Supporting Information

Optimized Electronic structure and p-band centre control engineering to Enhance the Surface Absorption and Inherent Conductivity for Accelerated Hydrogen Evolution over Wide pH Range

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Experimental section

Materials Preparation

All chemicals were purchased from aladdin Co., Ltd. and used as received.

As-MoS2 was fabricated via a facile one-pot hydrothermal method. Typically, 0.35 g of Na2MoO4, 2 g of thiourea, and 1 g of Arsenic sulfide (As2S2) were added to 43 mL of distilled water under vigorous stirring for 1 h to form a homogeneous solution. Then, the solution was transferred into a Teflon-lined stainless steel autoclave with a capacity of 75 mL for hydrothermal treatment at 350 °C. After 6 h, the autoclave was naturally cooled down to room temperature, and then the product was collected and washed with hydrochloric acid, distilled water and absolute ethanol several times to remove the impurities. Then, the product was dried in a vacuum oven at 70°C for several hours. Then, to determine the most suitable dosage of As2S2, 0.5 g and 1.5 g of As2S2 were used. To explore the major impacts of nitrogen and phosphorus, N-MoS2, and P-MoS2 were also prepared by replacing As2S2 with C2H4N4 and NaH2PO2.

Materials Characterization

The microtopography and atomistic structural information of the samples were characterized by scanning electron microscopy (SEM, Carl Zeiss SUPRA 55 SAPPHIRE, 15 kV), and transmission electron microscopy and (TEM, JEOL JEM-200EX 200 kV). Energy dispersive X-ray spectroscopy attached to the transmission electron microscope was used to obtain elemental contents. High-resolution transmission electron microscopy (HRTEM JEOL JEM-2010, 200kV)
and Raman spectroscopy (WITec, alpha300R, excited by a 512 nm laser) were also performed. X-ray diffraction (XRD) measurements were carried out using a Rigaku DMAX-2500 powder diffractometer with Cu-Kα radiation (λ = 0.154 nm) operated at 40 kV and 200 mA. X-ray photoelectron spectrum (XPS) was conducted using a Thermo Scientific ESCALAB 250Xi photoelectron spectrometer and Mg-Kα as the exciting source (1253.6 eV). Nitrogen adsorption-desorption isotherms were obtained on an ASAP 2020 HD88 (Micromeritics Instrument Corporation) instrument at 77K.

**Electrochemical Measurements**

All electrochemical measurements were performed in a standard three-electrode system using an electrochemical workstation (CHI760E). Typically, 5mg of the catalyst powders and 1 mg carbon black (Vulcan XC72) were dispersed in 1 mL of a water-ethanol mixed solvent (volume ratio of 3:1), along with 35 μL of Nafion solution, and the mixture was ultrasonicated for 1 h to form a homogeneous ink. Then, 20 μL of the prepared dispersion was drop onto the surface of a glassy carbon (GC) disk electrode (PINE AFE5T050GC) at a catalyst loading of 0.49 mg cm⁻². A graphite rod and SCE electrode were used as the reference and counter electrodes, respectively. Finally, the as-prepared catalyst was dried at room temperature. Linear sweep voltammetry and chronoamperometry with a scan rate of 5.0 mV s⁻¹ were conducted in 0.5 M H₂SO₄ and 1.0 M KOH (purged with pure N₂) using SCE as the reference electrode, respectively, graphite rod as the counter electrode. The electrochemical impedance spectroscopy (EIS) measurements were performed by applying an AC voltage with 5.0 mV amplitude in a frequency range from 106 to 0.1
Hz and recorded at -0.3 V (vs. SCE) in 0.5 M H2SO4. All the potentials were calibrated to a reversible hydrogen electrode (RHE) based on following equations:

\[ E \text{ (vs. RHE)} = E \text{ (vs. SCE)} + 0.059 \times \text{pH} + 0.242 \text{ V} \]

**MoS2 edge oxidation**

The preparation pristine MoS2 and As-MoS2 nanosheets is conducted by in situ negative linear sweeps from 0 to 0.9 V (vs. Hg/HgO) for five minutes at a scan rate of 5 mV s⁻¹ in 1 M KOH solution before electrochemical measurements. Oxidation was confirmed by the observation of peaks at 232.4 and 235.5 eV from Mo⁶⁺ 3d⁵/₂ and Mo⁶⁺ 3d³/₂, respectively, using XPS.

**Electrocatalytic HER mechanisms in acidic and alkaline solutions:**

**HER in acidic solution:**

\[
\begin{align*}
\text{H}^+ + e^- + \text{cat} & \rightarrow \text{H}^*\text{-cat} \quad \text{Volmer step} \\
2\text{H}^*\text{-cat} & \rightarrow \text{H}_2 \uparrow \quad \text{Tafel step} \\
\text{H}^*\text{-cat} + \text{H}^+ + e^- & \rightarrow \text{cat} + \text{H}_2 \uparrow \quad \text{Heyrovsky step}
\end{align*}
\]

**HER in alkaline solution**

\[
\begin{align*}
\text{H}_2\text{O} + e^- + \text{cat} & \rightarrow \text{H}^*\text{-cat} + \text{OH}^- \quad \text{Volmer step} \\
2\text{H}^*\text{-cat} & \rightarrow \text{H}_2 \uparrow \quad \text{Tafel step} \\
\text{H}^*\text{-cat} + \text{H}_2\text{O} + e^- & \rightarrow \text{cat} + \text{OH}^- + \text{H}_2 \uparrow \quad \text{Heyrovsky step}
\end{align*}
\]

**Theoretical Calculations**

We performed first-principles calculations using the Vienna ab initio Simulation Package (VASP)¹². All the results were obtained using the projector-augmented plane-wave (PAW) method within the Perdew, Burke, and Ernzerhof (PBE) parametrization scheme for the generalized gradient approximation (GGA)³⁻⁵. Monkhorst-Pack (MP) mesh of \(3 \times 3 \times 3\) is employed for geometry optimization. The pristine MoS2 monolayer is modeled by a \(4 \times 4\) supercell with lateral size of
12.75×12.75 Å², which contains 32 S and 16 Mo atoms. The distance between adjacent monolayers is 12.38 Å and hence the interaction between them can be eliminated. Full structural optimization was performed in which all lattice parameters and internal atomic positions were relaxed until the Hellmann-Feynman forces acting on each atom were less than 0.01 eV/Å and until the energy difference between two consecutive iterations was less than 0.0001 eV. Brillouin zone integrations were performed with a Gaussian broadening of 0.05 eV during all relaxations. For both structural and static electronic structure calculations, a plane-wave energy cut off of 400 eV was used for the GGA approach.

The free energy was calculated using the equation:

\[
G = E + ZPE - TS
\]

where G, E, ZPE and TS are the free energy, total energy from DFT calculations, zero point energy and entropic contributions (T was set to be 300K), respectively.

The hydrogen adsorption energy in acidic solution is calculated as follows: \( \Delta E_H = E(\text{MoS}_2+\text{H}) - E(\text{MoS}_2) - \frac{1}{2} E(\text{H}_2) \), where \( E(\text{MoS}_2+\text{H}) \) is the total energy of the non-metal atoms doped MoS2 with a hydrogen atom absorbed on the surface, \( E(\text{MoS}_2) \) is the total energy for the non-metal atoms doped MoS2 without an H atom absorbed and \( E(\text{H}_2) \) is the energy for an H2 molecule in the gas phase. \( \Delta G_H \) is calculated as:

\[
\Delta G_H = \Delta E_H + 0.2\text{eV}
\]

The key reaction steps in alkaline HER:

The free energy for step : \( \text{H}_2\text{O} + \text{e}^- + \text{cat} \to \text{H}^*\text{-cat} + \text{OH}^- \) and \( \text{H}^*\text{-cat} + \text{H}_2\text{O} + \text{e}^- \to \text{cat} + \text{OH}^- + \text{H}_2 \uparrow \) should be the same at equilibrium potential of HER. Under
this assumption, one can avoid computation of the exact free energy of OH\textsuperscript{-} in solutions by using computational hydrogen electrode\textsuperscript{8}. Herein, four main stage are considered: initial state, activated water adsorption, H\textsuperscript{*} intermediates formation, H\textsubscript{2} formation\textsuperscript{9}. The free energies in alkaline solution are calculated as:

\[ G_0 = G_{\text{cat}} + G_{\text{H}_2\text{O}} \]

\[ G_1 = G_{\text{cat}(H-OH)'} \]

\[ G_2 = G_{\text{cat}(H^*)} + G_{\text{OH}^-} \]

\[ G_3 = G_{\text{cat}} + G_{\text{OH}^-} + \frac{1}{2}G_{\text{H}_2} \]

And \[ G_3 = G_0 \].

Previous studies have proposed that there must be a balance between the transition state energies for water dissociation and the final state energies of adsorbed active species\textsuperscript{10,11}. Herein, the \( \Delta G_{\text{H}_2\text{O}} (\Delta G_{\text{H}_2\text{O}}=G_1-G_0) \) value is applied as an activity descriptor for the Volmer step. And the species H-OH is a ground state of activated water adsorption. The \( \Delta G_{\text{H}^*} (\Delta G_{\text{H}^*}=G_2-G_3) \) value is utilized as an activity descriptor for the Tafel step or Heyrovsky step\textsuperscript{8,9}. 
Fig. S1 Morphology characterization of the pristine MoS$_2$ catalysts. (a) SEM (b) TEM. The HRTEM is shown in the inset.
Fig. S2 Morphology characterization of the N-MoS\textsubscript{2} catalysts. (a) SEM (b) TEM and (c) HRTEM images of the N-MoS\textsubscript{2} nanosheets; (d-f) EDX elemental mapping of Mo, S, and N showing uniform distribution of the three elements.
Fig. S3 Morphology characterization of the P-MoS$_2$ catalysts. (a) SEM (b) TEM and (c) HRTEM images of the P-MoS$_2$ nanosheets; (d-f) EDX elemental mapping of Mo, S, and P showing uniform distribution of the three elements.
Fig. S4 EDX images of As-MoS$_2$
Fig. S5. Polarization curves of Electrochemical characterization of different dosage of As
Fig. S6 (a-d) cyclic voltammograms with various scan rate from 40-160 mV s\(^{-1}\) at E = 0.045–0.555 V (vs RHE)
Fig. S7 Mott-Schottky plots for as-prepared MoS$_2$ nanosheets
### Table. S1 The d-band-center of Mo atom for as-prepared samples

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Fig. S8(a) Projected d-orbital density of states of Mo atoms for S connect sites. (b) Projected p-orbital density of states of S atoms for Mo connect sites. (c) Projected orbital density of states of S atoms prior to the H adsorption of pristine MoS$_2$ and subsequent to the H adsorption.
Fig. S9(a) Projected d-orbital density of states of Mo atoms for B connect sites. (b) Projected p-orbital density of states of B atoms for Mo connect sites. (c) Projected orbital density of states of B atoms prior to the H adsorption of B-MoS$_2$ and subsequent to the H adsorption.
Fig. S10 (a) Projected d-orbital density of states of Mo atoms for C connect sites. (b) Projected p-orbital density of states of C atoms for Mo connect sites. (c) Projected orbital density of states of C atoms prior to the H adsorption of C-MoS$_2$ and subsequent to the H adsorption.
Fig. S11 (a) Projected d-orbital density of states of Mo atoms for N connect sites. (b) Projected p-orbital density of states of N atoms for Mo connect sites. (c) Projected orbital density of states of N atoms prior to the H adsorption of N-MoS$_2$ and subsequent to the H adsorption.
Fig. S12 (a) Projected d-orbital density of states of Mo atoms for P connect sites. (b) Projected p-orbital density of states of P atoms for Mo connect sites. (c) Projected orbital density of states of P atoms prior to the H adsorption of P-MoS$_2$ and subsequent to the H adsorption.
Fig. S13 (a) Projected d-orbital density of states of Mo atoms for As connect sites. (b) Projected p-orbital density of states of As atoms for Mo connect sites. (c) Projected orbital density of states of As atoms prior to the H adsorption of As-MoS$_2$ and subsequent to the H adsorption.
Fig. S14 (a) Projected d-orbital density of states of Mo atoms for Sb connect sites. (b) Projected p-orbital density of states of Sb atoms for Mo connect sites. (c) Projected orbital density of states of Sb atoms prior to the H adsorption of Sb-MoS$_2$ and subsequent to the H adsorption.
Fig. S15 Bader charge of different atoms for pristine MoS$_2$
Fig. S16 Bader charge of different atoms for B-MoS$_2$
Fig. S17 Bader charge of different atoms for C-MoS$_2$
Fig. S18 Bader charge of different atoms for N-MoS$_2$
Fig. S19 Bader charge of different atoms for P-MoS$_2$
Fig. S20 Bader charge of different atoms for As-MoS$_2$
Fig. S21 Bader charge of different atoms for Sb-MoS$_2$
Fig. S22 HER free energy diagram for different S sites in the basal plane of As-MoS$_2$ nanosheets.
Fig. S23 HER free energy diagram for different dosage of As for As-MoS$_2$. The above are the corresponding atomic configurations.
Fig. S24 LSV polarization curves for sample P-MoS$_2$ before (black line) and after (red line) 2000 CV cycles under alkaline solution.
Fig. S25 Projected p-orbital density of states of atoms prior to the H2O dissociation adsorption and subsequent to the H2O dissociation adsorption. (a) pristine MoS$_2$. (b) N-MoS$_2$. (c) P-MoS$_2$. (d) As-MoS$_2$. 
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<td>fractal-shaped singlelayer MoS₂</td>
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