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Abstract

The sluggish reaction kinetics of the hydrogen evolution reaction (HER) in alkaline media is a great obstacle to alkaline water electrolysis, and it remains a great challenge to develop precious metal-free efficient catalysts for the alkaline HER. Transition metal dichalcogenides (TMDs), in particular MoS₂ and MoSe₂, are promising catalysts for the HER in acidic media, but they exhibit much inferior catalytic activity for the alkaline HER owing to the slow water dissociation process. In this work, we, for the first time, demonstrate that TMD heterostructures with abundant edge sites deliver substantially accelerated alkaline HER kinetics, which is in great part due to the enhanced water adsorption/dissociation capability. As a proof of concept, MoS₂/MoSe₂ heterostructures with ultrasmall MoS₂ nanoclusters anchored on MoSe₂ nanosheets are synthesized via a solution-phase process and are investigated as alkaline HER catalysts in detail. MoSe₂ nanosheets serve as excellent substrates to hinder the agglomeration of MoS₂ nanoclusters, resulting in abundant edge sites. Benefiting from the decent water adsorption/dissociation capability of the edge sites, the optimal MoS₂/MoSe₂ heterostructure shows exceptional catalytic activity in 1 M KOH with an overpotential of 235 mV at 10 mA cm⁻² and a Tafel slope of 96 mV dec⁻¹, which is substantially improved as compared with the individual MoSe₂ (330 mV, 135 mV dec⁻¹) and MoS₂ (400 mV, 157 mV dec⁻¹). The success of this catalyst design strategy for enhancing alkaline HER kinetics is also demonstrated in MoSe₂/MoS₂ and MoS₂/MoS₂ heterostructures. The results suggest that engineering additional edge sites that have a strong affinity for H₂O is critical for TMDs towards enhanced alkaline HER activity, and also open new avenues in the design of precious metal-free efficient catalysts for the alkaline HER.

Disciplines

Engineering | Physical Sciences and Mathematics

Publication Details

Zhou, Q., Zhao, G., Rui, K., Chen, Y., Xu, X., Dou, S. Xue. & Sun, W. (2019). Engineering additional edge sites on molybdenum dichalcogenides toward accelerated alkaline hydrogen evolution kinetics. *Nanoscale*, 11 (2), 717-724.

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Engineering Additional Edge Sites on Molybdenum Dichalcogenides toward Accelerated Alkaline Hydrogen Evolution Kinetics

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Abstract

The sluggish reaction kinetics of hydrogen evolution reaction (HER) in alkaline media is a great obstacle to alkaline water electrolysis, and it remains a great challenge to develop precious metal-free efficient catalysts for alkaline HER. Transition metal dichalcogenides (TMDs), in particular MoS₂ and MoSe₂, are promising catalysts for HER in acidic media, but they exhibit much inferior catalytic activity for alkaline HER owing to the slow water dissociation process. In this work, we, for the first time, demonstrate that TMDs heterostructures with abundant edge sites deliver substantially accelerated alkaline HER kinetics, which is in great part due to the enhanced water adsorption/dissociation capability. As a proof of concept, MoS₂/MoSe₂ heterostructures with ultrasmall MoS₂ nanoclusters anchored on MoSe₂ nanosheets are synthesized via a solution-phase process and are investigated as alkaline HER catalysts in detail. MoSe₂ nanosheets serve as excellent substrates to hinder the agglomeration of MoS₂ nanoclusters, resulting in abundant edge sites. Benefiting from the decent water adsorption/dissociation capability of the edge sites, the optimal MoS₂/MoSe₂ heterostructure shows exceptional catalytic activity in 1 M KOH with an overpotential of 235 mV at 10 mA cm⁻² and a Tafel slope of 96 mV dec⁻¹, which is substantially improved as compared with the individual MoSe₂ (330 mV, 135 mV dec⁻¹) and MoS₂ (400 mV, 157 mV dec⁻¹). The success of this catalyst design strategy for enhancing

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alkaline HER kinetics is also demonstrated in MoSe₂/MoSe₂ and MoS₂/MoS₂ heterostructures. The results suggest that engineering additional edge sites that have a strong affinity for H₂O is critical for TMDs towards enhanced alkaline HER activity, and also open new avenues in the design of precious metal-free efficient catalysts for alkaline HER.

Keywords: heterostructure, edge site, molybdenum dichalcogenide, hydrogen evolution reaction, alkaline water electrolysis

1. Introduction

The energy crisis and environmental pollution problems have prompted the research for clean energy carrier.¹⁻⁴ Hydrogen has attracted significant attention owing to the zero greenhouse gas emission as well as high gravimetric energy density.^{5, 6} Among various hydrogen generation strategies, water electrolysis, particularly driven by renewable energies, has already demonstrated its feasibility in industrial processes.⁷⁻⁹ However, developing efficient and earth-abundant alternatives to noble metals which are the most satisfying electrocatalysts, are still the center for realizing the large-scale application of hydrogen generation via water electrolysis.^{10, 11} Practically, water electrolysis is more favoured in alkaline media which helps to promote the sluggish oxygen evolution reaction (OER) to achieve a high energy conversion efficiency.¹²⁻¹⁵ However, most earth-abundant electrocatalysts such as transition metal chalcogenides (TMDs),¹⁶⁻²⁰ nitrides,^{21, 22} carbides^{23, 24} and phosphides,²⁵⁻²⁸ despite of the performance comparable to noble metal that they may possess in acid media, exhibit inferior hydrogen evolution reaction (HER) activity in alkaline media due to the sluggish water adsorption/dissociation step.²⁹⁻³¹

Molybdenum dichalcogenides (MoS₂ and MoSe₂), as typical TMDs, are among the most efficient catalysts for HER in acid media owing to the moderate Gibbs free energy for hydrogen adsorption.^{32, 33} Both theoretical calculations and experimental results have demonstrated that unsaturated Mo–S sites possess the optimal hydrogen adsorption free

energy,³⁴⁻³⁷ which have stimulated the development of nanostructured TMDs-based catalysts with enriched edge sites.^{38, 39} As for alkaline HER, a recent theoretical study demonstrated that the water adsorption/dissociation process is more favoured on the edge sites rather than the basal plane of MoS₂.⁴⁰ Thus, increasing the exposure of TMDs edge sites might also be an effective strategy for promoting alkaline hydrogen evolution kinetics. Herein, as a proof of concept, a series of TMDs-based heterostructures (MoS₂/MoSe₂, MoSe₂/MoSe₂, and MoS₂/MoS₂) with MoS₂ or MoSe₂ quantum dots decorated on the basal planes of TMDs nanosheets were synthesized via a two-step chemical solution process. The MoS₂ or MoSe₂ quantum dots provide abundant edge sites which substantially enhance the affinity for H₂O, and the TMDs-based heterostructures exhibit significantly improved catalytic activities over the individual nanosheets in alkaline media. The results not only demonstrate the feasibility of engineering additional edges sites on molybdenum dichalcogenides toward the development of efficient alkaline HER electrocatalysts but also provide new insights into in-depth understanding of the HER mechanism.

2. Experiment section

2.1 Materials synthesis

Synthesis of MoSe₂ nanosheets: MoSe₂ nanosheets were synthesized by a hydrothermal method. Briefly, 2 mmol Se powder and 1 mmol Na₂MoO₄·2H₂O were dispersed in 30 mL deionized water (DI-W) under stirring at room temperature to form a dark red-brown suspension. Then, 2.5 mmol NaBH₄ was slowly added into the above suspension and dissolved completely. Subsequently, the mixture was transferred into a 50 mL Teflon stainless-steel autoclave with Ar purging for 30 min, and then the autoclave was heated at 180 °C for 24 h in an electric oven. After the reaction was completed, black products were

collected by centrifugation, washed with DI-W and ethanol three times, and eventually dried overnight in a vacuum oven at 60 °C.

Synthesis of MoS₂/MoSe₂ nanosheets: Typically, 0.1 mmol MoSe₂ was dispersed in 35 mL DI-W and treated by ultrasonication for 3 h to form a homogeneous suspension. Then various amount of Na₂MoO₄·2H₂O (0.025, 0.05 and 0.1 mmol) and L-cysteine (0.1, 0.2 and 0.4 mmol) dissolved in above suspension under stirring. Afterwards, the mixture was transferred into a 50 mL Teflon-lined stainless steel autoclave and was heated at 180 °C for 36 h. The products were collected by centrifugation, washed with DI-W and ethanol three times, and eventually dried overnight in a vacuum oven at 60 °C. Based on the molar ratio of MoS₂ to MoSe₂, the as-obtained hybrids are denoted as MoS₂/MoSe₂-0.25, MoS₂/MoSe₂-0.5, and MoS₂/MoSe₂-1, respectively.

Synthesis of MoS₂ nanosheets: The procedures for synthesizing MoS₂ nanosheets were the same as that of MoS₂/MoSe₂ nanosheets except that no MoSe₂ sheets were added.

Synthesis of MoSe₂/MoSe₂ nanosheets: A certain amount of MoSe₂ nanosheets was added into 35 mL water and treated with ultrasonication for 3 h to form a suspension. Then the following steps are the same as that of synthesising pure MoSe₂ nanosheets.

Synthesis of MoS₂/MoS₂ nanosheets: A certain amount of MoS₂ nanosheets was added into 35 mL water and treated with ultrasonication for 3 h to form a suspension. And the following steps are the same as that of synthesis of pure MoS₂ nanosheets.

2.2 Physical Characterization

The morphology and crystal structure of the as-prepared products were investigated using a JEM-2010 transmission electron microscope (TEM) operated at 200 kV. Scanning transmission electron microscopy (STEM) images were acquired on a probe-corrected JEOL

ARM200F TEM operated at 200 kV. Energy disperse X-ray (EDS) mapping images were acquired on FEI Talos F200X equipped with four symmetrical EDS signal detectors, operated at 200 kV. The powder X-ray diffraction (XRD) patterns were recorded on a GBC Scientific Equipment LLC X-ray powder diffractometer with Cu K α radiation ($\lambda=1.541$ Å, 25 mA, 40 kV, 2 °min⁻¹). The X-ray photoelectron spectroscopy (XPS) spectra of samples were performed on an XPS, Thermo ESCALAB 250Xi instrument with Al K α as the excitation source.

2.3 Electrochemical measurements

All the electrochemical experiments were conducted with a rotating disc electrode (RDE) systems using a three-electrode system at room temperature, where the electrochemical catalysts were used as the working electrodes, platinum wire as the counter electrode, and Hg/HgO and Ag/AgCl as the reference electrodes in 1.0 M KOH and 0.5 M H₂SO₄, respectively. The experiments were controlled by a WaveDriver 20 electrochemistry workstation (Pine Research Instruments, US). The working electrode was prepared via the method reported in our previous work.⁴¹ In brief, the as-synthesized catalyst (4 mg) was first added in 1 mL water-isopropanol mixed solution (volume ratio of 3:1) containing 30 μ L Nafion solution (5 wt%) and treated with ultrasonication to form a homogeneous ink. Then 10 μ L catalyst ink was drop-cast onto a glassy carbon electrode (GCE, 5 mm in diameter) and dried naturally (catalyst mass loading: 0.204 mg cm⁻²). LSV curves were obtained at a scan rate of 5 mV s⁻¹ at the rotation speed of 1600 rpm, and the results were corrected with 90% iR-compensation. All potentials were calibrated and reported with respect to reverse hydrogen electrode (RHE) by the equations: E(RHE)=E(Hg/HgO) +0.924 V and E(RHE)=E(Ag/AgCl) + 0.197 V. EIS measurements were carried out in the frequency range of 100 kHz to 100 mHz at potential of -0.3 V versus RHE. The turnover frequency is calculated using the following equations:⁴²

$$TOF = \frac{\text{Total number of H}_2 \text{ atoms per second}}{\text{Total number of active sites per unit area}} = \frac{\frac{j}{2 \times q}}{N}$$

Where j is the current density (A cm^{-2}) at a given overpotential, q is the elementary charge ($1.6 \times 10^{-19} \text{ C}$), N is the number of surface Mo atom per unit area which is estimated to be $1.06 \times 10^{15} \text{ cm}^{-2}$ and $1.15 \times 10^{15} \text{ cm}^{-2}$ for MoSe_2 and MoS_2 , respectively.

3. Results and discussion

Fig. 1a shows the schematic representation for the growth of 2D $\text{MoS}_2/\text{MoSe}_2$ vertical heterostructure. L-cysteine and MoO_4^{2-} firstly absorb on the surface of MoSe_2 nanosheets, and then MoO_4^{2-} is reduced to MoS_2 by L-cysteine during the hydrothermal process, during which process MoSe_2 nanosheets play an important role in the confined growth of MoS_2 quantum dots. As depicted in Fig. S1 (supporting information), pure MoSe_2 , MoS_2 , and $\text{MoS}_2/\text{MoSe}_2$ heterostructures show similar X-ray diffraction (XRD) patterns, in which peaks at around 32.0° , 38.3° , and 56.4° can be assigned to (100), (103), and (110) planes of molybdenum dichalcogenides. It is worth noting that the (002) peak of the pure MoSe_2 , unlike MoS_2 and $\text{MoS}_2/\text{MoSe}_2$, cannot be observed in the XRD patterns owing to the ultrathin thickness of MoSe_2 nanosheets.⁴³ The typical morphology of pristine MoSe_2 nanosheets is shown in Fig. S2a and b (Supporting Information), and the lattice fringes can be well assigned to MoSe_2 (Fig. S2c and d). Taking $\text{MoS}_2/\text{MoSe}_2\text{-0.5}$ as an example, as shown in Fig. 1b and Fig. S3a and b (Supporting Information), the $\text{MoS}_2/\text{MoSe}_2\text{-0.5}$ heterostructure inherits similar nanosheets morphology as MoSe_2 . The specific surface areas of MoSe_2 and $\text{MoS}_2\text{-MoSe}_2\text{-0.5}$ are determined to be 48 and $61 \text{ m}^2/\text{g}$ by BET (Fig. S3c, Supporting Information), respectively. The lattice fringe with spacing of 0.68 nm shown in Fig. 1b corresponds to the typical (002) planes of MoSe_2 substrates. However, it is difficult to distinguish MoS_2 species from MoSe_2 substrates because of the same crystal structure and

similar crystal parameters of MoS₂ and MoSe₂ in the high-resolution TEM (HRTEM) image (Fig. 1c). However, two sets of diffraction spots are shown in the corresponding fast Fourier transformation (FFT) patterns (Fig. 1d). Specifically, a set of six spots with a lattice spacing of about 0.27 nm can be ascribed to the {100} planes of MoS₂, and the other set with a lattice spacing of 0.28 nm can be assigned to {100} planes of MoSe₂. Two patterns are regenerated by applying inversed FFT (IFFT) on the selected FFT patterns (Fig. 1e), which show clear boundaries between MoS₂ and MoSe₂ as well as the ultrasmall size of MoS₂ quantum dots (<5 nm) on the MoSe₂ nanosheets. Both MoS₂/MoSe₂-0.25 and MoS₂/MoSe₂-1 show similar morphology to MoS₂/MoSe₂-0.5 heterostructure, as can be seen in Fig. S4 (Supporting Information). Owing to the dangling bond existing on the surface of MoSe₂ nanosheets, Mo-based precursors are prone to adsorb on the basal plane, resulting in the formation of MoS₂ quantum dots and ensuring the exposure of additional Mo-S edge sites. Without the confinement of MoSe₂ nanosheets, MoS₂ crystals grow freely and assemble micronized flower-like MoS₂ nanosheets (Fig. S5, Supporting Information). The STEM-EDS mappings (Fig. 1f) reveal the uniform distribution of Mo, Se, and S over the surface of MoS₂/MoSe₂-0.5 heterostructures, further demonstrating the homogeneous growth of MoS₂ over the MoSe₂ substrate.

The XPS survey spectrum of MoS₂/MoSe₂-0.5 in Fig. 1g reveals the existence of Mo, Se, and S. As illustrated in the high-resolution XPS spectra of Mo 3d, two peaks locate at 229.2 and 232.3 eV, corresponding to Mo 3d_{5/2} and Mo 3d_{3/2}, respectively, indicating that the valence state of Mo is +4.⁴⁴ In the meantime, the small shoulder peak at 226.4 eV, which is absent in the corresponding spectra of MoSe₂ (Fig. S6a, Supporting Information), is ascribed to S 2s,⁴⁴ further demonstrating the existence of MoS₂ species. The single doublet peak in the Se 3d spectra composes of Se 3d_{5/2} at 54.6 eV and Se 3d_{3/2} at 55.4 eV, while the fitted Se 3p peaks consist of Se 3p_{3/2} and Se 3p_{1/2} at 160.7 and 166.7 eV, respectively.⁴⁵ For the S 2p spectra, the

S 2p_{3/2} and S 2p_{1/2} peaks can be fitted at 161.8 and 164.1 eV, respectively.⁴⁵ The high-resolution XPS spectra of pure MoS₂, MoSe₂, and other MoS₂/MoSe₂ heterostructures can be found in Fig. S6 (Supporting Information).

Fig. 1. (a) Schematic illustration of the synthesis of MoS₂/MoSe₂ heterostructures. (b) TEM image of MoS₂/MoSe₂-0.5 heterostructure, showing the typical nanosheets morphology. (c) HRTEM image of MoS₂/MoSe₂-0.5 heterostructure. (d) the corresponding FFT patterns of (c). (e) IFFT image generated by the selected masked FFT patterns of MoSe₂ and MoS₂ (top) and the selected FFT patterns (down). (f) STEM image and the corresponding EDS mapping images. (g) XPS spectra of MoS₂/MoSe₂-0.5 heterostructure.

The electrochemical measurements were performed in N₂-saturated 1.0 M KOH and 0.5 M H₂SO₄ solution using a three-electrode setup. As shown in Fig. 2a, MoS₂/MoSe₂ heterostructures show notably enhanced performance compared to pure MoSe₂ and MoS₂ in alkaline solution. In particular, the MoS₂/MoSe₂-0.5 heterostructure exhibits the best HER activity with a small onset overpotential of 180 mV, which is much lower than that of pristine MoSe₂ (270 mV) and MoS₂ (310 mV). To achieve a cathodic current density of 10 mA cm⁻², the MoS₂/MoSe₂-0.5 only requires an overpotential of 235 mV (Fig. 2b), while large overpotentials of 330 mV and 400 mV are required for MoSe₂ and MoS₂, respectively. The performance of MoS₂/MoSe₂-0.5 heterostructure is among the best of the reported carbon-free MoS₂-based and MoSe₂-based materials without conductive substrates under the same test condition, and even comparable to a few conductive substrate-supported catalysts (Table S1, Supporting Information). Meanwhile, MoS₂/MoSe₂-0.5 delivers a current density as high as 36 mA cm⁻² at an overpotential of 300 mV, which is about 14 and 5 times higher than that of MoS₂ (2.5 mA cm⁻²) and MoSe₂ (6.5 mA cm⁻²), respectively. Due to the relatively lower activity of MoS₂, the catalytic activity of the MoS₂/MoSe₂ heterostructures decays as further increasing MoS₂. The improved catalytic kinetics of MoS₂/MoSe₂ heterostructures is also evidenced by the reduced Tafel slopes. The Tafel plots of MoSe₂, MoS₂, and MoS₂/MoSe₂ heterostructures are shown in Fig. 2c. The large Tafel slope of MoSe₂ (135 mV dec⁻¹) and MoS₂ (157 mV dec⁻¹) reveal that the rate-determining step of HER is the water adsorption and dissociation process. Compared with bare MoSe₂ and MoS₂, the decreased Tafel slope of MoS₂/MoSe₂-0.5 (96 mV dec⁻¹) suggests that the HER kinetics is determined by the combination of the Volmer step and the subsequent Heyrovsky step,⁴⁶ indicating an accelerated water adsorption/dissociation kinetics on the MoS₂/MoSe₂-0.5 surface. Electrochemical impedance spectroscopy (EIS) is employed to further investigate the reaction process. As shown in Fig. 2d, the reaction resistance of MoS₂/MoSe₂-0.5 (30 Ω) is smaller

than that of either pure MoSe₂ (98 Ω) or MoS₂ (486 Ω), indicating a substantially enhanced reaction kinetics due to the combination of MoS₂ quantum dots and MoSe₂ nanosheets. The activity durability of the electrocatalysts was evaluated by the chronopotentiometry test as shown in Fig. 2e. It can be observed that the overpotential of MoSe₂ rises distinctly within the initial 10 min and eventually increases by about 108 mV during the 3-h operation. In contrast, the overpotential of MoS₂/MoSe₂-0.5 is only elevated by 59 mV, manifesting that the stability is also improved after the incorporation of MoS₂ quantum dots. The HER turnover frequencies (TOFs) were calculated to evaluate the intrinsic activity of the electrocatalysts. Here, Mo⁴⁺ was employed as the active site for calculating TOFs, and the TOFs at the overpotential of 300 mV are shown in Fig. 2f. Remarkably, MoS₂/MoSe₂-0.5 heterostructure deliver a TOF as high as 102.3 s⁻¹, outperforming pure MoSe₂ (17.6 s⁻¹), MoS₂ (5.4 s⁻¹), MoS₂/MoSe₂-0.25 (66.7 s⁻¹) and MoS₂/MoSe₂-1 (53.7 s⁻¹).

Fig. 2. (a) iR-corrected LSV curves in 1M KOH solution of various electrocatalysts as indicated (scan rate: 5 mV s⁻¹, catalyst mass loading: 0.204 mg cm⁻²). (b) Overpotential

required at 10 mA cm^{-2} and current densities at an overpotential of 300 mV; (c) Tafel plots derived from LSV curves, (d) Nyquist plot measured at an overpotential of 300 mV; (e) chronopotentiometry curves conducted at a constant current density of 10 mA cm^{-2} ; (f) TOF of MoSe_2 , MoS_2 and $\text{MoS}_2/\text{MoSe}_2$ heterostructures at the overpotential of 0.3 V.

To investigate the origination of the promoted catalytic activity of MoSe_2 , the acidic HER performance evaluation was also carried out as shown in Fig. 3a. Interestingly, MoSe_2 exhibits the lowest overpotential (205 mV) at the current density of 10 mA cm^{-2} , and the electrocatalytic activity of $\text{MoS}_2/\text{MoSe}_2$ heterostructures is not improved. The catalytic activity variation at high current density region can be ascribed to the different hydrogen desorption behaviour at high hydrogen coverage.^{47, 48} To obtain deeper insight into the electrochemical behaviour, the electrochemical active surface areas (ECSA) of the catalysts were estimated through evaluating the electrochemical double layer capacitance (C_{dl}) in a non-Faraday region in alkaline as well as acidic solutions (Fig. S7, Supporting Information). As shown in Fig. 3b, $\text{MoS}_2/\text{MoSe}_2$ -0.5 and pure MoSe_2 possess similar C_{dl} in both alkaline and acidic solutions, demonstrating similar ECSA of $\text{MoS}_2/\text{MoSe}_2$ -0.5 and pure MoSe_2 . Therefore, the promoted alkaline HER activity can be ascribed to the accelerated water adsorption/dissociation process that originates from the additional edge sites in these molybdenum dichalcogenides.

Fig. 3. (a) iR-corrected LSV curves measured at a scan rate of 5 mV s⁻¹ in 0.5 M H₂SO₄ solution; (b) Fitted C_{dl} of MoSe₂ and MoS₂/MoSe₂-0.5 at 0 V vs. RHE (1 M KOH) and 0.05 V vs. RHE (0.5 M H₂SO₄).

To further verify the feasibility of engineering additional edge sites for promoting alkaline HER, MoSe₂/MoSe₂-0.5 and MoS₂/MoS₂-0.5 heterostructures were synthesized. As illustrated in Fig. S8 (Supporting Information), MoSe₂/MoSe₂-0.5 and MoS₂/MoS₂-0.5 possess the same diffraction peaks with pristine MoSe₂ and MoS₂, respectively. Both MoSe₂/MoSe₂-0.5 and MoS₂/MoS₂-0.5 maintain the graphene-like nanosheet morphology (Fig. S9 and S10, Supporting Information). MoSe₂ and MoS₂ quantum dots can be identified from the heterostructures in HRTEM images (Fig. S11a and c, Supporting Information). Also, the relative intensity variation in the selected area further demonstrates the presence of MoSe₂ and MoS₂ quantum dots on MoSe₂ nanosheets and MoS₂ nanosheets, respectively (Fig. S11b and d, Supporting Information). The LSV curves of MoSe₂/MoSe₂-0.5 and MoS₂/MoS₂-0.5 in 1 M KOH and 0.5 M H₂SO₄ were shown in Fig. 4a and b. Similar to MoS₂/MoSe₂ heterostructures, the overpotential to reach a current density of 10 mA cm⁻² of both MoSe₂/MoSe₂-0.5 (250 mV) and MoS₂/MoS₂-0.5 (331 mV) are substantially decreased as compared with MoSe₂ (330 mV) and MoS₂ (400 mV) in 1M KOH solution, in sharp

contrast with the negligible overpotential decrease in acidic solution. The reduction of the Tafel slopes (Fig. 4c and d) also verify the enhanced electrochemical reaction kinetics of the heterostructures. Furthermore, we prepared two control samples: pure MoSe₂ nanosheets treated with a second hydrothermal process in DI water at 180 °C for 24 h (denoted as MoSe₂-2) and a physical mixture of MoSe₂ and MoS₂ nanosheets (denoted as MoS₂/MoSe₂-m). As shown in Fig. S12 (Supporting Information), MoSe₂-2 exhibits almost the same electrocatalytic activity with pristine MoSe₂, proving that the HER performance is not affected by the additional hydrothermal treatment. On the other hand, the catalytic activity of MoS₂/MoSe₂-m is between pure MoS₂ and MoSe₂, confirming the significant role that the extra edge sites play in the enhanced HER activity in alkaline solution.

Fig. 4. iR-corrected LSV curves of MoSe₂, MoSe₂, MoSe₂/MoSe₂-0.5, and MoS₂/MoS₂-0.5 measured at a scan rate of 5 mV s⁻¹ in (a) 1M KOH solution and (b) 0.5 M H₂SO₄ solution; Tafel plots derived from LSV curves in (c) 1M KOH solution and (d) 0.5 M H₂SO₄ solution.

As has been reported, the adsorption/dissociation of H_2O is more favoured on the Mo-edges rather than the basal plane of molybdenum dichalcogenides.^{40, 49, 50} Thus, the improved alkaline HER performance for the TMDs-based heterostructures is derived from the additional edge sites provided by MoS_2 or MoSe_2 nanoclusters. As shown in Fig. 5, Mo-edge sites in MoS_2 act as a promoter for water adsorption and dissociation, while the produced hydrogen intermediates absorb on nearby MoSe_2 and subsequently combined to hydrogen gas. In this way, $\text{MoS}_2/\text{MoSe}_2$ heterostructure effectively reduces the energy barrier of the water dissociation and accelerates the alkaline HER process accordingly.

Fig. 5. HER mechanism on $\text{MoS}_2/\text{MoSe}_2$ heterostructure in alkaline solution.

4. Conclusion

In summary, TMDs-based heterostructures ($\text{MoS}_2/\text{MoSe}_2$, $\text{MoSe}_2/\text{MoSe}_2$ and $\text{MoS}_2/\text{MoS}_2$) with MoS_2 or MoSe_2 quantum dots anchored on TMDs nanosheets were synthesized via a two-step chemical solution process. The TMDs-based heterostructures delivered substantially improved catalytic activity over their single-component counterparts in alkaline media. The abundant edge sites in MoS_2 or MoSe_2 quantum dots would enhance the H_2O affinity of the TMDs-based heterostructures and hence promote the water adsorption/dissociation capability and alkaline HER kinetics accordingly. We believe the strategy for creating extra edge sites

by engineering hetero-nanostructures would provide new insights into designing efficient electrocatalysts for hydrogen evolution in alkaline media.

Acknowledgements

This work was financially supported by the Australian Research Council (ARC) DECRA Grant (DE160100596), ARC Discovery Project (DP160102627), and AIIM FOR GOLD Grant (2017, 2018). The authors also acknowledge the use of facilities within the UOW Electron Microscopy Centre.

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Figure captions

Figure 1 (a) Schematic illustration of the synthesis of MoS₂/MoSe₂ heterostructures. (b) TEM image of MoS₂/MoSe₂-0.5 heterostructure, showing the typical nanosheets morphology. (c) HRTEM image of MoS₂/MoSe₂-0.5 heterostructure. (d) the corresponding FFT patterns of (c). (e) IFFT image generated by the selected masked FFT patterns of MoSe₂ and MoS₂ (top) and the selected FFT patterns (down). (f) STEM image and the corresponding EDS mapping images. (g) XPS spectra of MoS₂/MoSe₂-0.5 heterostructure.

Figure 2 (a) iR-corrected LSV curves in 1M KOH solution of various electrocatalysts as indicated (scan rate: 5 mV s⁻¹, catalyst mass loading: 0.204 mg cm⁻²). (b) Overpotential required at 10 mA cm⁻² and current densities at an overpotential of 300 mV; (c) Tafel plots derived from LSV curves, (d) Nyquist plot measured at an overpotential of 300 mV; (e) chronopotentiometry curves conducted at a constant current density of 10 mA cm⁻²; (f) TOF of MoSe₂, MoS₂ and MoS₂/MoSe₂ heterostructures at the overpotential of 0.3 V.

Figure 3 (a) iR-corrected LSV curves measured at a scan rate of 5 mV s⁻¹ in 0.5 M H₂SO₄ solution; (b) Fitted C_{dl} of MoSe₂ and MoS₂/MoSe₂-0.5 at 0 V vs. RHE (1 M KOH) and 0.05 V vs. RHE (0.5 M H₂SO₄).

Fig. 4. iR-corrected LSV curves of MoSe₂, MoSe₂, MoSe₂/MoSe₂-0.5, and MoS₂/MoSe₂-0.5 measured at a scan rate of 5 mV s⁻¹ in (a) 1M KOH solution and (b) 0.5 M H₂SO₄ solution; Tafel plots derived from LSV curves in (c) 1M KOH solution and (d) 0.5 M H₂SO₄ solution.

Figure 5 HER mechanism on MoS₂/MoSe₂ heterostructure in alkaline solution.