Magnetic Co-Doped MoS$_2$ Nanosheets for Efficient Catalysis of Nitroarene Reduction

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Supporting Information

ABSTRACT: Co-doped MoS$_2$ nanosheets have been synthesized through the hydrothermal reaction of ammonium tetrathiomolybdate and hydrazine in the presence of cobalt acetate. These nanosheets exhibit a dominant metallic 1T phase with cobalt ion-activated defective basal planes and S-edges. In addition, the nanosheets are dispersible in polar solvents like water and methanol. With increased active sites, Co-doped MoS$_2$ nanosheets exhibit exceptional catalytic activity in the reduction of nitroarenes by NaBH$_4$ with impressive turnover frequencies of 8.4, 3.2, and 20.2 min$^{-1}$ for 4-nitrophenol, 4-nitroaniline, and nitrobenzene, respectively. The catalyst is magnetic, enabling its easy separation from the reaction mixture, thus making its recycling and reusability simple and efficient. The enhanced catalytic activity of the Co-doped 1T MoS$_2$ nanosheets suggests that incorporation of cobalt ions in the MoS$_2$ lattice is the major reason for the efficiency of the catalyst. The dopant, Co, plays a dual role. In addition to providing active sites where electron transfer is assisted through redox cycling, it renders the nanosheets magnetic, enabling their easy removal from the reaction mixture.

1. INTRODUCTION

Two-dimensional (2D) MoS$_2$ nanosheets$^1$ have garnered interest as a potential noble-metal-free catalyst for the electrochemical generation of hydrogen from water$^2$ and hydrodesulfurization of petroleum.$^3$ Theoretical and experimental studies indicate that the catalytic activity of the thermodynamically stable 2H polymorph of MoS$_2$ is associated with its metallic edges, whereas its semiconducting basal plane is catalytically inert.$^4, 5$

In this context, nanostuctures of MoS$_2$ amorphous$^6, 7$ crystalline, and vertically aligned structures$^8, 9$ have been explored to maximize the number of active edge sites. MoS$_2$ is also hybridized with conducting/semiconducting/magnetic materials (graphene$^{10–13}$/CoSe$_2^{14–17}$/CoS$_2^{18}$, $^{20}$/CoS$_2^{21–24}$/CdS$^{25}$, $^{26}$/Fe$_3$O$_4^{27}$) to enhance the catalytic activity through synergetic coupling effects. Metastable, intrinsically metallic, octahedral 1T MoS$_2$ obtained through exfoliation of trigonal prismatic 2H MoS$_2$ has proven to be an excellent catalyst for H$_2$ evolution reactions as the 1T phase facilitates electrode kinetics by increasing the electric conductivity and proliferation of the catalytic active sites.$^{28–30}$ Introducing transition metal ions (Co, Ni, Fe) into the MoS$_2$ matrix has been the classic route to maximize the catalytic activity of MoS$_2$ as the doped ions alter the electronic properties at the coordinatively unsaturated catalytic S-edges.$^{31–33}$ These strategies have been designed, largely, to either optimize the density of active edge sites by reducing the dimensions along the z direction or xy direction (nanostructures) or increase the conductivity by stabilizing the 1T MoS$_2$ polytype.$^{19, 28, 29}$ The question is, would it be possible to tune both the structural features and electronic properties simultaneously to increase the catalytic active sites? Doping 2H MoS$_2$ with Co has been shown to increase its catalytic efficiency through increased active sites in the basal planes in addition to edges.$^{34}$ It would be of interest to prepare Co-doped 1T MoS$_2$ because in addition to all of the above effects, there would be increased conductivity.

One of the standard reactions to test the electron transfer catalytic action is the reduction of nitroarenes by NaBH$_4$. Nitroarenes, with aromatic rings associated with H-bonding $\equiv$NH$_2$ and $\equiv$OH groups, enable the reduction to be carried out in water, making it a green reaction. This study demonstrates a single-step robust strategy to synthesizing 1T Co-doped MoS$_2$ nanosheets. With increased active sites, Co-doped MoS$_2$ nanosheets exhibit exceptional catalytic activity in the reduction of nitroarenes. The observed turnover frequency (TOF) is far superior in comparison to that of other MoS$_2$ architectures and noble-metal-based catalysts, reported so far.

2. RESULTS AND DISCUSSION

The XRD pattern of as-prepared Co-doped MoS$_2$ nanosheets (Figure 1A,a) exhibits a broad 002 reflection at 11.0 Å, indicating the presence of guest species in the interlayer.$^{35, 36}$
The guest entity could possibly be NH₃/NH₄⁺ ions released as byproducts of hydrazine used as a reductant in the hydrothermal reaction. On treating Co-doped MoS₂ nanosheets with 1 N HCl solution, the 002 reflection (Figure 1A,b) disappears, indicating deintercalation of the guest species. However, the low intensity of the 002 reflection or its absence (Figure 1A,a,b) suggests that Co-doped MoS₂ nanosheets are poorly ordered along the stacking direction and comprise largely exfoliated layers. The asymmetric 2D reflections at 2θ = 33 and 57° reveal the presence of stacking faults within the few-layered Co-doped MoS₂. The undoped MoS₂ is also poorly ordered and exhibits increased basal spacing due to NH₃/NH₄⁺ intercalation (Figure 1A,c).

The Raman spectrum of Co-doped MoS₂ (Figure 1B) exhibits the in-plane E₂g (380 cm⁻¹) and out-of-plane A₁g (406 cm⁻¹) Mo–S vibration modes, characteristic of the MoS₂ layered structure. An additional peak at 220 cm⁻¹ in Figure S1 indicates the presence of stacking faults within the few-layered Co-doped MoS₂. The undoped MoS₂ is also poorly ordered and exhibits increased basal spacing due to NH₃/NH₄⁺ intercalation (Figure 1A,c).

The XPS spectra of acid-treated Co-doped MoS₂ (Figure S2) indicate that whereas the nitrogen-containing species, NH₃ and NH₄⁺ ions, are absent, Co²⁺ and 1T phase of MoS₂ nanosheets are retained. These further suggest that Co²⁺ is present in the MoS₂ lattice. Hydrothermally synthesized MoS₂ has been shown to have a defective basal plane as well as unsaturated S-edges. Recent studies by Liu et al. demonstrate that Co²⁺ is doped at S vacancies in basal planes as well as at the unsaturated S-edges.

The magnetic hysteresis loop measured on the powder sample indicates a weak ferromagnetic behavior (Figure 3). The saturation magnetization (Mₛ) at 300 K of Co-doped MoS₂ nanosheets is 0.0029 emu g⁻¹, which is comparable to that of exfoliated 1T MoS₂ reported in the literature. Because our control 1T MoS₂ is nonmagnetic, it is fair to assume that the magnetism in Co-doped MoS₂ arises as a consequence of doping. The magnetism in monolayer MoS₂ and its doped analogues depends on the nature of edges, type of edge defects, lattice strain, and the dopant concentration. Theoretical
calculations by Wang et al.\textsuperscript{44} reveal that low concentrations of 4 and 6\% of \textsuperscript{6}Co\textsuperscript{2+} doping in the Mo vacant sites of the basal planes result in stable magnetic moments at room temperature. Yun et al.\textsuperscript{45} and Saab et al.\textsuperscript{46} also reported tuning of electronic and magnetic properties due to doping of metal ions in the MoS\textsubscript{2} lattice. The very low M\textsubscript{S} observed for Co-doped MoS\textsubscript{2} suggests that the weak ferromagnetism here originates from the strain in the layer rather than from ordering of Co\textsuperscript{2+} ions. Co-doped MoS\textsubscript{2} (Figure 3) as well as the acid-leached product is weakly magnetic, suggesting that Co\textsuperscript{2+} ions are doped in the MoS\textsubscript{2} layers. In addition, the presence of Co\textsuperscript{2+} in the MoS\textsubscript{2} lattice could be the reason for the retention of metastable 1T structure even after deintercalation of the intercalants (SI, Figure S2). All of these results indicate that Co\textsuperscript{2+} is possibly doped in the basal plane and S-edge planes of MoS\textsubscript{2} layers.

Clusters of layers are observed in the SEM image (Figure 4a) of as-synthesized Co-doped MoS\textsubscript{2}. The bright-field transmission electron microscopy (TEM) image (Figure 4b) indicates that the transparent layers are few-layer thick and few hundred nanometers in lateral dimensions. The HRTEM image (Figure 4c) shows lattice fringes with a spacing of 1.1 nm, which correlate with the basal spacing observed in the XRD pattern (Figure 1a), suggesting the presence of intercalants. The HRTEM image in Figure 4d clearly shows that the layers are crystalline, exhibiting (100) lattice planes. Except for the circled regions representing the 2H phase, the layers largely exist as the 1T polytype.\textsuperscript{\textsuperscript{43}}

Figure 5 schematically depicts the catalytic reduction of nitroarenes. Catalytic performance of Co-doped MoS\textsubscript{2} in the reduction of 4-nitrophenol (4-NP) in water is summarized in Figure 6a–d. UV–visible absorption spectra (Figure 6a) of the reaction mixture indicate that 4-nitrophenol converts to 4-aminophenol within 7 min. The absorption peak at 400 nm is due to the nitro phenolate ion, and the intensity of this peak decreases with time and disappears completely at 7 min. Peaks at 235 and 308 nm emerge due to the formation of amino phenolate, and their intensities increase with time. The log (absorbance) versus time plot (Figure 6e) is linear (R\textsuperscript{2} = 0.979), indicating a pseudo-first-order kinetics with a rate constant of 1.976 \times 10^{-3} s\textsuperscript{-1}. The turnover frequency (TOF) values, defined as the number of moles of the product formed per unit time per mole of the catalyst, of the materials studied are given in Table 2.

Apart from exhibiting a high TOF, the catalyst also has the advantage of recyclability. As the catalyst is weakly magnetic, it is easily separated from the reaction mixture using a strong magnet, enabling easy recycling (Figure 5). The catalytic activity of Co-doped MoS\textsubscript{2} remains nearly constant over a number of cycles (Figure 6f). The morphology and composition of the catalyst remain almost the same after six cycles of catalysis. Earlier attempts to make MoS\textsubscript{2}-based catalysts magnetic have been through hybridization of MoS\textsubscript{2} nanosheets with magnetic nanoparticles such as Fe\textsubscript{3}O\textsubscript{4}.\textsuperscript{27} One

| binding energy (eV) | Mo 3d | phase | S 2p | Co 2p | N 1s |
|---------------------|-------|-------|------|-------|------|
| Mo\textsubscript{0.83}Co\textsubscript{0.16}S\textsubscript{2}(NH\textsubscript{3})\textsubscript{0.38} | 228.6 & 231.8 | 1T | 161.49 & 162.80 | 779.2 & 794.0 | 397.6 – NH\textsubscript{3} |
| Mo\textsubscript{0.85}Co\textsubscript{0.15}S\textsubscript{2}(NH\textsubscript{4})\textsubscript{0.3} | 229.0 & 232.5 | 2H | 163.97 & 164.77 | 400.4 – NH\textsubscript{4}\textsuperscript{+} |

Figure 3. Hysteresis loop of the Co-doped MoS\textsubscript{2} nanosheets at 300 K.

Figure 4. (a) SEM image, (b) low-magnification bright-field TEM image, and (c, d) HRTEM images of Co-doped MoS\textsubscript{2}.

Figure 5. Schematic representation of the catalytic reduction of nitroarenes using Co-doped 1T MoS\textsubscript{2}.  

Table 1. Summary of the Binding Energies of Mo, S, Co and N in Co-doped MoS\textsubscript{2}.
of the shortcomings of such approaches is the increased net weight of the catalyst because the magnetic component of the hybrid does not provide sites for catalytic action. Here, the advantage is that the dopant that improves the catalytic efficiency also makes the catalyst magnetic.

Treating Co-doped MoS2 with an acid leads to deintercalation of interlayer NH3/NH4+ and removal of about 30% of Co2+, which were either intercalated or in the edge planes. Catalytic reduction of 4-NP using acid-leached Co-doped MoS2 exhibits a slight decrease in catalytic activity (Table 2). In contrast, ammoniated 1T-MoS2 synthesized in the absence of a cobalt source exhibits relatively very poor catalytic activity toward 4-NP reduction (Table 2). The comparison of the catalytic activities (Table 2) of the catalysts used in 4-NP reduction suggests that incorporation of cobalt ions in the MoS2 lattice is crucial to maximizing the efficiency of the catalyst.

Figure 6b,c traces the reduction of nitroaniline and nitrobenzene, respectively, in the presence of as-prepared Co-doped MoS2. The results show that the catalyst is universally effective in the reduction of nitro groups in different substrates and in at least two polar solvents. In fact, the catalyst is most efficient in the reduction of nitrobenzene, a reaction that is of importance in the removal of toxic nitrobenzene from effluents. In all of the cases, reduction of nitroarene does not occur in the absence of the catalyst.

In comparison to what has so far been reported in the literature (Table 3), the enhanced TOF and recyclability make Co-doped MoS2 a superior catalyst. The TOF of Co-doped MoS2 is 1 order greater than that of the best MoS2-based catalyst and ∼20% higher than the best value reported so far.

In Co-doped MoS2, Co2+ takes residence at the coordinately unsaturated sulfur vacancies on the basal plane and edge sites.10,58 This leads to a conversion of a fraction of Mo4+ to Mo3+, thus stabilizing the 1T polytype.15 Doped Co2+ distorts the close-packed sulfur layer of MoS2 and induces lattice strain.39,60 These sites would lower the reaction free energy.28 Nitroarenes are adsorbed at the strained active sites of the MoS2 surface.39–61 At these sites, the electron transfer to the substrate is facilitated by Co2+/Co3+ redox couple. The electrons generated by the hydrolysis of NaBH4 are transferred...
to the Co\textsuperscript{2+}-accommodated basal and edge sites of 1T MoS\textsubscript{2} and are promoted into the MoS\textsubscript{2} conduction band.\textsuperscript{59} The Co-substituted sites not only instigate faster electron transfer for nitroarene reduction through reversible reduction–oxidation reactions but also serve as an electron reserve and aid in the retention of the 1T phase with enhanced electrical conductivity.

The role of Co in improving the catalytic efficiency is very clear from the fact that the control MoS\textsubscript{2}, which has retention of the 1T phase with enhanced electrical conductivity, exhibited exceptional catalytic activity toward reduction of nitroarenes at ambient temperature. The preparation was repeated using 0.107 and 0.054 g of cobalt acetate to vary the cobalt content in the product.

### 4.3. Preparation of MoS\textsubscript{2} Nanosheets

As a control experiment, the synthesis was repeated in the absence of cobalt acetate, which results in ammoniated MoS\textsubscript{2} nanosheets.

### 4.4. Reduction of Nitroarenes Using Co-Doped MoS\textsubscript{2} Nanosheets as a Catalyst

#### 4.4.1. Reduction of 4-Nitrophenol (4-NP)

Cobalt acetate (0.214 g) was dissolved in 45 mL of water. Ammonium tetrahexylammonium (0.442 g) was added to the pink Co\textsuperscript{2+} solution, and the mixture was stirred for 15 min. Hydrazine hydrate (5 mL) was added to the solution, and stirring was continued for another 15 min. The black-brown solution was transferred to a teflon-lined autoclave and sealed in a stainless steel canister. The autoclave was heated in a hot-air oven at 180 °C for 24 h and cooled to room temperature under ambient conditions. The pH of the supernatant at the end of the reaction was ∼12. The black precipitate was washed with distilled water till the pH of the washings is ∼7, followed by washing with acetone. The product was dried in air at ambient temperature. The preparation was repeated using Co-MoS\textsubscript{2} nanosheets as a catalyst, and (c) acid-treated Co-MoS\textsubscript{2} nanosheets.

#### 4.4.2. Reduction of 4-nitroaniline (4-NA)

The catalyst (10 mg) was dispersed in 100 mL of water by stirring for 1 h. 4-NA (192 mg, 37 mM) was dissolved in 100 mL of the catalytic dispersion. An excess of NaBH\textsubscript{4} (1.51 g, 400 mM) was added with constant stirring. The progress of the reaction was monitored by measuring the absorbance at 380 nm. The catalyst (10 mg) was dispersed in 100 mL of methanol by stirring for 1 h. 4-NA (192 mg, 14 mM) was dissolved in 100 mL of the catalytic dispersion. An excess of NaBH\textsubscript{4} (1.51 g, 400 mM) was added with constant stirring. The progress of the reaction was monitored by measuring the absorbance at 400 nm.

#### 4.4.3. Reduction of Nitrobenzene (NB)

The catalyst (10 mg) was dispersed in 100 mL of methanol by stirring for 1 h. Nitrobenzene (0.52 mL, 50 mM) was dissolved in the dispersion. An excess of NaBH\textsubscript{4} (1.51 g, 400 mM) was added with constant stirring. The progress of the reaction was monitored by measuring the absorbance at 259 nm.

### 4.5. Characterization

All of the samples were analyzed by recording powder X-ray diffraction (XRD) patterns using a PANalytical X\textsuperscript{pert} pro diffractometer (Cu Kα radiation, \ DOI: 10.1021/acsomega.7b00848

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secondary graphite monochromator, scanning rate of 1° 2θ/min. The amount of Co2+ was estimated by a Varian AA240 atomic absorption spectrometer using a Co hollow cathode lamp in an air–acetylene flame at a wavelength of 324.4 nm. X-ray photoelectron spectroscopy (XPS) measurements were carried out with Kratos axis Ultra DLD. All spectra were acquired with Tecnai T20 operated at 200 kV. UV microscope equipped with energy-dispersive X-ray spectroscopy (EDS). Transmission electron microscopy (TEM) images were acquired with Tecnai T20 operated at 200 kV. UV−visible spectra of the reaction mixtures were recorded on HORIBA Jobin-Yvon JY-35 spectrophotometer. The UV−visible spectra were acquired with Tecnai T20 operated at 200 kV. UV−visible spectrometer. The Raman spectrum of the samples was recorded on HORIBA Jobin-Yvon LabRAM HR800 at 532 nm excitation wavelength. Isothermal magnetization [M vs H] was measured using a superconducting quantum interference device (SQUID) magnetometer.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.omega.7b00848.

Raman spectrum of Co-doped MoS2 and XPS data of acid leached Co-doped MoS2 (PDF)

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Notes
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REFERENCES

(1) Chhowalla, M.; Shin, H. S.; Eda, G.; Li, L.-J.; Loh, K. P.; Zhang, H. The Chemistry of Two-Dimensional Layered Transition Metal Dichalcogenide Nanosheets. Nat. Chem. 2013, 5, 263−275.
(2) Hinnemann, B.; Moses, P. G.; Bonde, J.; Jørgensen, K. P.; Nielsen, J. H.; Horch, S.; Chorkendorff, I.; Nørskov, J. K. Biomimetic Hydrogen Evolution: MoS2 Nanoparticles as Catalyst for Hydrogen Evolution. J. Am. Chem. Soc. 2005, 127, S308−S309.
(3) Chia, X.; Eng, A. Y. S.; Ambrozi, A.; Tan, S. M.; Pumera, M. Electrochemistry of Nanostructured Layered Transition-Metal Dichalcogenides. Chem. Rev. 2015, 115, 1941−1966.
(4) Jaramillo, T. F.; Jørgensen, K. P.; Bonde, J.; Nielsen, J. H.; Horch, S.; Chorkendorff, I. Identification of Active Edge Sites for Electrochemical H2 Evolution from MoS2 Nanocatalysts. Science 2007, 317, 100−102.
(5) Prins, R.; De Beer, V. H. J.; Somorjai, G. A. Structure and Function of the Catalyst and The Promoter In Co–Mo Hydrodesulfurization Catalysts. Catal. Rev. 1989, 31, 1−41.
(6) Grange, P. Catalytic Hydrodesulfurization. Catal. Rev. 1980, 21, 135−181.
(7) Benck, J. D.; Chen, Z. B.; Kuritzky, L. Y.; Forman, A. J.; Jaramillo, T. F. Amorphous Molybdenum Sulfide Catalysts for Electrochemical Hydrogen Production: Insights Into The Origin of Their Catalytic Activity. ACS Catal. 2012, 2, 1916−1923.
(8) Merki, D.; Hu, X. L. Recent Developments of Molybdenum and Tungsten Sulphides As Hydrogen Evolution Catalysts. Energy Environ. Sci. 2011, 4, 3878−3888.
(9) Morales-Guio, C. G.; Hu, X. L. Amorphous Molybdenum Sulphides As Hydrogen Evolution Catalysts. Acc. Chem. Res. 2014, 47, 2671−2681.
(10) Bonde, J.; Moses, P. G.; Jaramillo, T. F.; Nørskov, J. K.; Chorkendorff, I. Hydrogen Evolution on Nano-Particulate Transition Metal Sulphides. Faraday Discuss. 2012, 5, 219−231.
(11) Kibsgaard, J.; Chen, Z. B.; Reinecke, B. N.; Jaramillo, T. F. Engineering the Surface Structure of MoS2 to Preferentially Expose Active Edge Sites for Electrocatalysis. Nat. Mater. 2012, 11, 963−969.
(12) Xie, J.; Zhang, H.; Li, S.; Wang, R.; Sun, X.; Zhou, M.; Zhou, J.; Lou, X. W.; Xie, Y. Defect-Rich MoS2 Ultrathin Nanosheets with Additional Active Edge Sites for Enhanced Electrocatalytic Hydrogen Evolution. Adv. Mater. 2013, 25, 5807−5813.
(13) Xie, J.; Zhang, J.; Li, S.; Grote, F.; Zhang, X.; Zhang, H.; Wang, R.; Lei, Y.; Pan, B.; Xie, Y. Controllable Disorder Engineering in Oxygen- Incorporated MoS2 Ultrathin Nanosheets for Efficient Hydrogen Evolution. J. Am. Chem. Soc. 2013, 135, 17881−17888.
(14) Kong, D.; Wang, H.; Cha, J. J.; Pasta, M.; Koski, K. J.; Yao, J.; Cui, Y. Synthesis of MoS2 and MoS2 Films with Vertically Aligned Layers. Nano Lett. 2013, 13, 1341−1347.
(15) Wang, H.; Lu, Z.; Xu, S.; Kong, D.; Cha, J. J.; Zhang, G.; Hsu, P.-C.; Yan, K.; Bradshaw, D.; Prinz, F. B.; Cui, Y. Electrochemical Tuning of Vertically Aligned MoS2 Nanofilms and Its Application In Improving Hydrogen Evolution Reaction. Proc. Natl Acad. Sci. U.S.A. 2013, 110, 19701−19706.
(16) Li, Y.; Wang, H.; Xie, L.; Liang, Y.; Hong, G.; Dai, H. MoS2 Nanoparticles Grown on Graphene: An Advanced Catalyst for The Hydrogen Evolution Reaction. J. Am. Chem. Soc. 2011, 133, 7296−7299.
(17) Wang, H. T.; Lu, Z.; Kong, D.; Sun, J.; Hyneel, T. M.; Cui, Y. Electrochemical Tuning of MoS2 Nanoparticles on Three-Dimensional Substrate for Efficient Hydrogen Evolution. ACS Nano 2014, 8, 4940−4947.
(18) Jeffrey, A. A.; Rao, S. R.; Rajamath, M. Preparation of MoS2 Reduced Graphene Oxide (rGO) Hybrid Paper For Catalytic Applications by Simple Exfoliation-Costacking. Carbon 2017, 112, 8−16.
(19) Wang, F. Z.; Zheng, M. J.; Zhang, B.; Zhu, C. Q.; Li, Q. J.; Ma, L.; Shen, W. Z. Ammonia Intercalated Flower-like MoS2 Nanosheet Film As Electrocatalyst For Highly Efficient and Stable Hydrogen Evolution. Sci. Rep. 2016, 6, No. 31092.
(20) Gao, M.-R.; Liang, J.-X.; Zheng, Y.-R.; Xu, Y.-F.; Jiang, J.; Gao, Q.; Li, J.; Yu, S.-H. An Efficient Molybdenum Disulfide/Cobalt Diselenide Hybrid Catalyst For Electrochemical Hydrogen Generation. Nat. Commun. 2015, 6, No. 5982.
(21) Huang, J.; Hou, D.; Zhou, Y.; Zhou, W.; Li, G.; Tang, Z.; Lia, L.; Chen, S. MoS2 Nanosheet-Coated CoS2 Nanowire Arrays on Carbon Cloth As Three-Dimensional Electrodes For Efficient Electrocatalytic Hydrogen Evolution. J. Mater. Chem. A 2015, 3, 22886−22891.
(22) Ranjith, B.; Jin, Z.; Shin, S.; Kim, S.; Lee, S.; Min, Y.-S. Catalytic Effects of CoS2 on the Activity of the MoS2 Catalyst for Electrochemical Hydrogen Evolution. Langmuir 2017, 33, 5626−5635.
(23) Wang, W.; Li, L.; Wu, K.; Zhu, F.; Tan, S.; Liu, Y.; Yang, Y. Highly Selective Catalytic Conversion of Phenols to Aromatic Hydrocarbons on CoS2/MoS2 Synthesized using a Two Step Hydrothermal Method. RSC Adv. 2016, 6, 31265−31271.
(24) Sorribes, I.; Liu, L.; Corma, A. Nanolayered Co-Mo-S Catalysts for Chemoselective Hydrogenation of Nitroarenes. ACS Catal. 2017, 7, 2698−2708.
(25) Yin, X.-L.; Li, L.-L.; Jiang, W. J.; Zhang, Y.; Zhang, X.; Wan, L.-J.; Hu, J.-S. MoS2/CoS2 Nanosheets-on-Nanorod Heterostructure for Highly Efficient Photocatalytic H2 Generation under Visible Light Irradiation. ACS Appl. Mater. Interfaces 2016, 8, 15258−15266.
(26) Liu, Y.; Yu, Y.-X.; Zhang, W.-D. MoS2/Cds Heterojunction with High Photoelectrochemical Activity for H2 Evolution under Visible Light: The Role of MoS2. J. Phys. Chem. C 2013, 11, 12949−12957.
(27) Lin, T.; Wang, J.; Guo, L.; Fu, F. FeO4@MoS2 Core−Shell Composites: Preparation, Characterization and Catalytic Application. J. Phys. Chem. C 2015, 119, 13658−13664.
(28) Voiry, D.; Yamaguchi, H.; Li, J.; Silva, R.; Alves, D. C. B.; Fujita, T.; Chen, M.; Asea, T.; Shenoy, V. B.; Eda, G.; Chhowalla, M. Enhanced Catalytic Activity in Strained Chemically Exfoliated WS\textsubscript{2} Nanosheets for Hydrogen Evolution. Nat. Mater. 2013, 12, 850–855.

(29) Lükowski, M. A.; Daniel, A. S.; Meng, F.; Fortiaca, A.; Li, L.; Jin, S. Enhanced Hydrogen Evolution Catalysis from Chemically Exfoliated Metallic MoS\textsubscript{2} Nanosheets. J. Am. Chem. Soc. 2013, 135, 10274–10277.

(30) Wang, Y.; Carey, B. J.; Zhang, W.; Chrimes, A. F.; Chen, L.; Kalantar-Zadeh, K.; Ou, J. Z.; Daeneke, T. Intercalated 2D MoS\textsubscript{2} Utilizing a Simulated Sun Assisted Process: Reducing the HER Overpotential. J. Phys. Chem. C 2016, 120, 2447–2455.

(31) Yan, Y.; Xia, Y. X.; Xu, Z.; Wang, X. Recent Development of Molybdenum Sulphides as Advanced Electrocatalysts For Hydrogen Evolution Reaction. ACS Catal. 2014, 4, 1693–1705.

(32) Merki, D.; Vrubel, H.; Rovelli, L.; Fierro, S.; Hu, X. L. Fe, Co, and Ni Ions Promote The Catalytic Activity of Amorphous Molybdenum Sulfide Films For Hydrogen Evolution. Chem. Sci. 2013, 3, 2515–2525.

(33) Wang, H.; Yuan, H.; Hong, S. S.; Li, Y.; Cui, Y. Physical and Chemical Tuning of Two-Dimensional Transition Metal Dichalcogenides. Chem. Soc. Rev. 2015, 44, 2664–2680.

(34) Liu, G.; Robertson, A. W.; Li, M. M.-J.; Kuo, W. C. H.; Darby, M. T.; Muhieddine, M. H.; Lin, Y.-C.; Suenga, K.; Stamatakis, M.; Warner, J. H.; Tsang, S. C. E. MoS\textsubscript{2} Monolayer Catalyst Doped with Isolated Co Atoms For The Hydrodeoxygenation Reaction. Nat. Chem. 2017, 9, 810–816.

(35) Jeffrey, A. A.; Nethravathi, C.; Rajamathi, M.; Two-Dimensional Nanosheets and Layered Hybrids of MoS\textsubscript{2} and WS\textsubscript{2} through Exfoliation of Ammoniated MS\textsubscript{2} (M = Mo, W). J. Phys. Chem. C 2014, 118, 1386–1396.

(36) Dungey, K. E.; Curtis, M. D.; Penner-Hahn, J. E. Structural Characterization and Thermal Stability of MoS\textsubscript{2} Intercalation Compounds. Chem. Mater. 1998, 10, 2125–2161.

(37) Warren, B. E.; Bodenstein, P. The Diffraction Pattern of Fine Particle Carbon Blacks. Acta Crystallogr. 1965, 18, 282–286.

(38) Rajamathi, M.; Kamath, P. V.; Seshadri, R. Polymorphism in Nickel Hydroxide: Role of Interstratification. J. Mater. Chem. 2000, 10, 503–506.

(39) Ramakrishna Matte, H. S. S.; Gomathi, A.; Manna, A. K.; Late, D. J.; Datta, R.; Pain, S. K.; Rao, C. N. R. MoS\textsubscript{2} and WS\textsubscript{2} Analogues of Graphene. Angew. Chem. Int. Ed. 2010, 49, 4059–4062.

(40) Lee, C.; Yan, H. Z.; Brus, L. E.; Heinz, T. F.; Hone, J.; Ryu, S. Anomalous Lattice Vibrations of Single- and Few-Layer MoS\textsubscript{2}, ACS Nano 2010, 4, 2695–2700.

(41) Eda, G.; Yamaguchi, H.; Voiry, D.; Fujita, T.; Chen, M.; Chhowalla, M. Photoluminescence from Chemically Exfoliated MoS\textsubscript{2}. Nano Lett. 2011, 11, 5111–5116.

(42) Yan, Y.; Xia, B. Y.; Ge, X.; Liu, Z.; Wang, J.-Y.; Wang, X. Ultrathin MoS\textsubscript{2} Nanoplates With Rich Active Sites As Highly Efficient Catalyst For Hydrogen Evolution. ACS Appl. Mater. Interfaces 2013, 5, 12794–12798.

(43) Luxa, J.; Jankovsky, O.; Sedmidubsky, D.; Medlin, R.; Marysko, M.; Pumera, M.; Sofer, Z. Origin of Exotic Ferromagnetic Metal Dichalcogenides MoS\textsubscript{2} and WS\textsubscript{2}, Nanoscale 2016, 8, 1960–67.

(44) Wang, Y.; Li, S.; Yi, J. Electronic and Magnetic Properties of Co Doped MoS\textsubscript{2} Monolayer. Sci. Rep. 2017, 6, No. 24153.

(45) Yun, W. S.; Lee, J. D. Strain-Induced Magnetism in Single-Layer MoS\textsubscript{2}: Origin and Manipulation. J. Phys. Chem. C 2015, 119, 2822–2827.

(46) Saab, M.; Raybaud, P. Tuning the Magnetic Properties of MoS\textsubscript{2} Single Nanolayers by 3d Metals Edge Doping. J. Phys. Chem. C 2016, 120, 10691–10697.

(47) Gu, X.; Qi, W.; Xu, X.; Sun, Z.; Zhang, L.; Liu, W.; Pan, X.; Su, D. Covalently functionalized carbon nanotube supported Pd nanoparticles for catalytic reduction of 4-nitrophenol. Nanoscale 2014, 6, 6609–6616.

(48) Huang, J.; Zhu, Y.; Lin, M.; Wang, Q.; Zhao, L.; Yang, Y.; Yao, X. Nanorode: A Platform for Highly Sensitive Monitoring of Catalytic Reactions by Surface Enhancement Raman Spectroscopy. J. Am. Chem. Soc. 2013, 135, 8552–8561.