Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information of Exfoliation of MoS_2 by zero-valent transition metal intercalation

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1. Experimental sections

Materials. Commercially available MoS_2 powder and dicobalt octacarbonyl ($Co_2(CO)_8$) were purchased from Macklin (product number M813146) and Aladdin (product number C189362), respectively. Acetonitrile (purchased from Rosen), ethanol and other organic solvents were used as purchased without further purification. Deionized water was used for all aqueous experiments and characterizations.

Preparation of MoS_2 Nanosheets. Exfoliation of MoS_2 was achieved with the assistance of zero-valent transition metal complex ($Co_2(CO)_8$) intercalation. Specifically, MoS_2 powder (50 mg, 0.31 mmol) and $Co_2(CO)_8$ powder (106.8 mg, 0.31 mmol) were added to dry acetonitrile (5ml) under Ar atmosphere in a Schlenk flask. After the Schlenk flask was sealed and sonicated for 3 h to make a good dispersion, the mixture was stirred overnight at room temperature under Ar to complete the intercalation process. After centrifugation (10000 r/min, 10 min), excess HCl (4 M, 6 mL, 24 mmol) was added to the precipitate and sonicated for 1 h to complete the exfoliation of MoS_2. Subsequently, the precipitate was collected by centrifugation (10000 r/min, 10 min) and washed by H_2O twice (10000 r/min, 30 min) to remove excess HCl and other side products. The product collected after the H_2O wash was proposed to be the exfoliated MoS_2 and used for further experiments.

Ni and Cu intercalation into bulk MoS_2 were accomplished according to literature[1]. Similar to the protocol of Co intercalation assisted exfoliation, the Ni and Cu intercalated MoS_2 were treated with excess HNO_3 and HCl, respectively to separate the MoS_2 layers and produce MoS_2 nanosheets for electrocatalytic HER investigations.

Characterization. The morphology of the exfoliated MoS_2 nanosheets was characterized by AFM (Bruker Dimension Icon), TEM (Tecnai G20). Additional chemical and structural characterizations of MoS_2 was accomplished by XRD (Bruker D8 Advance), XPS (KRATOS AXIS Ultra DLD) and Raman spectroscopy (LabRAM Soleil nano).

Electrochemical Measurements. All the electrochemical experiments were

implemented in a three-electrode system with an electrochemical station (CHI760E, Shanghai Chenhua Instrument Factory, China). The glassy carbon (GC) electrode (diameter 5 mm) deposited with MoS_2 nanosheets was used as the working electrode. Platinum wire and Ag/AgCl (3 M KCl-filled) electrode were served as counter and reference electrodes, respectively. All measurements were performed in Ar saturated H_2SO_4 aqueous solution (0.1 M).

The exfoliated MoS_2 nanosheets (catalyst) were deposited onto the GC electrode through the following steps: 5 mg MoS_2 nanosheets was ultrasonicated in 2 mL ethanol containing 0.1 wt% Nafion for 30 mins. Subsequently, 7 μL of the homogeneous catalyst ink was then transferred onto the GC electrode, dried under air for linear sweep voltammetry (LSV) characterizations.

2. Supplementary Figures

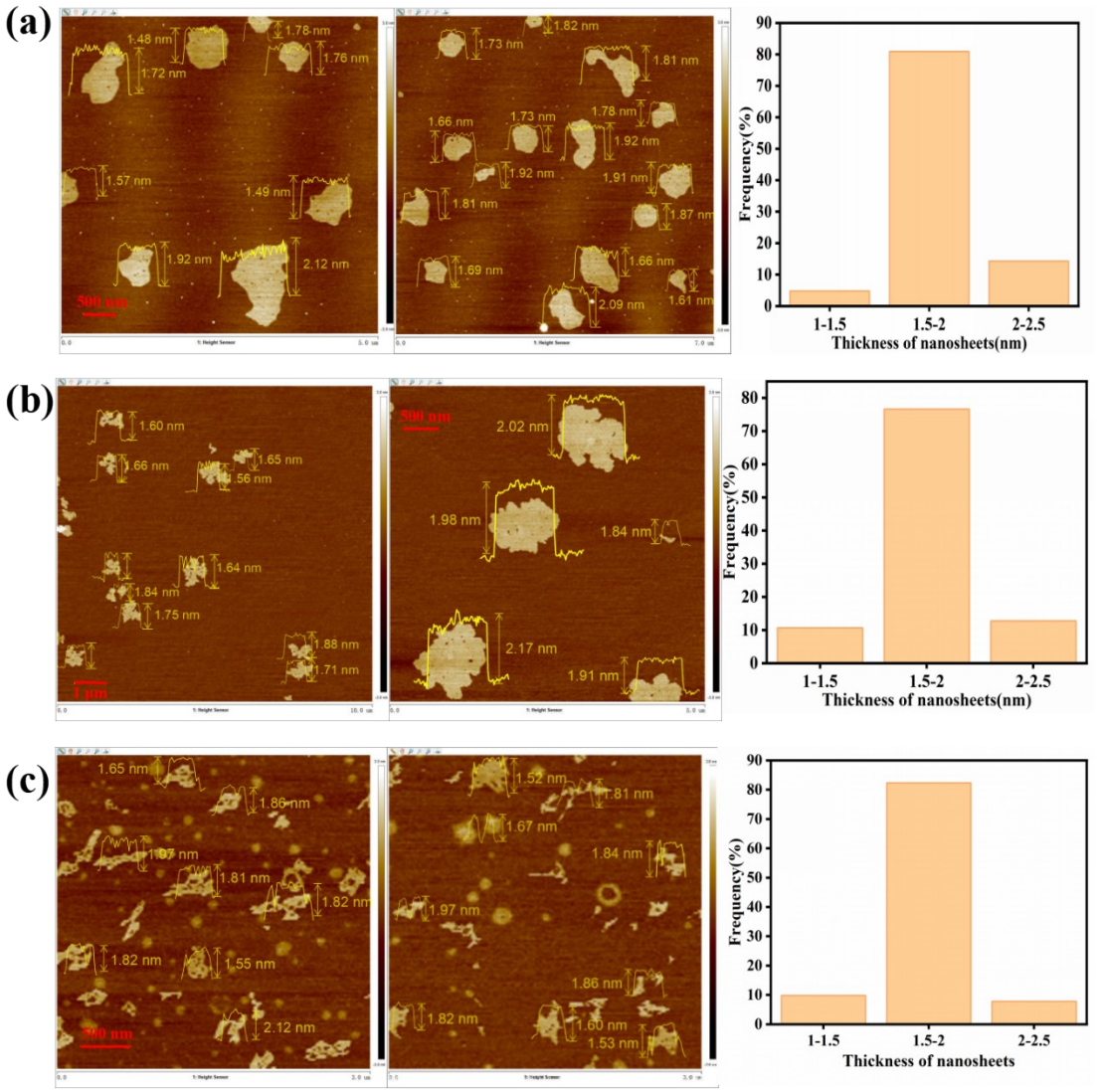

Figure S1. (a) The AFM of Co assisted exfoliated MoS_2 nanosheets. (b) The AFM of Cu assisted exfoliated MoS_2 nanosheets. (c) The AFM of Ni assisted exfoliated MoS_2 nanosheets. To make the statistic Figure on the right side, 84, 47 and 53 counts of Co, Cu, Ni assisted exfoliated MoS_2 nanosheets were analyzed and summarized, respectively.

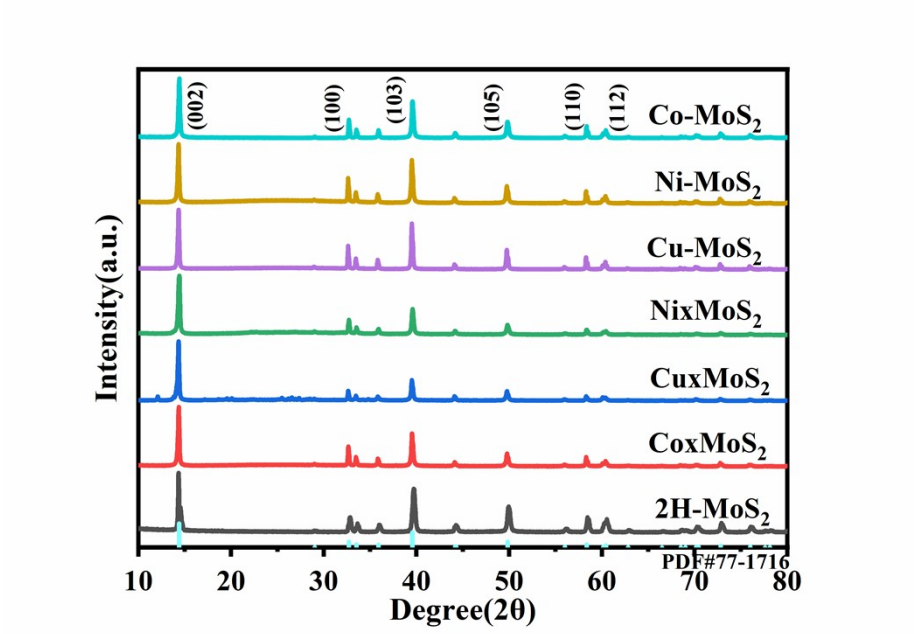

Figure S2. XRD characterizations of pristine 2H-MoS_2, intercalated Co_xMoS_2, Cu_xMoS_2 and Ni_xMoS_2, and Co, Cu, Ni assisted exfoliated MoS_2 nanosheets. Crystallographic data for MoS_2 reference is directly retrieved from the database of JADE.

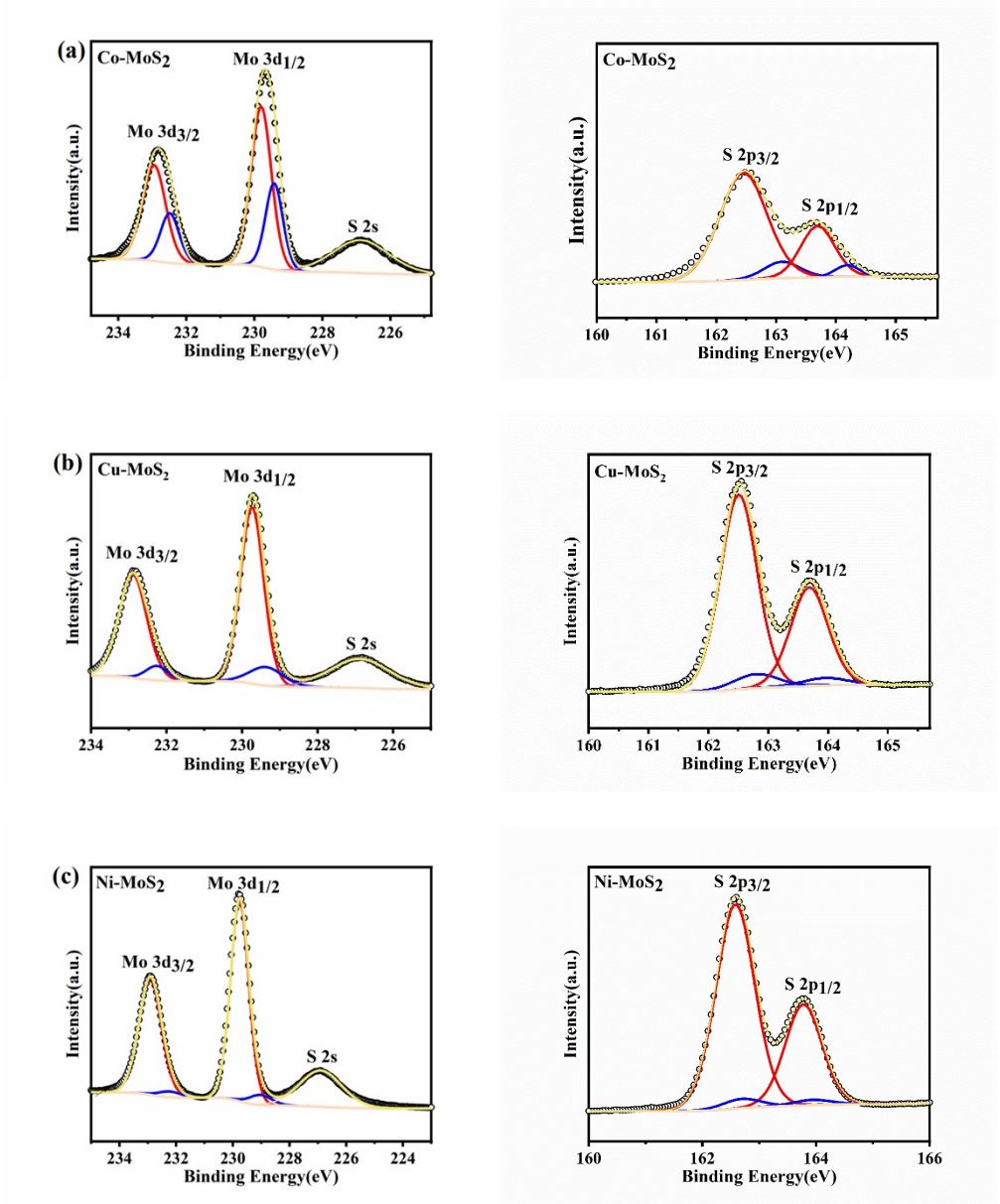

Figure S3. (a) The XPS of Mo 3d and S 2p of Co assisted exfoliated MoS_2 nanosheets. (b) The XPS of Mo 3d and S 2p of Cu assisted exfoliated MoS_2 nanosheets. (c) The XPS of Ni 3d and S 2p of Co assisted exfoliated MoS_2 nanosheets.

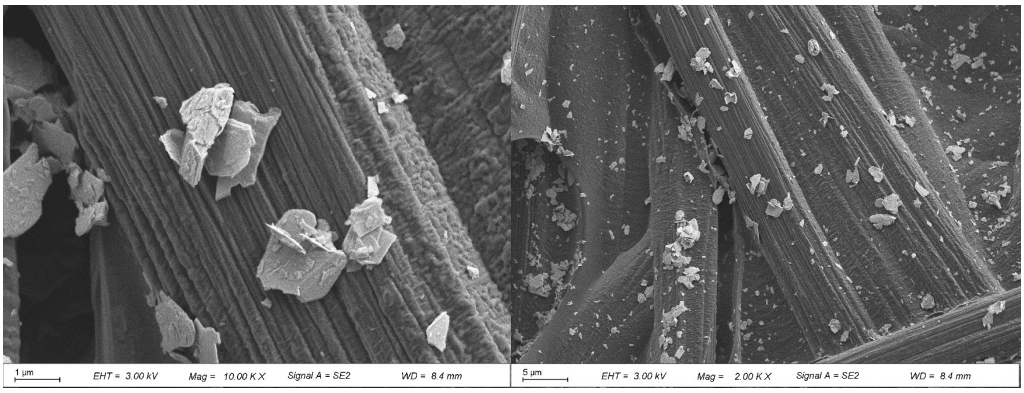

Figure S4. The SEM images of Co intercalation assisted exfoliated MoS_2 nanosheets (e-MoS_2).

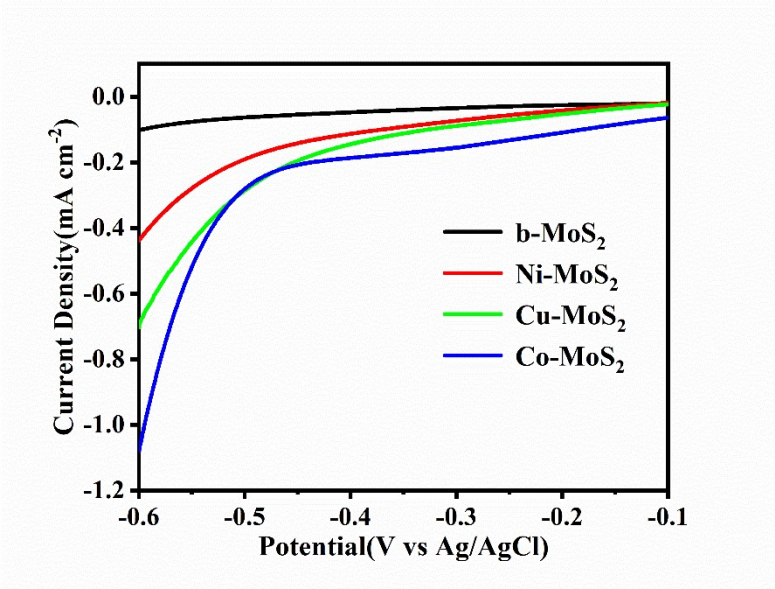

Figure S5. Linear sweep voltammetry (LSV) characterizations of pristine and exfoliated MoS_2 exfoliated by the intercalation of Co, Ni, Cu.

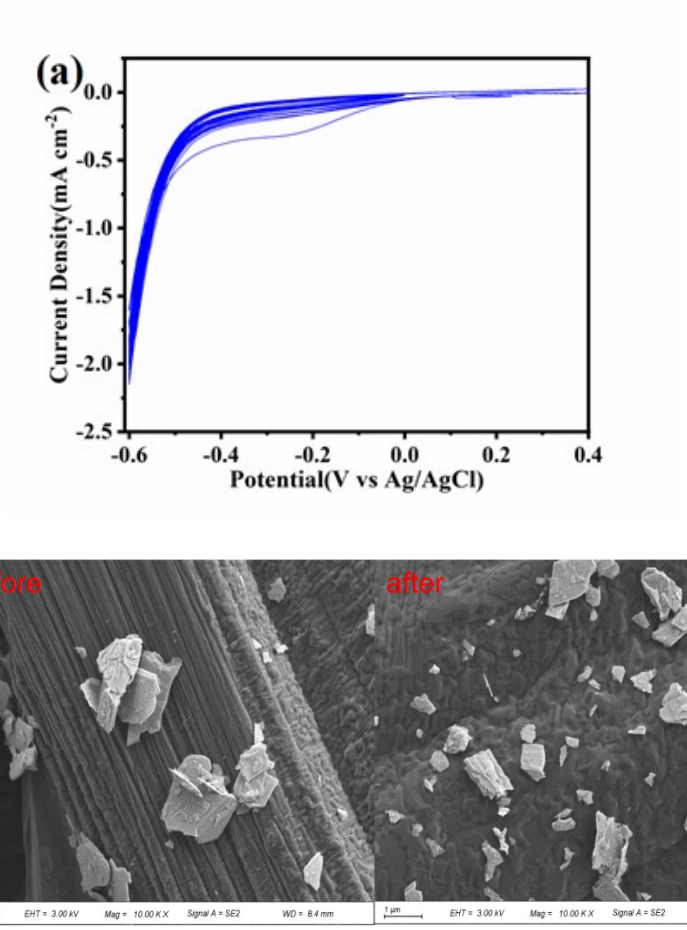

Figure S6. (a) Cyclic voltammogram of e-MoS_2 (100 cycles). (b) The SEM images of e-MoS_2 before and after 100 cycles of cyclic voltammetry.

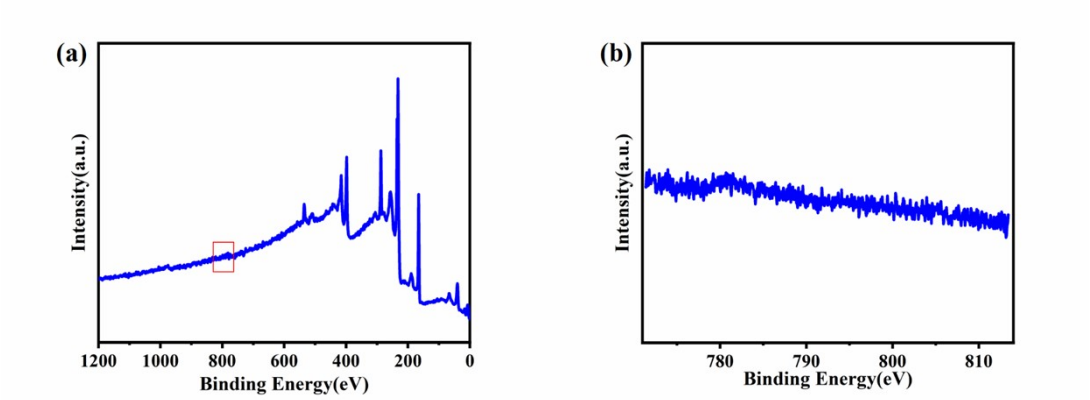

Figure S7. (a) XPS spectrum of Co assisted exfoliated MoS_2 nanosheets (survey scan) and (b) the XPS of Co 2p of Co assisted exfoliated MoS_2 nanosheets.

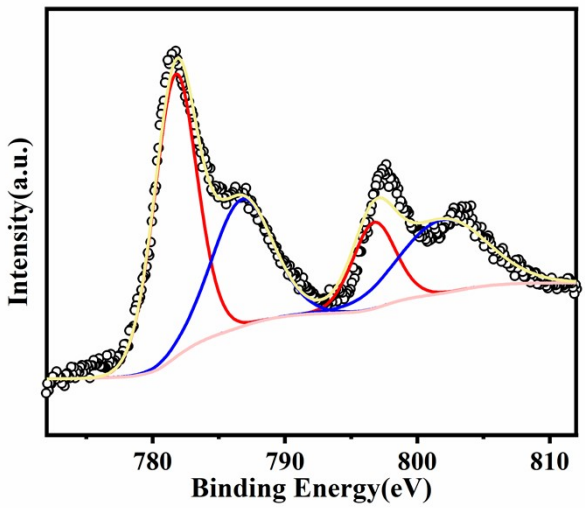

Figure S8. The XPS of Co 2p of intermediate Co_xMoS_2.

Reference

1. K. J. Koski, C. D. Wessells, B. W. Reed, J. J. Cha, D. Kong and Y. Cui, *J. Am. Chem. Soc.*, 2012, **134**, 13773-13779.