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# Single-atom cobalt array bound to distorted 1T MoS<sub>2</sub> with ensemble effect for hydrogen evolution catalysis

Kun Qi<sup>1</sup>, Xiaoqiang Cui<sup>1\*</sup>, Lin Gu<sup>2</sup>, Shansheng Yu<sup>1</sup>, Xiaofeng Fan<sup>1</sup>, Mingchuan Luo<sup>3,4</sup>, Shan Xu<sup>1</sup>, Ningbo Li<sup>1</sup>, Lirong Zheng<sup>5</sup>, Qinghua Zhang<sup>2</sup>, Jingyuan Ma<sup>6</sup>, Yue Gong<sup>2</sup>, Fan Lv<sup>3,4</sup>, Kai Wang<sup>3,4</sup>, Haihua Huang<sup>1</sup>, Wei Zhang<sup>1</sup>, Shaojun Guo<sup>3,4\*</sup>, Weitao Zheng<sup>1\*</sup> & Ping Liu<sup>7</sup>

The grand challenge in the development of atomically dispersed metallic catalysts is their low metal-atom loading density, uncontrollable localization and ambiguous interactions with supports, posing difficulty in maximizing their catalytic performance. Here, we achieve an interface catalyst consisting of atomic cobalt array covalently bound to distorted 1T MoS<sub>2</sub> nanosheets (SA Co-D 1T MoS<sub>2</sub>). The phase of MoS<sub>2</sub> transforming from 2H to D-1T, induced by strain from lattice mismatch and formation of Co-S covalent bond between Co and MoS<sub>2</sub> during the assembly, is found to be essential to form the highly active single-atom array catalyst. SA Co-D 1T MoS<sub>2</sub> achieves Pt-like activity toward HER and high long-term stability. Active-site blocking experiment together with density functional theory (DFT) calculations reveal that the superior catalytic behaviour is associated with an ensemble effect via the synergy of Co adatom and S of the D-1T MoS<sub>2</sub> support by tuning hydrogen binding mode at the interface.

<sup>1</sup>State Key Laboratory of Automotive Simulation and Control, Department of Materials Science, Key Laboratory of Automobile Materials of MOE, Jilin University, Changchun 130012, China. <sup>2</sup>Key Laboratory for Renewable Energy, Beijing Key Laboratory for New Energy Materials and Devices, Laboratory of Advanced Materials and Electron Microscopy, Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China. <sup>3</sup>Department of Materials Science and Engineering, Peking University, Beijing 100871, China. <sup>4</sup>4BIC-ESAT, College of Engineering, Peking University, Beijing 100871, China. <sup>5</sup>Beijing Synchrotron Radiation Facility, Institute of High Energy Physics, Chinese Academy of Sciences, Beijing 100049, China. <sup>6</sup>Shanghai Synchrotron Radiation Facility, Shanghai Institute of Applied Physics, Chinese Academy of Sciences, Shanghai 200120, China. <sup>7</sup>Department of Chemistry, Brookhaven National Laboratory, Upton, NY 11973, USA. \*email: [xqcui@jlu.edu.cn](mailto:xqcui@jlu.edu.cn); [guosj@pku.edu.cn](mailto:guosj@pku.edu.cn); [wztzheng@jlu.edu.cn](mailto:wztzheng@jlu.edu.cn)

Hydrogen ( $H_2$ ), as a zero-emission, renewable energy source, has attracted increasingly extensive attention owing to its important role in solving the environmental issues<sup>1,2</sup>. Water splitting catalysis is one of the most efficient approaches for  $H_2$  generation because of its high-efficiency energy conversion<sup>3</sup>. Platinum (Pt) is the best catalyst for the hydrogen evolution reaction (HER); however, the high cost and limited earth abundance of Pt expose tremendous limitations for large-scale implementation<sup>4</sup>. Therefore, the critical determinant for energy storage in electrolytic systems is the development of robust and efficient alternative catalysts that are cheap and earth-abundant. Remarkable advances have been made in developing efficient non-noble materials as Pt substitutes for HER<sup>5</sup>. Unfortunately, a large gap in their HER catalytic performance still exists for completely substituting Pt owing to their lack of more efficient active sites and difficulty in maximizing the intrinsic activity of their active sites<sup>6,7</sup>. Atomically dispersed catalysts with single metal atoms or mononuclear metal complexes anchored on supports represent the lowest size limit to achieve maximum atom efficiency, providing the most ideal platform for catalysis<sup>8–10</sup>. However, the biggest issue is that previously reported atomically dispersed catalysts have been primarily in the form of atomic clusters, especially at high loading amounts, owing to the ambiguous interactions between the metal atoms and supports, posing a difficulty in maximizing the catalytic efficiency<sup>11–15</sup>.

Herein, we report the procedure for making single-atom cobalt (Co) array covalently bound onto distorted 1T  $MoS_2$  nanosheets (denoted as SA Co-D 1T  $MoS_2$ ) via Co-S bonds through electrochemical cyclic voltammetry (CV) leaching of Co nanodisks (NDs)- $MoS_2$  nanosheet hybrids. The strain induced by lattice mismatch and the formation of Co-S covalent bond between Co and  $MoS_2$  in the Co ND- $MoS_2$  nanosheet hybrids are shown to be critical for achieving the phase transformation of  $MoS_2$  from the semiconductive 2H to metallic distorted 1T (D-1T) phase<sup>16</sup>. The SA Co-D 1T  $MoS_2$  catalyst exhibits the Pt-like electrocatalytic activity for HER in acid electrolyte with a very low overpotential of 42 mV at 10 mA  $cm^{-2}$ , low Tafel slope of 32 mV  $dec^{-1}$  and excellent long-term and cycling stability. The HER activity of SA Co-D 1T  $MoS_2$  is very close to that of commercial Pt<sup>17</sup>. The ultrahigh activity is proved to be the ensemble effect through the synergy of single Co atom and S in distorted 1T phase of  $MoS_2$  that possesses the optimal hydrogen-binding energy.

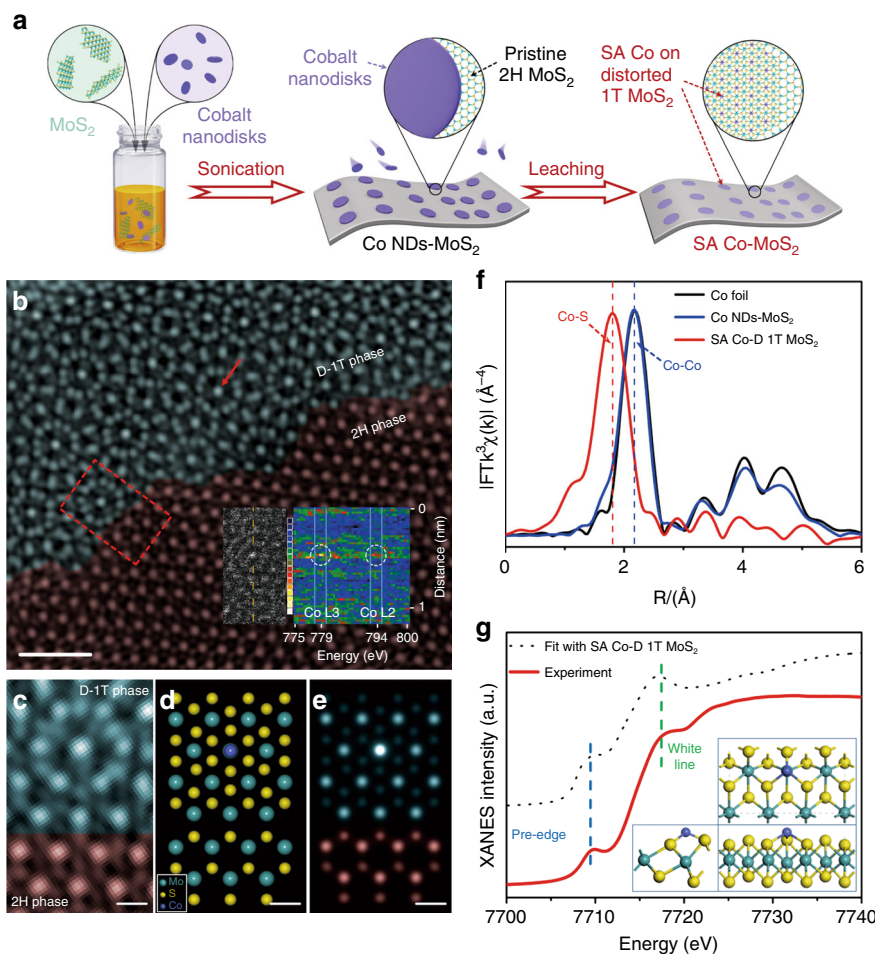
## Results

**Synthesis and characterization of SA Co-D 1T  $MoS_2$ .** Figure 1a shows the schematic illustration of the preparation of the SA Co-D 1T  $MoS_2$  catalysts using an assembly/leaching process, which ensures the successful introduction of Co atoms on the basal plane other than on the defect or edged sites of  $MoS_2$ . Ordered Co NDs with an average diameter of 12 nm and height of 4.5 nm (Supplementary Fig. 1) were first assembled onto the surface of  $MoS_2$  nanosheets by sonication-induced Co-S bonding, in which the assembling amount is highly dependent on the sonication power (Supplementary Fig. 2). Phonons at ultrasonic power may help to closely contact Co nanodisks with  $MoS_2$  nanosheets, and provide the energy for the Co-S bond formation through ultrasonic cavitation (Supplementary Figs. 3 and 4, Supplementary Table 1)<sup>18,19</sup>. The Co ND-modified  $MoS_2$  heterostructures (Co NDs/ $MoS_2$ ) were further treated by electrochemical CV cycles (Supplementary Fig. 5)<sup>20</sup>. This electrochemical CV leaching resulted in the disappearance of Co-Co bond and remaining of Co-S bond in the resultant SA Co-D 1T  $MoS_2$  (Supplementary Figs 6 and 7 and Supplementary Table 2). Single-atom Co array was formed and in situ anchored onto the  $MoS_2$  surface, where the Co NDs were assembled. Transmission electron microscopy

(TEM) image, selected area electron diffraction pattern (Supplementary Fig. 8) and X-ray diffraction (XRD) pattern (Supplementary Fig. 9) show that the Co nanodisks is well contacted with the  $MoS_2$  by forming heterostructures, and there is no Co nanocrystal after the electrochemical leaching. Energy-dispersive X-ray spectroscopy mapping analysis reveals that Co is evenly dispersed in SA Co-D 1T  $MoS_2$  (Supplementary Fig. 8f–h). High-resolution TEM (HRTEM) image shows that  $MoS_2$  is intensely disordered after bonding with Co atoms (Supplementary Fig. 8i). High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) was further used to intuitively observe the atomic dispersion of Co and the phase transition of  $MoS_2$  (Fig. 1b–e). The disordered structure of SA Co-D 1T  $MoS_2$  is totally different from the Moiré patterns when two or few layers of  $MoS_2$  aggregate with random orientation (Supplementary Fig. 10). The atomically isolated Co species (bright spots marked by the red arrow) are dispersed on the D-1T  $MoS_2$  matrix, and the obvious interface between SA Co-D 1T  $MoS_2$  and the 2H  $MoS_2$  is confirmed by both the HAADF-STEM image (Fig. 1c) and simulated pattern (Fig. 1d, e). Atomically electron energy loss spectroscopy (EELS) line scanning was also conducted (inset of Fig. 1b), showing two Co peaks at 779 eV and 794 eV, which correspond to Co L3 and Co L2, respectively<sup>21</sup>. The statistics for the size of bright dots (Co atom) were determined to be in the range of  $\sim 2\text{--}3 \text{ \AA}$ , close to that of a single Co atom (Supplementary Fig. 11)<sup>22</sup>. These results indicate that single Co atoms are uniformly bound to the top of the Mo atoms on the  $MoS_2$  slab (Supplementary Fig. 12)<sup>23</sup>. The Co mass loading amount on SA Co-D 1T  $MoS_2$  is determined to be 3.54 wt.% by inductively coupled plasma mass spectrometry technique, being in agreement with those determined by EDX technique (3.60 wt.%, Supplementary Fig. 13) and XAFS spectrum simulation (4.07 wt.%, Supplementary Fig. 14). In addition, using the same assembly/leaching strategy, we also successfully prepared SA Ni D-1T  $MoS_2$  and SA Fe D-1T  $MoS_2$  catalysts (Supplementary Figs 15–25, Supplementary Table 3 and 4) on the premise that the Ni and Fe nanoplates were used to ensure their large area sufficient contact with  $MoS_2$  instead of their nanoparticles counterparts, further indicating that the method is universal and can be extended to any 2D metals or metal oxides, which meets the criterions.

## Coordination environment confirmation of SA Co-D 1T $MoS_2$ .

To verify the coordination environment of atomic Co dispersed on SA Co-D 1T  $MoS_2$ , the extended X-ray absorption fine structure (EXAFS) and X-ray absorption near-edge structure (XANES) spectroscopies were performed (Fig. 1f–g)<sup>24</sup>. A single strong shell at 1.79  $\text{\AA}$  in R-space of the EXAFS spectrum indicates the exclusive existence of Co-S bond for SA Co-D 1T  $MoS_2$  (Fig. 1f)<sup>25,26</sup>. The charge density difference from the first-principle calculation also confirms the existence of the Co-S covalent bond (Supplementary Fig. 26)<sup>27</sup>. We also characterized the cross-section structure and interactions for the side view of the heterostructures. Supplementary Fig. 27 shows the TEM and HRTEM images of the Co NDs- $MoS_2$ . The crystal alignment between Co nanodisks and  $MoS_2$  nanosheets is that the contact layer of Co was covalently bonded with the S atom on the surface of  $MoS_2$ , and also the contact layer of  $MoS_2$  nearest to Co nanodisks shows a phase transformation from 2H to distorted 1T phase. We can also observe from the cross-section views of Co nanodisks- $MoS_2$  that there is a well-defined covalently bounded interface between the counterparts. Using the SA Co-D 1T  $MoS_2$  (Co atom was coordinated with three adjacent sulfur atoms, and located at the site directly above the center Mo atom) as a model, we also simulated its XANES spectrum (dotted lines in Fig. 1g)<sup>28</sup>. The fitting results for SA



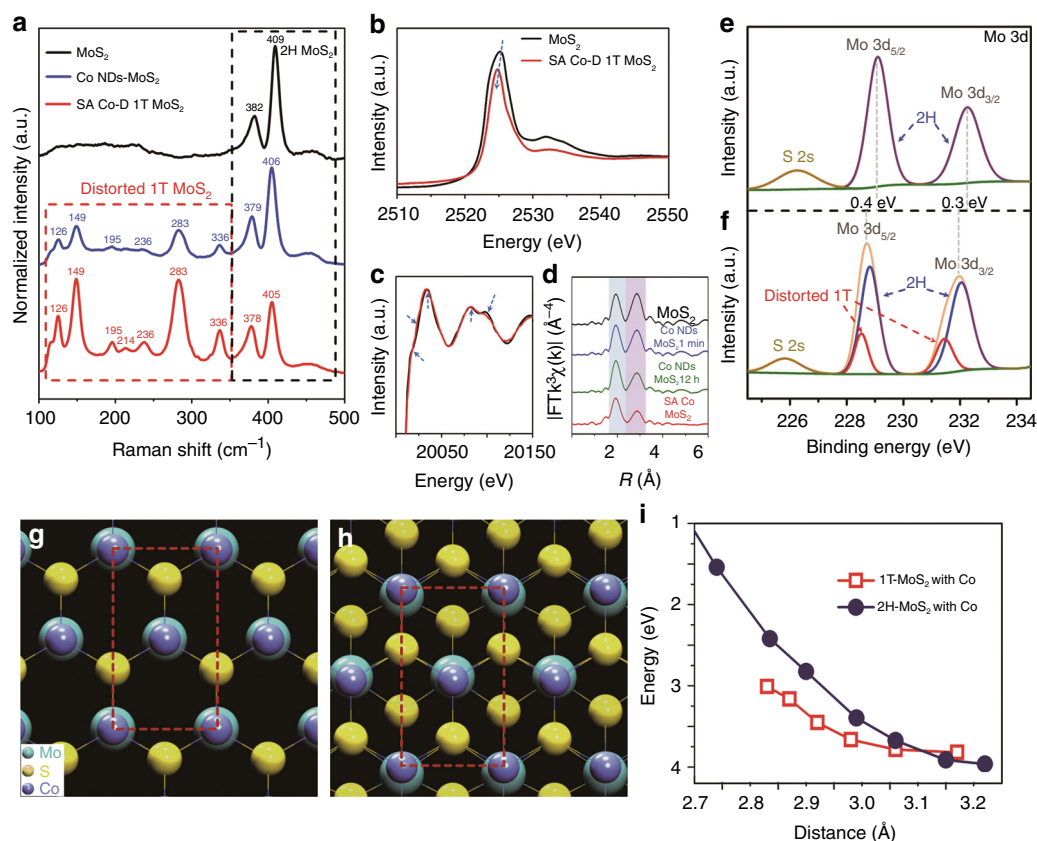
**Fig. 1** Schematic illustration of synthetic method for SA Co-D 1T MoS<sub>2</sub> and its characterization. **a** Schematic diagram of the fabrication process for SA Co-D 1T MoS<sub>2</sub>. **b** Aberration-corrected HAADF-STEM image of SA Co-D 1T MoS<sub>2</sub>, showing the obvious junction between SA Co-D 1T MoS<sub>2</sub> (dark cyan) and pristine 2H MoS<sub>2</sub> (wine). The inset shows the HRTEM and EELS spectrum of SA Co-D 1T MoS<sub>2</sub> (scale bar: 1 nm). **c** Enlarged HAADF-STEM image in the red square area of **b** (scale bar: 2 Å). **d** Theoretical model and **e** simulated STEM images using QSTEM simulation software (scale bar: 2 Å). **f** FT-EXAFS spectra of SA Co-D 1T MoS<sub>2</sub> and bulk cobalt foil at the Co K-edge. **g** Co K-edge XANES of SA Co-D 1T MoS<sub>2</sub> and fitted curve. The inset shows the atomic structure of SA Co-D 1T MoS<sub>2</sub>

Co-D 1T MoS<sub>2</sub> with a Co concentration of 3.70% show the same two main energy features at 7710 eV (pre-edge) and 7718 eV (white line) as those of the experimental results, further proving that the Co atom is right on the top of Mo atom instead of the replacement of Mo atom. All these extensive experimental and simulation results reveal that, in SA Co-D 1T MoS<sub>2</sub>, a single Co atom is coordinated to three adjacent sulfur atoms and located at the site directly above the Mo atom.

**Phase transition observation during the synthesis of SA Co-D 1T MoS<sub>2</sub>.** Raman spectra of Co ND/MoS<sub>2</sub> and SA Co-D 1T MoS<sub>2</sub> show peak shifts of E<sub>1g</sub><sup>1</sup> and A<sub>1g</sub>, and new peaks between 100 and 350 cm<sup>-1</sup> (i.e., 126, 149, 195, 214, 236, 283, and 336 cm<sup>-1</sup>) compared with those of pristine MoS<sub>2</sub> (Fig. 2a), resulting from the phase transformation of the MoS<sub>2</sub><sup>29</sup>. The results from time-dependent evolution of Raman spectra reveal that the phase transformation happened during the assembly process of Co NDs on MoS<sub>2</sub> (Supplementary Fig. 28). The Mo L<sub>3</sub>-edge XANES spectrum (Fig. 2b) of SA Co-D 1T MoS<sub>2</sub> shows a decreased peak intensity and blue shift to ~2525.12 eV, indicating the phase transformation from 2H to D-1T MoS<sub>2</sub><sup>30</sup>. The Mo K-edge XANES spectrum (Fig. 2c) of SA Co-D 1T MoS<sub>2</sub> also indicates a considerably widened energy-state distribution related to the Mo

4d electrons with the appearance of some unoccupied Mo 4d states after bonding with the SA Co (as labeled by the arrows)<sup>31</sup>. Fig. 2d shows that the second shell intensity of Mo K-edge EXAFS spectrum decreases after the Co NDs assembly. When SA Co-D 1T MoS<sub>2</sub> was produced after CV leaching, the second shell intensity decreases more, indicating the further phase transformation from pristine 2H to D 1T of MoS<sub>2</sub><sup>32</sup>.

The two polymorphs of MoS<sub>2</sub> (pristine 2H phase and distorted 1T phase) can be identified by the XPS spectra of Mo 3d and S 2p. The binding energies of Mo 3d for the pristine 2H MoS<sub>2</sub> (Fig. 2e) are obviously different from those of SA Co-D 1T MoS<sub>2</sub> (Fig. 2f). The peaks at ~229.1 and 232.3 eV, corresponding to the binding energies of Mo<sup>4+</sup> 3d<sub>5/2</sub> and 3d<sub>3/2</sub>, shift to lower energy by 0.4 and 0.3 eV, respectively, and also a new doublet of Mo 3d spectrum located at 228.5 and 231.5 eV appears, which indicate the production of distorted 1T MoS<sub>2</sub>. The S 2p spectrum also shows a new doublet at 161.6 and 162.7 eV (Supplementary Fig. 29). These new doublets in Mo 3d and S 2p spectra can be assigned to the characteristic peaks of distorted 1T phase MoS<sub>2</sub>, further confirming the phase transformation from the pristine 2H to D 1T<sup>33</sup>. The evolution of Co 2P spectrum during the assembly and CV leaching process also confirms the formation of the Co-S bond (Supplementary Fig. 30).

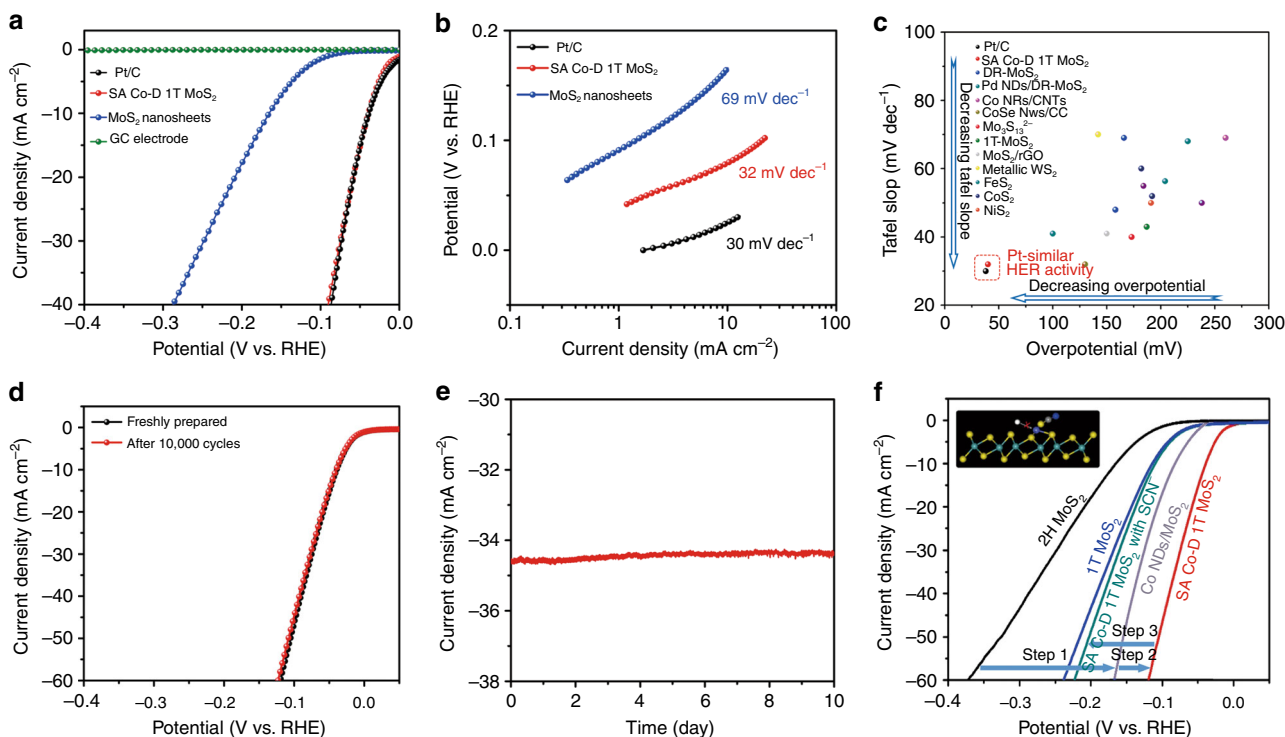


**Fig. 2** Characterization techniques and DFT calculation for the phase transformation of MoS<sub>2</sub>. **a** Raman spectra of pristine MoS<sub>2</sub>, Co NDs/MoS<sub>2</sub>, and SA Co-D 1T MoS<sub>2</sub>. **b, c** Mo L<sub>3</sub>-edge and K-edge XANES spectra of SA Co-D 1T MoS<sub>2</sub> and pristine MoS<sub>2</sub>. **d** Mo K-edge EXAFS spectra variation during the preparation of SA Co-D 1T MoS<sub>2</sub>. **e, f** Mo 3d XPS spectra show the surface-binding state variation before **e** and **f** after the MoS<sub>2</sub> phase transformation. **g, h** 2H and 1T atomic structures of MoS<sub>2</sub> assembled with Co atomic layer calculated by first-principles. **i** Energies of 2H MoS<sub>2</sub> and 1T MoS<sub>2</sub> assembled with Co atomic layer as a function of Co-Co distance calculated by first-principles method based on the single layer 2H MoS<sub>2</sub> and atomic Co as the reference state with the formula  $\Delta E = E_{2H-MS} + E_{Co} - E_{MS-Co}$

**Phase transition mechanism of MoS<sub>2</sub> during the synthesis of SA Co-D 1T MoS<sub>2</sub>.** Density functional theory (DFT) calculations were conducted to reveal the mechanism of the phase transition of MoS<sub>2</sub> after assembling Co NDs. On the basal plane of MoS<sub>2</sub> surface, it is found that there is strong interaction between the Co adatom and S atom. As shown in Fig. 2g, the Co atom prefers to occupy the top site of 2H MoS<sub>2</sub>. The adsorption energy is 3.96 eV/Co by the formula,  $\Delta E_{ad} = E_{MS} + E_{Co} - E_{MS-Co}$ , where  $E_{MS}$ ,  $E_{Co}$ , and  $E_{MS-Co}$  are the energies of the isolated MoS<sub>2</sub>, isolated Co atom and MoS<sub>2</sub> with adsorbed Co atom, respectively. Interestingly, the adsorption energy (4.37 eV/Co) of Co on 1T MoS<sub>2</sub> (Fig. 2h) is larger than that on 2H MoS<sub>2</sub>. This means that Co atoms prefer to bond on 1T MoS<sub>2</sub> than 2H MoS<sub>2</sub>. With the adsorption of Co atoms, the energy difference between 2H and 1T ( $\Delta E = E_{MS(1T)} - E_{MS(2H)}$ ) is 184 meV/atom. That is, the phase transformation of MoS<sub>2</sub> from 2H to 1T is still not thermodynamically favorable, but should be driven by the external force. According to the previous theoretical work, the strain can be used to modulate the phase transition from 2H phase to 1T<sup>34</sup>. In Fig. 2i, the stability of 2H and 1T phases varies with the coverage of Co or the Co-Co distance in the nearest neighbor. Only under the Co-Co distance lesser than 3.10 Å with a strain of ~3.70%, the 1T phase becomes to be more stable (Fig. 2i). It is noticed that the Co-Co distance on (111) facet of Co is about 2.51 Å and the lattice constant of MoS<sub>2</sub> is ~3.16 Å. The mismatch between the lattice of metallic Co and pristine 2H MoS<sub>2</sub> is large enough for the strain generation (Supplementary Fig. 31). In this case, the anchoring of Co atoms induces the coordination

reconstruction of the MoS<sub>2</sub> support to D-1T MoS<sub>2</sub> owing to a charge density wave (CDW) state<sup>35</sup>. Such CDW state of D-1T MoS<sub>2</sub> can trap the system into the deeper energy minimum on the potential energy surface. The CDW structures with different Co coverages are illustrated in Supplementary Fig. 32. These DFT results strongly support the experimental observation that phase transition happens after the assembly of Co NDs on MoS<sub>2</sub> surface, during which the Co-S bond was formed with the assistance of sonication.

**HER activity of SA Co-D 1T MoS<sub>2</sub>.** The HER activities of the catalysts were studied in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution. SA Co-D 1T MoS<sub>2</sub> with 3.54% Co loading amount exhibits an extremely small onset overpotential ( $\eta$ ) of 42 mV vs. the reversible hydrogen electrode (RHE) for HER, much smaller than those of other non-precious metal catalysts and even comparable to that of 10% Pt/C (Fig. 3a, Supplementary Fig. 33, Supplementary Table 5 and 6). To gain a quantitative insight into the HER activity, the turnover frequency (TOF), which can reveal the intrinsic catalytic activity of a single active site of the catalyst, was calculated (Supplementary Fig. 34). SA Co-D 1T MoS<sub>2</sub> shows a TOF of 7.82 s<sup>-1</sup> at an overpotential of 100 mV vs. RHE. Also, after the SA Co atom bonding, the catalyst shows a lower EIS response than the MoS<sub>2</sub> (Supplementary Fig. 35), indicating a fast kinetics for hydrogen evolution<sup>36</sup>. The Tafel slope of SA Co-D 1T MoS<sub>2</sub> is 32 mV dec<sup>-1</sup> (Fig. 3b), similar to that of Pt/C (30 mV dec<sup>-1</sup>), and surpassing those of previously reported non-Pt-based materials (Fig. 3c) that using a graphite rod as the counter electrode instead of Pt foil to avoid Pt contamination<sup>37</sup>. The low



**Fig. 3** HER performance of SA Co-D 1T MoS<sub>2</sub>. **a** Polarization curves of different catalysts tested in Ar-saturated 0.5 M H<sub>2</sub>SO<sub>4</sub>. **b** Tafel plots for the catalysts derived from **a**. **c** HER activity comparison using the Tafel slope (mV dec<sup>-1</sup>) vs. overpotential at a current density of 10 mA cm<sup>-2</sup>. **d** Polarization curves of the SA Co-D 1T MoS<sub>2</sub> after 10,000 CV cycles. **e** Time dependence of the current density for SA Co-D 1T MoS<sub>2</sub> at a static overpotential of 100 mV vs. RHE. **f** HER polarization plots of MoS<sub>2</sub>, 1T MoS<sub>2</sub> prepared by lithiation, Co NDs/MoS<sub>2</sub> and SA Co-D 1T MoS<sub>2</sub> without and with SCN<sup>-</sup> ions. The inset shows that the cobalt HER active centers are blocked by SCN<sup>-</sup> ions

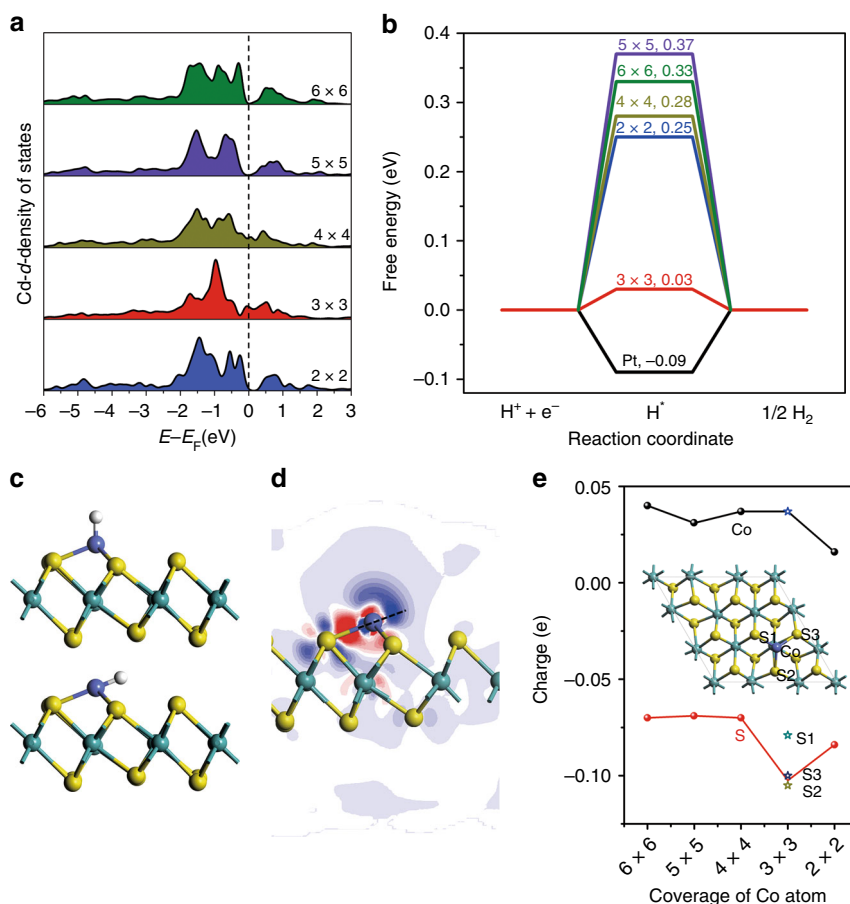
Tafel slope indicates that SA Co-D 1T MoS<sub>2</sub> processes a Tafel rate-determining-step mechanism for HER, instead of the common Volmer reaction<sup>38</sup>. In addition, a series of control experiments and DFT calculations prove that other MoS<sub>2</sub>/Co catalysts prepared by using Co clusters, nanoparticles, or ions on MoS<sub>2</sub> cannot achieve such high HER performance (Supplementary Figs 36–45, Supplementary Table 7). The SA Ni D-1T MoS<sub>2</sub> and SA Fe D-1T MoS<sub>2</sub> catalysts also show enhanced HER activity relative to pristine MoS<sub>2</sub>, but lower than SA Co-D-1T MoS<sub>2</sub> (Supplementary Fig. 46 and Supplementary Table 8).

**HER stability of SA Co-D 1T MoS<sub>2</sub>.** SA Co-D 1T MoS<sub>2</sub> shows excellent cycling stability and long-term durability for HER in acidic media. The linear sweep voltammetry (LSV) curves measured for SA Co-D 1T MoS<sub>2</sub> before and after 10,000 CV cycles between 0.1 and -0.3 V vs. RHE exhibit a negligible current density loss (Fig. 3d). Figure 3e shows the long-term durability measured by performing continuous HER at a static overpotential of 100 mV. Consistent H<sub>2</sub> generation was observed during the HER process (inset of Fig. 3e), and the current density remained without any decrease as the reaction proceeded for 10 days. The high stability of SA Co-D 1T MoS<sub>2</sub> catalyst was also confirmed by HAADF-STEM (atomic structure stability), XPS (valence state and phase stability), XANES, and FT-EXAFS (coordination environment stability) after accelerating stability measurements, long-term air storage and heating treatment (Supplementary Figs 47–52 and Supplementary Table 9).

**The identification of reaction active site.** The nature of the high activity of SA Co-D-1T MoS<sub>2</sub> was disclosed by comparing the HER polarization plots of different catalysts (Fig. 3f). The HER activity of MoS<sub>2</sub> was first improved by the assembly of Co NDs (Step 1, Co

NDs/MoS<sub>2</sub>) that induced the phase transformation from 2H to D-1T (onset overpotential decreases from 162 mV to 85 mV at 10 mA cm<sup>-2</sup>) because the metallic 1T MoS<sub>2</sub> can give higher conductivity and more active sites for better HER<sup>39</sup>. The HER performance of MoS<sub>2</sub> was further improved to a Pt-like activity (onset overpotential decreases from 85 mV to 42 mV, similar to the Pt/C, by CV leaching to form single-atom Co sites on D-1T MoS<sub>2</sub> (Step 2, SA Co-D-1T MoS<sub>2</sub>). Thiocyanate ion (SCN<sup>-</sup>, poisoning agent) was then used to block the Co active sites<sup>40</sup>. The addition of 10 mM SCN<sup>-</sup> resulted in an increase of onset overpotential from 42 mV to 112 mV (Step 3, SA Co-D 1T MoS<sub>2</sub> with SCN<sup>-</sup>), close to that of the 1T MoS<sub>2</sub> prepared by lithiation. Therefore, the high HER activity of the SA Co-D 1T MoS<sub>2</sub> catalyst is a synergetic effect of both the single Co atom and the D-1T MoS<sub>2</sub>, that is to say, both single Co atom site and 2H to D-1T phase transformation of MoS<sub>2</sub> are contributory. Nevertheless, single-atom Co sites give the dominant contribution to Pt-like HER activity.

**Ensemble effect enhancing HER activity.** DFT calculations were further performed to explore the origin of the high electrocatalytic activity of SA Co-D 1T MoS<sub>2</sub> for the HER in acidic solution. According to the DFT calculations, the PDOS of Co 3d near the Fermi level for 3 × 3 and 4 × 4 cases are remarkably different from the others (Fig. 4a). It indicates that the Co adatoms are transformed from cationic to metallic with the coverage increasing to 2.08 and 3.70% (corresponding to 4 × 4 and 3 × 3 models) because of their transition CDW structures. In particular, the resulted increase in the empty state of Co close to the Fermi level for the 3 × 3 case is the most significant among the systems studies, being able to promote the hybridization between Co adatom and the hydrogen atom, and thus enhance the corresponding hydrogen binding. In addition, the d-peak at the Fermi



**Fig. 4** Theoretical calculation of SA Co-D 1T MoS<sub>2</sub> for HER. **a** Calculated Co projected d-density of states for different coverage. **b** Calculated free-energy diagram for HER at a potential of  $U = 0$  relative to the standard hydrogen electrode at  $\text{pH} = 0$  for different atomic Co loading amounts. **c** Hydrogen adsorption modes on the single-atom Co-MoS<sub>2</sub> 3 × 3 case. **d** The electron density difference of 3 × 3 case and **e** the electron charge of Co and S adjacent to Co as a function of Co coverage

level for the 3 × 3 case is stronger than that for 4 × 4 case, indicating the stronger hydrogen adsorption on cobalt. Such variation in Co 3d with the coverage strongly depends on the Co-MoS<sub>2</sub> interaction, which corresponds to the so called electronic or ligand effect. The  $|\Delta G_{\text{H}^+}|$  value is dependent on the Co coverage on D-1T MoS<sub>2</sub> (Fig. 4b). SA Co-D 1T MoS<sub>2</sub> with a Co coverage of 3.70% (3 × 3 superstructure) shows the lowest  $|\Delta G_{\text{H}^+}|$  value of 0.03 eV, enabling the HER energy profile even closer to the ideal than Pt (111) with the  $|\Delta G_{\text{H}^+}^{\text{Pt}}| = 0.09$  eV. Thus, a superior HER activity of SA Co-D 1T MoS<sub>2</sub> catalyst over Pt is expected from a thermodynamics viewpoint (Supplementary Figs 53–55).

Most importantly, the prominent HER activity of SA Co-D 1T MoS<sub>2</sub> in a 3 × 3 superstructure is attributed to the ensemble effect of D-1T MoS<sub>2</sub> support and Co single-atom. Our calculation results show that the hydrogen adsorption at the upright position of Co on MoS<sub>2</sub> (111) is not as favorable as that at the tilted top site toward the adjacent S atom on the surface (Fig. 4c) by 0.68 eV/unit. The preference for the tilted top site is associated with the ensemble effect at the Co-MoS<sub>2</sub> (111) interface. The energy gain by moving from the upright to the tilted position is associated with the electrostatic attraction between the positively charged proton and negatively charged S adjacent to Co. Figure 4e plots the variation in Hirshfeld charge of Co and adjacent S as a function of Co coverage<sup>41</sup>. The positive Co atom is beneficial to the protonation process. Among the S ions, the one in a 3 × 3 superstructure displays the most negative charge, and therefore contributes the most to stabilize adsorbed H via the electrostatic interaction. Our DFT calculations highlight the importance of

ensemble effect via the synergy of Co adatom and S of the MoS<sub>2</sub> (111) support in tuning hydrogen-binding mode at the interface and thus achieving superior HER activity.

## Discussion

In summary, we report a unique designed single-atom array catalyst, SA Co-D 1T MoS<sub>2</sub>, with Pt-like HER performance by the top-down assembly/leaching strategy. During the assembly process, the strain induced by lattice mismatch and the formation of the covalent Co-S bond between Co ND and 2H MoS<sub>2</sub> nanosheet are identified as the main reasons for 2H to D 1T phase transformation. The 2D morphology of Co NDs is the key in the preparation of SA Co-D 1T MoS<sub>2</sub> because that the large area contact of Co with the basal plane of MoS<sub>2</sub> is essential to generate enough compressive strain for phase transformation. The active site blocking experiment reveals that the single-atom Co in SA Co-D 1T MoS<sub>2</sub> is the principal catalytic center, although both single Co atom and 2H to D-1T phase transformation of MoS<sub>2</sub> are contributory for HER catalysis. DFT calculations confirm that the high HER activity of this single-atom catalyst is mainly owing to an ensemble effect via the synergy of Co adatom and S of the MoS<sub>2</sub> (111) support by tuning hydrogen-binding mode at the interface. The discovery of this SA Co-D 1T MoS<sub>2</sub> catalyst highlights the area of tuning the structure and functionality of metal-TMD catalysts at the atomic scale, which holds promise for applications in large-scale water splitting electrolyzers.

## Methods

**Synthesis of MoS<sub>2</sub> nanosheets.** MoS<sub>2</sub> was synthesized using standard solvothermal procedures<sup>42</sup>. In a typical synthesis, 24.7 mg of ammonium molybdate tetrahydrate ((NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>·4H<sub>2</sub>O, ACS Grade, Sigma Aldrich) and 53.2 mg of thiourea (CH<sub>4</sub>N<sub>2</sub>S, ACS Grade, Sigma Aldrich) were dissolved in 20 mL of Millipore water (18.2 MΩ cm) under vigorous stirring to form a homogeneous solution. The solution was then transferred into a 30 mL Teflon-lined stainless-steel autoclave and maintained at 220 °C for 18 h before the reaction system was allowed to cool down to room temperature. The final product was washed several times with water and ethanol to remove any possible ions and finally suspended in ethanol.

**Synthesis of Co nanodisks.** Co nanodisks were synthesized using standard air-free procedures<sup>18</sup>. In a typical synthesis, 0.1 g of trioctylphosphine oxide (TOPO, Technical Grade, Sigma Aldrich) was degassed with argon (High purity) for 20 min in a three-neck flask, followed by the introduction of 15 mL of anhydrous *o*-dichloride benzene (DCB, Technical Grade, Sigma Aldrich) and 0.1 mL of oleylamine (OA, Technical Grade, Sigma Aldrich) under argon, heating to reflux (182 °C) and then rapidly injecting 0.54 g of cobalt carbonyl (Co<sub>2</sub>(CO)<sub>8</sub>, Co content ≥90%, Sigma Aldrich) containing 1–5% hexane diluted in 3 mL of DCB (precursor solution). After 10 min, the reaction was stopped by quenching in an ice water bath. The final products were processed by extracting the solution, washing several times with water and methanol to remove the possible ions and organic component, and finally suspending in argon-saturated water for storage.

**Synthesis of Ni nanodisks.** Ni nanodisks were synthesized using a standard air-free procedure<sup>43</sup>. In a typical synthesis, 0.257 g of nickel(II) acetylacetonate (Ni(acac)<sub>2</sub>, Technical Grade, Sigma Aldrich) and 0.109 g of tungsten hexacarbonyl (W(CO)<sub>6</sub>, 97%, Sigma Aldrich) were added to 7 mL of oleylamine in a two neck flask. Then the mixture was pre-heated to 60 °C under an argon atmosphere with strong magnetic stirring for the air degassing. After 30 min, the solution mixture was slowly heated up to 160 °C, and then immediately cooled down to room temperature in a water bath. Subsequently, the dark solution obtained was washed with a mixture of *n*-hexane and ethanol twice. The obtained product was separated by centrifugation, further washed twice and dried under ambient conditions to acquire dark powders. Finally, the Ni nanodisks powder was stored in an argon-saturated glass bottle for further use.

**Synthesis of Fe<sub>2</sub>O<sub>3</sub> nanodisks.** Fe<sub>2</sub>O<sub>3</sub> nanodisks were synthesized using standard hydrothermal procedures<sup>44</sup>. In a typical synthetic procedure, 0.8 g of Iron(III) nitrate nonahydrate (Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O, ACS Grade, Sigma Aldrich) and 1.0 g of urea (NH<sub>2</sub>CONH<sub>2</sub>, Sigma Aldrich) were dissolved in 70 mL of Millipore water. Then, 8.28 g of Tween 80 (C<sub>24</sub>H<sub>44</sub>O<sub>6</sub>, AR, Adamas-beta Chemical Co.) and 1.3 g of P123 (Poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol), Mav ~ 5800, Sigma Aldrich) were added under magnetic stirring. When Tween 80 and Pluronic amphiphilic triblock copolymer were dissolved completely, the obtained red solution was carefully transferred into a 100 mL Teflon-lined stainless-steel autoclave, then sealed and maintained at 180 °C for 24 h. After cooled to room temperature, the dark-red colloidal suspension was obtained. The precipitate was collected by centrifugation at 8000 rpm for 10 min, and then resuspended in the isometric mixture of distilled water and ethanol. The washing centrifugation process was repeated for at least three times. Finally, the Fe<sub>2</sub>O<sub>3</sub> nanodisks powder was stored in an argon-saturated glass bottle for further use.

**Assembly of Co/Ni/Fe<sub>2</sub>O<sub>3</sub> nanodisks on MoS<sub>2</sub>.** For the assembly of Co/Ni/Fe<sub>2</sub>O<sub>3</sub> nanodisks onto MoS<sub>2</sub>, the Co/Ni/Fe<sub>2</sub>O<sub>3</sub> nanodisks and MoS<sub>2</sub> solution with an appropriate mass ratio were mixed together in a 20 mL bottle. The reaction system was degassed with argon for at least 20 min. Then, it was ultrasonically treated for 24 h in a thermostat reaction system with a constant temperature of 4 °C, power of 800 W and frequency of 40 KHz. The final product was collected by extraction from the solution, washed with water several times to remove the possible ions and organic component, and finally suspended in argon-saturated water for storage.

**Synthesis of SA Co/Ni/Fe D 1T MoS<sub>2</sub>.** The Co/Ni/Fe<sub>2</sub>O<sub>3</sub> ND-MoS<sub>2</sub> solution was drop casted onto a carbon fiber paper electrode. Then, the electrode was immersed in a 0.5 M H<sub>2</sub>SO<sub>4</sub> solution, and the electrochemical leaching between 0.1 V to -0.4 V was performed for 50 cycles. The electrode was then dipped into an ethanol solution and sonicated for 30 min. The suspension was separated after being left to stand for 6 h. The entire process was repeated twice.

**Synthesis of Co NPs/MoS<sub>2</sub> by self-assembly.** Co NPs were obtained by a standard air-free procedures<sup>45</sup>. In the typical synthesis, 0.6 g of octadecylamine (ODA, Technical Grade, Acros Organics) and 0.2 g of TOPO were degassed with argon, and then 15 mL of DCB was added under argon. The resulting solution was heated to 182 °C, and 0.45 g Co<sub>2</sub>(CO)<sub>8</sub> dissolved in 3 mL of DCB was rapidly injected into the hot solution. After 5 min heating at 182 °C, a black colloidal solution was obtained. The particles were isolated by centrifugation and washed with alcohol. Then, the obtained Co NPs and MoS<sub>2</sub> solution with an appropriate

mass ratio were mixed together in a 20 mL conical flask. The reaction system was degassed with argon for at least 20 min. Then, it was ultrasonically treated for 24 h in a thermostat reaction system with a constant temperature of 4 °C, power of 800 W and frequency of 40 KHz. The final product was collected by extraction from the solution, washed several times with water to remove the possible ions and organic component, and finally suspended in argon-saturated water for storage.

**Synthesis of Co NPs/MoS<sub>2</sub> by in situ growth.** For the Co NPs/MoS<sub>2</sub> synthesized by a refined in situ growth method<sup>46</sup>, 0.1 mg of MoS<sub>2</sub> was suspended in 10 mL water, followed by adding 0.03 mg of cobalt (II) chloride hexahydrate (CoCl<sub>2</sub>·6H<sub>2</sub>O, Technical Grade, Sigma Aldrich). Then, 5 mL of freshly prepared sodium borohydride (NaBH<sub>4</sub>, Technical Grade, Adamas-beta Chemical Co.) solution was injected. The solution was shaken for 5 s and stayed for aging. After 1 h reaction, a black colloidal solution was obtained. The nanostructures were isolated by centrifugation and washed with water. Then, the obtained Co NPs and MoS<sub>2</sub> solution with an appropriate mass ratio were mixed together in a 20 mL conical flask. The reaction system was degassed with argon for at least 20 min. Then, it was ultrasonically treated for 24 h in a thermostat reaction system with a constant temperature of 4 °C, power of 800 W and frequency of 40 KHz. The final product was collected by extraction from the solution, washed several times with water to remove the possible ions and organic component, and finally suspended in argon-saturated water for storage.

**Synthesis of Co clusters/MoS<sub>2</sub>.** Co clusters/MoS<sub>2</sub> was synthesized according to a refined reported procedure<sup>47</sup>. In a typical synthesis, 24.7 mg of (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>·4H<sub>2</sub>O, 53.2 mg of CH<sub>4</sub>N<sub>2</sub>S and 0.3 mg of CoCl<sub>2</sub>·6H<sub>2</sub>O were dissolved in 20 mL of Millipore water under vigorous stirring to form a homogeneous solution. The solution was then transferred into a 30 mL Teflon-lined stainless-steel autoclave and maintained at 220 °C for 18 h before the reaction system was allowed to cool to room temperature. The final product was washed several times with water and ethanol to remove any possible ions and finally suspended in ethanol.

**Materials characterization.** TEM, HRTEM, and energy-dispersive X-ray (EDX) spectroscopy were performed on the FEI Tecnai G<sup>2</sup> F20 TEM operating at 200 kV. The samples were prepared by dropping ethanol dispersions of the samples onto 300 mesh carbon-coated copper grids and then evaporating the solvent. Fast Fourier transform (FFT) masked contrast refined HRTEM images were obtained using Gatan digital micrograph software. HRTEM images were acquired using a JEOL-ARM200F TEM operated at 200 kV. The attainable spatial resolution of the microscope was 78 pm with a probe spherical-aberration corrector. High-angle annular dark-field (HAADF) images were acquired with an illumination semi-angle of 25 mrad and probe current of 100 pA. The dwell time for image acquisition was set at 10 μs per pixel to ensure a desirable signal-to-noise ratio. The collection angles for the HAADF images were fixed at 90–250 mrad. To obtain high-quality scanning transmission electron microscopy (STEM) images with atomic resolution, SA Co-D 1T MoS<sub>2</sub> was pre-treated at 80 °C in a vacuum oven for 4 h to remove any organic ligands on its surface. The high-resolution STEM simulations were performed using the multi-slice JEMS software (copyright P.J.A. Stadelmann, EPFL, Switzerland). A supercell of ~15 × 8 Å was built using the coordinates supplied in Fig. 1d. The pixel sampling used for the supercell was 2048 × 2048. The electron optical parameters used in the simulation were consistent with experimental conditions, including an electron energy of 200 kV, spherical-aberration coefficient of 78 pm, illumination semi-angle of 25 mrad and probe current of 100 pA. The FFT-filtered images were obtained by transposition of the HRTEM images into reciprocal space. To form the FFT patterns, reciprocal spots from the patterns (typically-type reflections) were selected, masked with a five pixel filter, and then transformed into real space with inverse FFT. The powder XRD experiments were conducted on a Bragg-Brentano diffractometer (D8-tools, Germany), and the source was a Cu-Kα line at 0.15418 nm. The scanning speed was set to 8° per min. Inductively coupled plasma mass spectrometry (ICP-MS) data were determined using an ELAN 9000/DRC ICP-MS system (Perkinelmer, USA). X-ray photoelectron spectroscopy (XPS) was performed using an ESCALAB-250 instrument (Thermo Fisher Scientific, USA), performed with a monochromatic Al-Kα (1486.6 eV) radiation source and a hemisphere detector with an energy resolution of 0.1 eV. Peak positions were all corrected by the C 1 s spectrum at 284.8 eV. Atomic force microscope images were obtained by the deposition of sample on freshly cleaved mica and investigated by using tapping mode in air (Dimension Icon, Veeco Instruments/Bruker, Germany). The Raman measurements with an excitation laser line of 532 nm were performed using a WITTEC alpha 300 R Confocal Raman system and power of <0.1 mW to prevent the phase transition during measurement under ambient conditions.

**Electrochemical measurements.** The electrochemical measurements were performed using a glassy carbon (GC) rotating disk electrode (RDE, Pine research instrumentation) connected to a CHI760D potentiostat (Shanghai, Chenhua Co., China) in a three-electrode cell. The working electrode (WE) was prepared by loading the ink containing 20 μg of the catalyst onto a GC RDE (3 mm in diameter). An Ag/AgCl (KCl saturated) electrode and graphite rod (3 cm in diameter) were used as the reference and counter electrodes, respectively. All potentials were

calibrated to the RHE by the equation:

$$E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.059 \text{ pH} + 0.197 \quad (1)$$

LSV was conducted in Ar-saturated 0.5 M H<sub>2</sub>SO<sub>4</sub> solution between 0.1 and -0.6 V vs RHE to investigate the HER activity. The electrochemical impedance measurements were performed in the frequency range from 100 kHz to 0.1 Hz at an overpotential of 250 mV. All the impedance data were fitted by a simplified Randles circuit to extract the series and charge-transfer resistance. CV was conducted between 0.1 and -0.3 V vs RHE at 50 mV s<sup>-1</sup> to investigate the cycling stability. A long-term stability test was recorded by taking a chronoamperometric curve at a constant overpotential of 150 mV. The onset overpotential was determined based on the potential when the current density reached 10 mA cm<sup>-2</sup>. All data are presented without IR-compensation. All the electrochemical tests were performed at room temperature.

**XAFS measurements.** X-ray absorption spectra were collected at Beijing Synchrotron Radiation Facility (BSRF) on beamline 1W1B and Shanghai Synchrotron Radiation Facility (SSRF) on beamline BL14W1. The storage ring is operated at electron energy of 2.5 GeV with a beam current of 250 mA. A Si (111) double-crystal monochromatic was applied. The beam size used at the sample position was ~900 × 300 μm<sup>2</sup>. All the data were collected at ambient temperature applied in the transmission mode. Curve fitting and data analysis were performed with Artemis and IFEFFIT software<sup>48,49</sup>. The energy resolution (ΔE/E) for the incident X-ray photons was estimated to be 2 × 10<sup>-4</sup>. Conventional transmission mode was adopted for the Co, Ni and Fe K-edge EXAFS measurements. To ascertain the reproducibility of the experimental data, at least two scan sets were collected and compared for each sample.

**XAFS analysis.** Each sample of XAS data was aligned, and processed using the Athena program. Spectra were baseline corrected using a linear pre-edge function between -200 and -50 eV and normalized using a linear or quadratic function between 150 and 700 eV, including a flattening function in the post-edge region. The XAFS signal was isolated from the adsorption edge background using a fit to a cubic spline with nodes defined by the AUTOBK function in IFEFFIT, with a *k*-weight of 3 and with the Rbkg parameter set to 1. Fourier transformations of *k*<sup>3</sup>-weighted spectra were using a Kaiser-Bessel window with a 1 Å<sup>-1</sup> sill width. The magnitude parts of the Fourier transformed spectra are shown throughout this manuscript with a radial distance scale that is not corrected for phase shift.

For EXAFS fitting, theoretical scattering paths were calculated with FEFF6 using Artemis. All EXAFS spectra were fit for distances (ΔR), CN, and mean-square displacement of interatomic distance (σ<sup>2</sup>) using the Artemis interface with a fixed amplitude reduction factor (S<sub>0</sub><sup>2</sup>) of 0.707 ~ 1.000. The parameters such as interatomic distance (*R*), coordination number (CN), the difference in threshold energy (ΔE<sub>0</sub>) and Debye-Waller factor (σ<sup>2</sup>) were first established with reasonable guesses, and then were fitted in R-space. The error in the overall fits was determined using the R-factor, the goodness-of-fit parameter, in which R-factor = Σ(χ<sub>data</sub> - χ<sub>fit</sub>)<sup>2</sup>/Σ(χ<sub>data</sub>)<sup>2</sup> and good fits occur for R-factor < 0.05.

**Mechanism of phase transition of MoS<sub>2</sub>.** The first-principle calculations about structural stability and phase transition were carried out by using accurate frozen-core full-potential projector augmented-wave pseudopotentials method on the basis of DFT, as implemented in the VASP code<sup>50-52</sup>. The 3d and 4s electrons of Co atom, 4p, 4d, and 5s electrons of Mo atom, and 3s and 3p electrons of S atom were treated as the valence electrons. We used the generalized gradient approximation (GGA) with Perdew-Burke-Ernzerhof (PBE) parameterization for the exchange and correlation potential<sup>53</sup>. A kinetic energy cutoff of 500 eV for the plane wave expansion and a Monkhorst-Pack grid with a *k*-point spacing of 0.01 Å<sup>-1</sup> were found to be sufficient to ensure that the total energy was converged at 1 meV/atom level. The slab model with a vacuum layer larger than 20 Å was used to avoid the artificial coupling between the periodically repeated cells along *z* direction. The structures were fully optimized by using the conjugate gradient algorithm until the maximum energy difference converge to 10<sup>-6</sup> eV. The effect of spin polarization was considered in our calculation.

**Hydrogen binding free-energy calculations.** All theoretical calculations about hydrogen-binding free energy were performed using DFT by DMOL3 code<sup>54,55</sup>. In the DFT calculations, the all-electron Kohn-Sham wave functions were expanded in the double numerical polarized atomic orbital basis, and GGA with PBE for describing the exchange and correlation energy was employed. Effective core potentials were considered during calculations. Self-consistent field procedure was done until the change of energy was > 10<sup>-6</sup> Hartree, and the geometrical optimization of the structure was done with an energy convergence criterion of 10<sup>-5</sup> Hartree. Long range nonlocal effects were taken into account by applying semi-empirical dispersion-correction approach through the DFT-D scheme with Grimme parameters<sup>56</sup>. In our models, the experimental in-plane lattice constant of 3.16 Å for the in-plane unit cell of MoS<sub>2</sub> monolayers has been used. A vacuum region of 20 Å along the *z* direction is enough to ensure negligible interaction between the MoS<sub>2</sub> monolayer and its periodic images. We used one cobalt dopant in 2 × 2, 3 × 3, 4 × 4, 5 × 5 and 6 × 6 MoS<sub>2</sub> supercell as the models to present different Co doping coverage, corresponding to

8.33%, 3.70%, 2.08%, 1.33%, and 0.93%, respectively. The spin-unrestricted calculations were carried out. The Brillouin zone was sampled by Monkhorst-Pack 10 × 10 × 1, 7 × 7 × 1, 5 × 5 × 1, 4 × 4 × 1, and 3 × 3 × 1 *k*-point grids for 2 × 2, 3 × 3, 4 × 4, 5 × 5, and 6 × 6 MoS<sub>2</sub> supercell, respectively<sup>57</sup>.

**Charge density difference calculations.** The charge density difference (Δρ) for Co adsorbed MoS<sub>2</sub> system was obtained using the following equation: Δρ = ρ(MoS<sub>2</sub> + Co) - ρ(MoS<sub>2</sub>) - ρ(Co), where ρ(MoS<sub>2</sub> + Co), ρ(MoS<sub>2</sub>) and ρ(Co) are the total charge density of the Co adsorbed MoS<sub>2</sub> system, MoS<sub>2</sub> substrate and single Co atom, respectively. The charge density difference quantifies the redistribution of electron charge due to the interaction between adatom Co and MoS<sub>2</sub> substrate.

## Data availability

The data that support the findings of this study are available from the corresponding authors upon reasonable request.

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## Author contributions

X.Q.C., S.J.G., and W.T.Z. co-directed this research. X.Q.C. and K.Q. designed preparation and characterization of the material. K.Q., S.X., and N. B.L. synthesized the materials. K.Q., F.L., M.C.L., K.W., and N.B.L. performed the materials property characterization. L.G., W.Z., Q.H.Z. and Y.G. performed the TEM and HAADF-STEM characterization. S.S.Y., X.F.F., H.H.H., and P.L. carried out and analyzed the theoretical results. J.Y.M., K.Q., and L.R.Z. designed and analyzed the XAS experiments. K.Q. and M.C.L. wrote the manuscript. X.Q.C., S.J.G. and W.T.Z. supervised the project and established the final version of the paper. All authors discussed the results and commented on the manuscript. All authors have approved the final version of the manuscript.

## Competing interests

The authors declare no competing interests.

## Additional information


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Correspondence and requests for materials should be addressed to X.C., S.G. or W.Z.

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