZQ, Liu YJ, Chen Z, Warrender G, Tian JH. Amorphous Ni-S-Mn alloy as hydrogen evolution reaction cathode in alkaline medium. *International Journal of Hydrogen Energy*, 2008, 33(1): 28-33.
- [15] Paseka I. Evolution of hydrogen and its sorption on remarkable active amorphous smooth Ni-P(x) electrodes. *Electrochimica Acta*, 1995, 40(11): 1633 - 1640.
- [16] Shibli SMA, Dilimon VS. Effect of phosphorous content and TiO₂-reinforcement on Ni-P electroless plates for hydrogen evolution reaction. *International Journal of Hydrogen Energy*, 2007, 32 (12): 1694 -1700.
- [17] A.S.M.A. Haseeb, p. Chakraborty I. Ahmed a, F. Caccavale b, R. Bertoncello, XRD, XPS and SIMS investigations on electrodeposited nickel-phosphorous alloy coatings. *Thin Solid Films* 283 (1996) 140 -144
- [18] T.F. Jaramillo, K.P. Jorgensen, J. Bonde, J.H. Nielsen, S. Horch, I. Chorkendorff, *Science* 317 (2007) 100-102.
- [19] Merki D, Vrabel H, Rovelli L, Fierro S, Hu XL. Fe, Co, and Ni ions promote the catalytic activity of amorphous molybdenum sulfide films for hydrogen evolution. *Chem Sci* 2012; 3: 2515-25.
- [20] Bian XJ, Zhu J, Liao L, Scanlon MD, Ge PY, Ji C, Girault HH, Liu BH. Nanocomposite of MoS₂ on ordered mesoporous carbon nanospheres: a highly active catalyst for electrochemical hydrogen evolution. *Electrochem Commun* 2012, 22:128 - 32.
- [21] Wang HT, Lu ZY, Kong DS, Sun J, Hymel TM, Cui Y. Electrochemical tuning of MoS₂ nanoparticles on threedimensional substrate for efficient hydrogen evolution. *ACS Nano* 2014, 8: 4940 - 7.
- [22] Xie JF, Zhang JJ, Li S, Grote F, Zhang XD, Zhang H, Wang RX, Lei Y, Pan B, Xie Y. Controllable disorder engineering in oxygen-incorporated MoS₂ ultrathin nanosheets for efficient hydrogen evolution. *JAm Chem Soc* 2013; 135:17881-8.
- [23] Lukowski MA, Daniel AS, Meng F, Forticaux A, Li L, Jin S. Enhanced hydrogen evolution catalysis from chemically exfoliated metallic MoS₂ nanosheets. *J Am Chem Soc* 2013, 135:10274 -7.
- [24] Tsai C, Abild-Pedersen F, Nørskov JK. Tuning the MoS₂ edgesite activity for hydrogen evolution via support interactions. *Nano Lett* 2014, 14:1381-7.
- [25] Chen ZB, Cummins D, Reinecke BN, Clark E, Sunkara MK, Jaramillo TF. Core-shell MoO₃-MoS₂ nanowires for hydrogen evolution: a functional design for electrocatalytic materials. *Nano Lett* 2011, 11:4168 -75.
- [26] Kim JH, Fang BZ, Song MY, Yu J-S. Topological transformation of thioether-bridged organosilicas into nanostructured functional materials. *Chem Mater* 2012, 24: 2256 - 64.

- [27] Li XD, Yu S, Wu SQ, Wen YH, Zhou S, Zhu ZZ. Structural and electronic properties of superlattice composed of grapheme and monolayer MoS₂. J Phys Chem C 2013, 117: 15347 - 53.
- [28] Pan Y, Yang N, Chen YJ, Lin Y, Li YP, Liu YQ, et al. Nickel phosphide nanoparticles-nitrogen-doped graphene hybrid as an efficient catalyst for enhanced hydrogen evolution activity. J Power Sources 2015, 297: 45 - 52.
- [29] C. Lee, H. Yan, L.E. Brus, T.F. Heinz, J. Hone, S. Ryu, ACS Nano. 4 (2010) 2695 - 2700.
- [30] B.C. Windom, W.G. Sawyer, D.W. Hahn, Tribol. Lett. 42 (2011) 301-310.
- [31] K. Liu, W. Zhang, Y. Lee, Y. Lin, M. Chang, C. Su, C. Chang, H. Li, Y. Shi, H. Zhang, C. Lai, L. Li, Nano. Lett. 12 (2012) 1538 -1544.
- [32] Sabela R, Paseka I. Properties of Ni-Sx electrodes for hydrogen evolution from alkaline medium. Journal of applied electrochemistry, 1990, 20 (3): 500 - 505.