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Electronic Supplementary Information

Realizing the Electronic Modulation on Mo Sites for Efficient Hydrogen Evolution Reaction

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Experimental section

Chemicals and Reagents

Nickel nitrate hexahydrate ($Ni(NO_3)_2 \cdot 6H_2O$), hexamethylenetetramine ($C_6H_{12}N_4$), ammonium heptamolybdate ($(NH_4)_6Mo_7O_{24} \cdot 4H_2O$), Ammonium hydroxide ($NH_3 \cdot H_2O$) and sulfuric acid ($H_2SO_4$) were purchased from Chengdu Kelong Chemical Regent Co. Ltd (China). Carbon nanotube (multi-walled, >90%) was purchased from Aladdin Industrial Corporation. Nafion solution (5 wt%) and Poly (vinilidene fluoride) (PVDF) was obtained from Sigma-Aldrich. N-methyl-2-pyrrolidone (NMP) was available from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). Pt/C (20 wt%) was purchased from Alfa Aesar. De-ionized water MilliQ UV-plus water (Millipore) was used throughout all experiments. All chemicals were analytical grade and used without further purification.

Synthesis of pristine Mo_2C

The pristine Mo_2C was synthesized based on our previous study.[1] Typically, 2.48 g ammonium heptamolybdate (AHM) was dissolved in 25 mL deionized water. Then, 20 ml aqueous solution containing 0.5626 g hexamethylenetetramine (HMT) was added and continuously stirred for 2 hours at room temperature. After another 3 hours aging, the solvent was removed by evaporation at 80 °C for 24 h, and a white solid precursor was obtained. Subsequently, the precursor was transferred into a tubular furnace. For obtaining the vacuum condition, Ar flow was introduced for 1 h and the precursor was heated to 800 °C and kept for 2 h with a ramping rate 5 °C min^{-1}. The obtained black solid product was denoted as pristine Mo_2C.

Synthesis of Mo_2C/CNTs

The preparation methods for pristine Mo_2C, Mo_2C/CNTs, Ni-Mo_2C and Ni-Mo_2C/CNTs were based on our previous work with a light modification.[1] Briefly, a certain amount of multi-walled carbon nanotube (CNTs) was dispersed in 25 mL H_2O. After the ultrasonic treatment process of 30 min, 2.48 g ammonium heptamolybdate (AHM) was added. 20 mL of hexamethylenetetramine (HMT) aqueous solution (28.13 mg/mL) was added the above solution dropwise under magnetic stirring. Then $NH_3 \cdot H_2O$ was added dropwise with magnetic stirring until the pH was changed from 5.8 to 10. After stirring for 2 hours and another 3 hours aging at room temperature, the above solution was heated in water bath to 90 ℃ and kept at this temperature under constant stirring for 30 min. Then the solution was evaporated slowly to dehydrate at 80 ℃ for 24 hours, and a black solid precursor was obtained. Subsequently, the precursor was transferred into a tubular furnace. For obtaining the vacuum condition, Ar flow was introduced for 1 h and the precursor was heated to 700 ℃ and kept for 2 hours with a ramping rate 5 ℃ min^{-1}. According to the different mass ratio between AHM and CNTs (1:0.10, 1:0.15 and 1:0.20), three samples denoted as Mo_2C/CNTs-0.10, Mo_2C/CNTs-0.15 and Mo_2C/CNTs-0.20 were obtained, respectively.

Synthesis of Ni-Mo_2C

For introducing Ni-doping, 2.48 g AHM was dispersed in 25 mL H_2O. After 20 mL of HMT aqueous solution (28.13 mg/mL) was added the above solution dropwise under magnetic stirring, $NH_3 \cdot H_2O$ was added dropwise with magnetic stirring until the pH was changed from 5.8 to 10. Subsequently, a certain amount of $Ni(NO_3)_2 \cdot 6H_2O$ was added the above system. After stirring for 2 hours and another 3 hours aging at room temperature, the solution was evaporated slowly to dehydrate at 80 °C for 24 hours, and a blue-green solid precursor was obtained. Subsequently, the precursor was transferred into a tubular furnace. For obtaining the vacuum condition, Ar flow was introduced for 1 h and the precursor was heated to 700 °C and kept for 2 hours with a ramping rate 5 °C min^{-1}. According to the different molar ratio between Mo and Ni (1:0.063, 1:0.125, 1.:0.25 and 1:0.5), four samples denoted as Ni-Mo_2C-0.063, Ni-Mo_2C-0.125, Ni-Mo_2C-0.25 and Ni-Mo_2C-0.5 were obtained, respectively.

Synthesis of Ni-Mo_2C/CNTs

For the synthesis of Ni-Mo_2C/CNTs, 0.372 g CNTs was dispersed in 25 mL H_2O. After the ultrasonic treatment process of 30 min, 2.48 g AHM was added. 20 mL of HMT aqueous solution (28.13 mg/mL) was added the above solution dropwise under magnetic stirring. Then $NH_3 \cdot H_2O$ was added dropwise with magnetic stirring until the pH was changed from 5.8 to 10. Subsequently, a certain amount of $Ni(NO_3)_2 \cdot 6H_2O$ was added the above system. After stirring for 2 hours and another 3 hours aging at room temperature, the above solution was heated in water bath to 90 °C and kept at this temperature under constant stirring for 30min. Then the solution was evaporated slowly to dehydrate at 80 °C for 24 hours, and a black solid precursor was obtained. Subsequently, the precursor was transferred into a tubular furnace. For obtaining the vacuum condition, Ar flow was introduced for 1 h and the precursor was heated to 700 ℃ and kept for 2 hours with a ramping rate 5 ℃ min^{-1}. Finally, the Ni-Mo_2C/CNTs was obtained.

Synthesis of N-CNTs, Ni-NCNTs, Ni-CNTs and Ni-NC

To clarify the real active sites, the N-CNTs, Ni-NCNTs, Ni-CNTs and Ni-NC were synthesized. In detail, N-CNTs was synthesized through the same method as Mo_2C/CNTs-0.15 without using AHM; Ni-NCNTs was synthesized through the same method as Ni-Mo_2C/CNTs without using AHM; Ni-CNTs was synthesized through the same method as Ni-Mo_2C/CNTs without using AHM and HMT; Ni-NC was synthesized through the same method as Ni-Mo_2C-0.125 without using AHM.

Sample characterizations

The phase composition was identified by a Shimadzu XRD-6100 diffractometer using a Cu Kα radiation (λ = 0.15406 nm). The Raman spectra were recorded using a Raman spectrometer (Andor SR-500i, λ = 532 nm). Thermogravimetric analysis curves (TGA curves) were obtained by Thermogravimetric Analyzer (TGA, STA 449F3, Netzsch) in the temperature range of 30-700 ℃ in air at a heating rate of 10 ℃ min^{-1}. To quantify the produced H_2 and Faradaic efficiency, the constant current measurement at the current density of 100 mA cm^{-2} using the Titanium foil (with dimensions of 1.0 × 2.0 cm^2) as the working electrodes was performed. The gas collected by the drainage method during electrolysis was diluted with N_2. Then, the mixture gas was analyzed by gas chromatography (Fuli Instruments, FL 9790II), with a thermal conductivity detector (TCD). The morphology of different samples was studied using scanning electron microscopy (SEM, Hitachi S-4800) and transmission electron microscope (TEM, FEI Titan G^2 60-300). X-ray photoelectron spectroscopy (XPS) was carried out with an EscaLab 250Xi system. To conduct the XPS calibration, for CNTs-containing samples, we use 284.6 eV as binding energy for C=C (sp^2 C) due to the high graphitization and the existence of a large number of C=C (sp^2 C) in CNTs. As for the samples without CNTs, the carbon is mainly consisted of C-C (sp^3 C), which stems from amorphous carbon in samples and contamination carbon in the air, a higher binding energy 284.7 eV is adopted for C-C (sp^3 C).The N_2 adsorption/desorption isotherm was measured at 77 K using an Automated Surface Area and Porosity Analyzer (ASAP 2460, Micromeritics). Before the measurement of the isotherm, the samples were degased under the vacuum condition for 12 hours at 150 °C. The specific surface area and the corresponding pore size distribution were calculated by Brunauer-Emmet-Teller (BET) and Barrett-Joyner-Halenda (BJH) methods.

Electrochemical measurements

All the electrochemical measurements were conducted on an electrochemical workstation (VersaStat3, Princeton Applied Research, USA) in a three-electrochemical system. The saturated calomel electrode (SCE) and standard Hg/HgO electrode were used as reference electrodes in 0.5 M H_2SO_4 and 1 M KOH, respectively. Graphite rod was used as the counter electrode. And the glassy carbon electrode (GCE, 5 mm diameter, 0.19625 cm^2) with catalyst was used as the working electrode. To prepare the catalyst ink, the catalyst (5 mg) was mixed with 30 μL Nafion solution (5 wt%), 0.5 mL H_2O and 0.5 mL ethanol by sonication for 1 hour, followed by 10 μL PVDF solution (5 wt%, the solvent is NMP) was added and sonication for another 1 min to form a homogeneous ink. For preparing the working electrode, 10 μL catalysts ink was dispersed onto the GCE, which was dried under ambient condition (the catalyst loading was 0.25 mg cm^{-2}). Before characterization, the electrolytes (0.5 M H_2SO_4 and 1 M KOH) were bubbled with pure Ar (99.99%) for 15 min at room temperature. Linear Sweep Voltammetry (LSV) was obtained at a scan rate of 5 mV s^{-1}. Electrochemical impedance spectroscopy (EIS) was performed at AC voltage of -0.2 V from 10^5 - 10^{-1} Hz with an AC potential amplitude of 5 mV In this study, all polarization curves were iR-corrected and all potentials were corrected with regard to reversible hydrogen electrode (RHE), according to E (RHE) = E (SCE) + 0.242 + 0.059*pH or E (RHE) = E (Hg/HgO) + 0.098 + 0.059*pH.

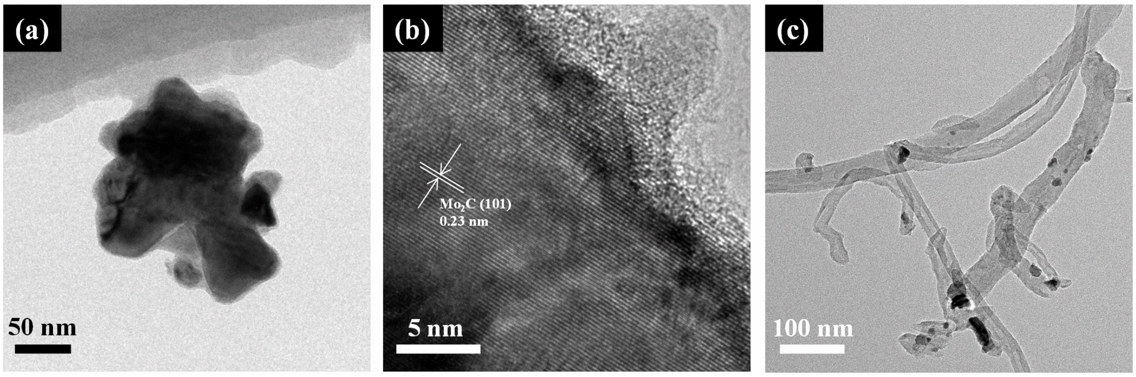

Fig. S1. (a, b) The TEM and HRTEM images of pristine Mo_2C; (c) the TEM image of Mo_2C/CNTs-0.15.

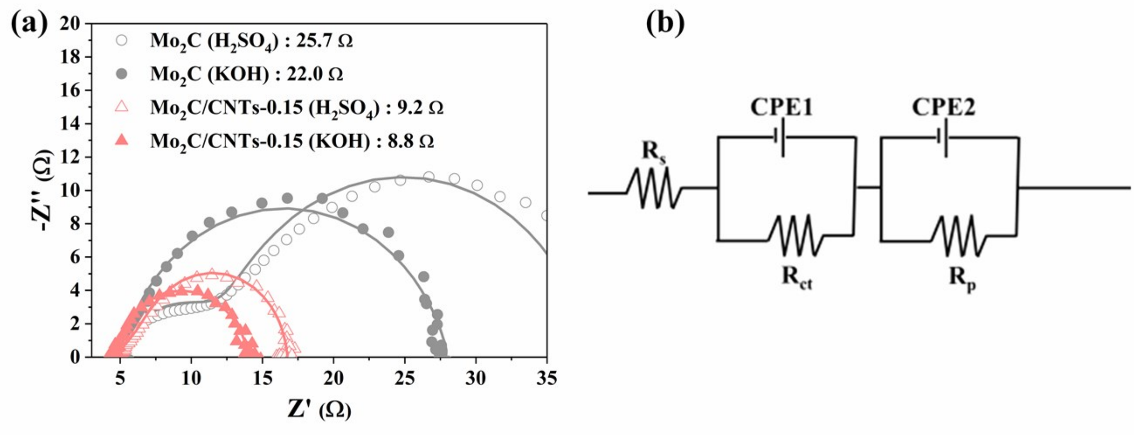

Fig. S2. (a) Electrochemical impedance spectroscopy (EIS) Nyquist plots of pristine Mo_2C and Mo_2C/CNTs-0.15 in 0.5 M H_2SO_4 and 1 M KOH, (b) the equivalent circuit model for fitting the EIS response of HER.

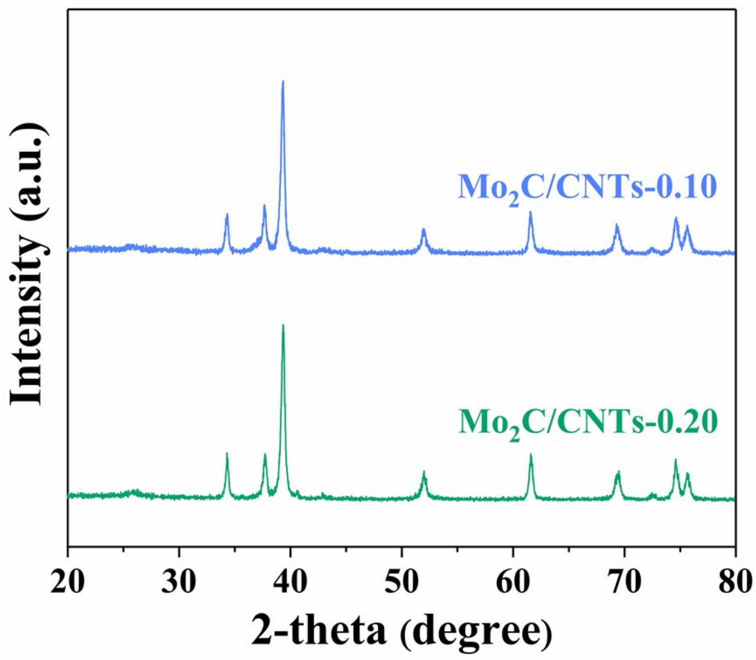

Fig. S3. XRD patterns of Mo_2C/CNTs-0.10 and Mo_2C/CNTs-0.20.

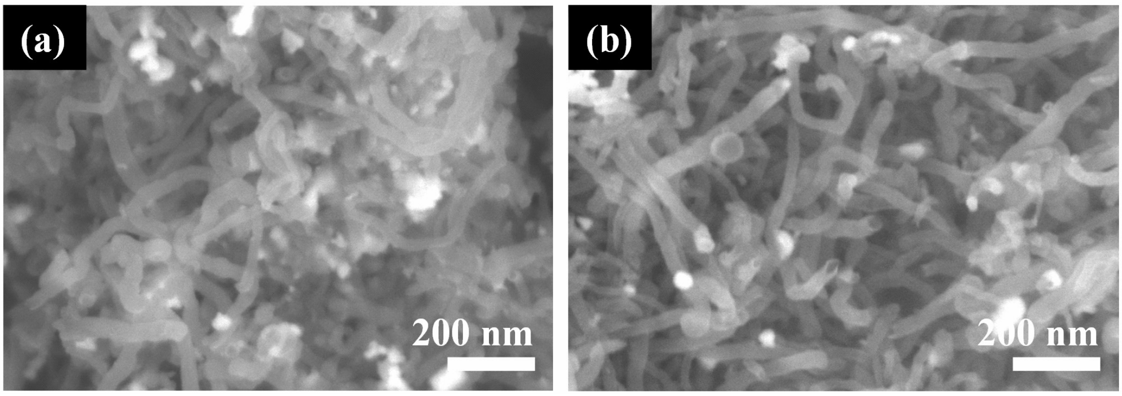

Fig. S4. SEM images of (a) Mo_2C/CNTs-0.10 and (b) Mo_2C/CNTs-0.20.

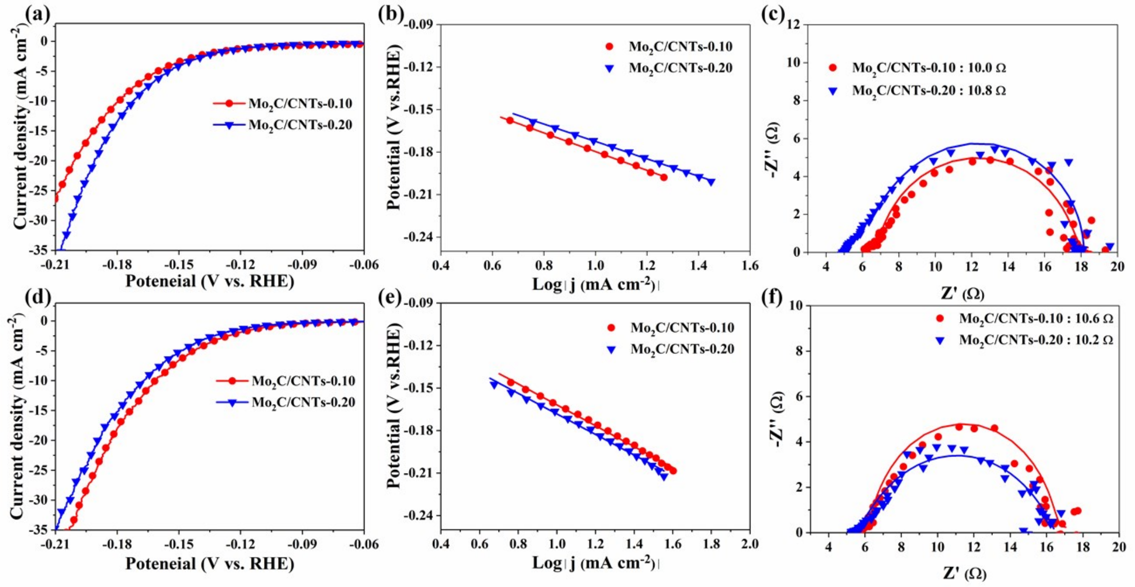

Fig. S5. HER performance of different samples. (a) Polarization curves, (b) Tafel plots and (c) Electrochemical impedance spectroscopy (EIS) Nyquist plots of Mo_2C/CNTs-0.10 and Mo_2C/CNTs-0.20 in 0.5 M H_2SO_4; (d) Polarization curves, (e) Tafel plots and (f) EIS Nyquist plots of Mo_2C/CNTs-0.10 and Mo_2C/CNTs-0.20 in 1 M KOH.

Table S1 Summary of the HER activity of Pristine Mo_2C, Mo_2C/CNTs-0.10, Mo_2C/CNTs-0.15 and Mo_2C/CNTs-0.20 in 0.5 M H_2SO_4 and 1 M KOH.

Samples	**0.5 M H_2SO_4**			**1 M KOH**		
	η_{10} (mV)	**Tafel slopes (mV dec^{-1})**	**R_{ct} (Ω)**	**η_{10} (mV)**	**Tafel slopes (mV dec^{-1})**	**R_{ct} (Ω)**
Pristine Mo_2C	212	82.7	25.7	187	77.2	22.0
Mo_2C/CNTs-0.10	179	66.0	10.0	161	73.7	10.6
Mo_2C/CNTs-0.15	152	59.2	9.2	135	55.3	8.8
Mo_2C/CNTs-0.20	172	61.3	10.8	167	72.5	10.2

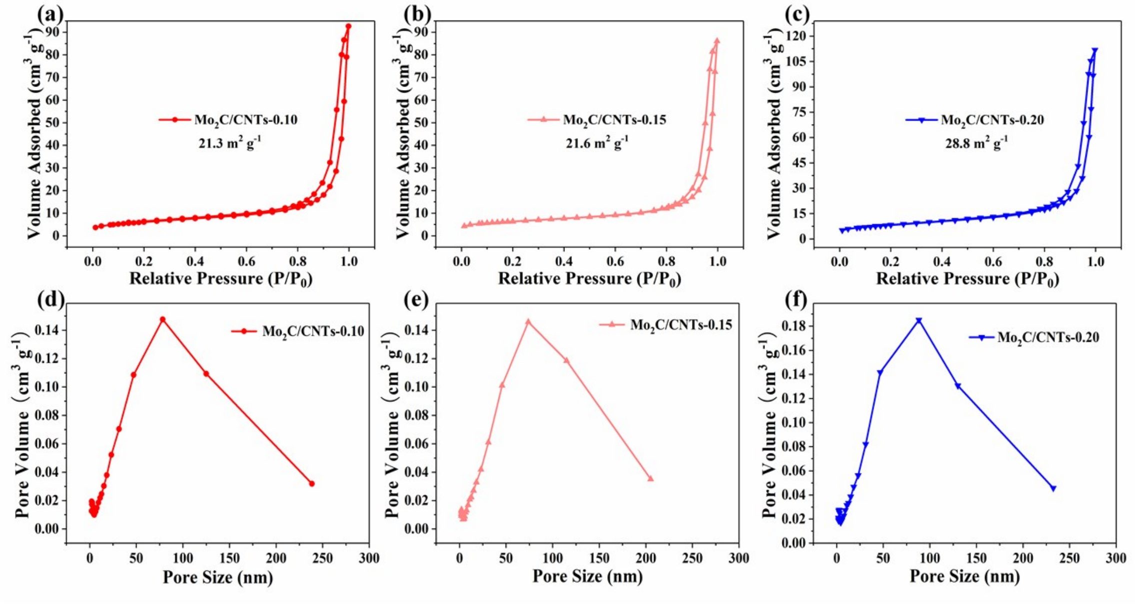

Fig. S6. (a-c) N_2 adsorption-desorption isotherms and (d-f) the pore size distribution of Mo_2C/CNTs-0.10, Mo_2C/CNTs-0.15 and Mo_2C/CNTs-0.20.

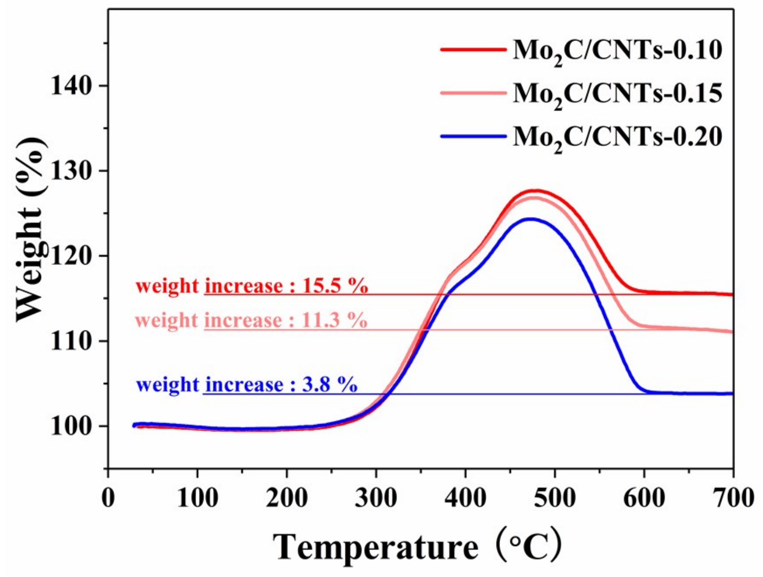

Fig. S7. TG curves of Mo_2C/CNTs-0.10, Mo_2C/CNTs-0.15 and Mo_2C/CNTs-0.20.

According to our previous studies, the content of β-Mo_2C in the final products can be identified by TG analysis under air atmosphere. With arising temperature, Mo_2C

reacts with oxygen to produce MoO_3, thus causing the weight gain. While the combustion of carbon leads to the weight loss. Finally, the weight remains stable, which means the carbon is completely converted into carbon dioxide and MoO_3 exists as the final residue. The weight fraction of Mo_2C present in the as-prepared powders are determinate as follows:

$$Mo_2C(\%) = m_{MoO_3} * \frac{M_{Mo_2C}}{2 * M_{MoO_3}} * 100\%$$

The results show that the content of β-Mo_2C in Mo_2C/CNTs-0.10, Mo_2C/CNTs-0.15 and Mo_2C/CNTs-0.20 is estimated to be 81.8%, 78.8% and 73.5%, respectively.

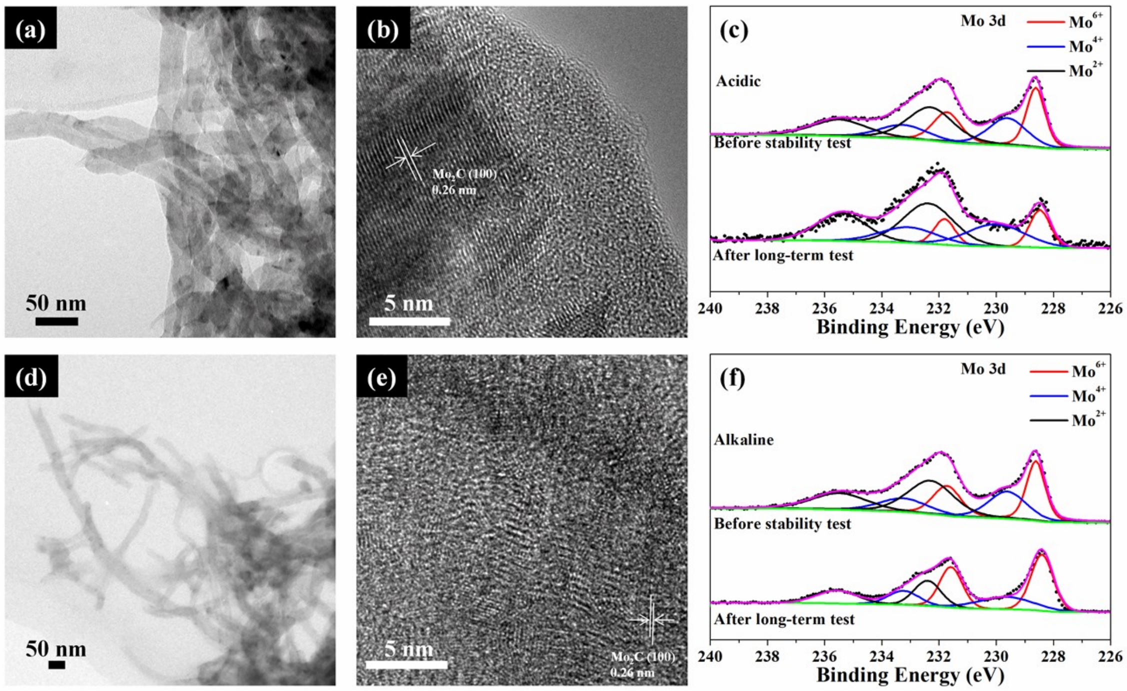

Fig. S8. TEM, HRTEM images and XPS spectra of Mo_2C/CNTs-0.15 after HER stability test in 0.5 M H_2SO_4 (a-c) and 1 M KOH (d-f).

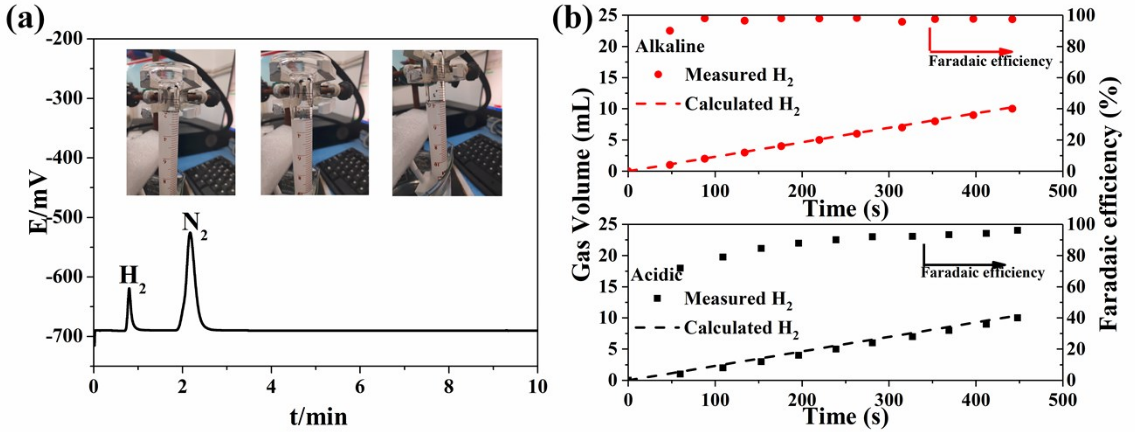

Fig. S9. (a) Gas chromatography (GC) result of mixture gas diluted with N_2; (b) the drainage method-measured H_2 quantity compared with theoretically calculated value in acidic and alkaline media.

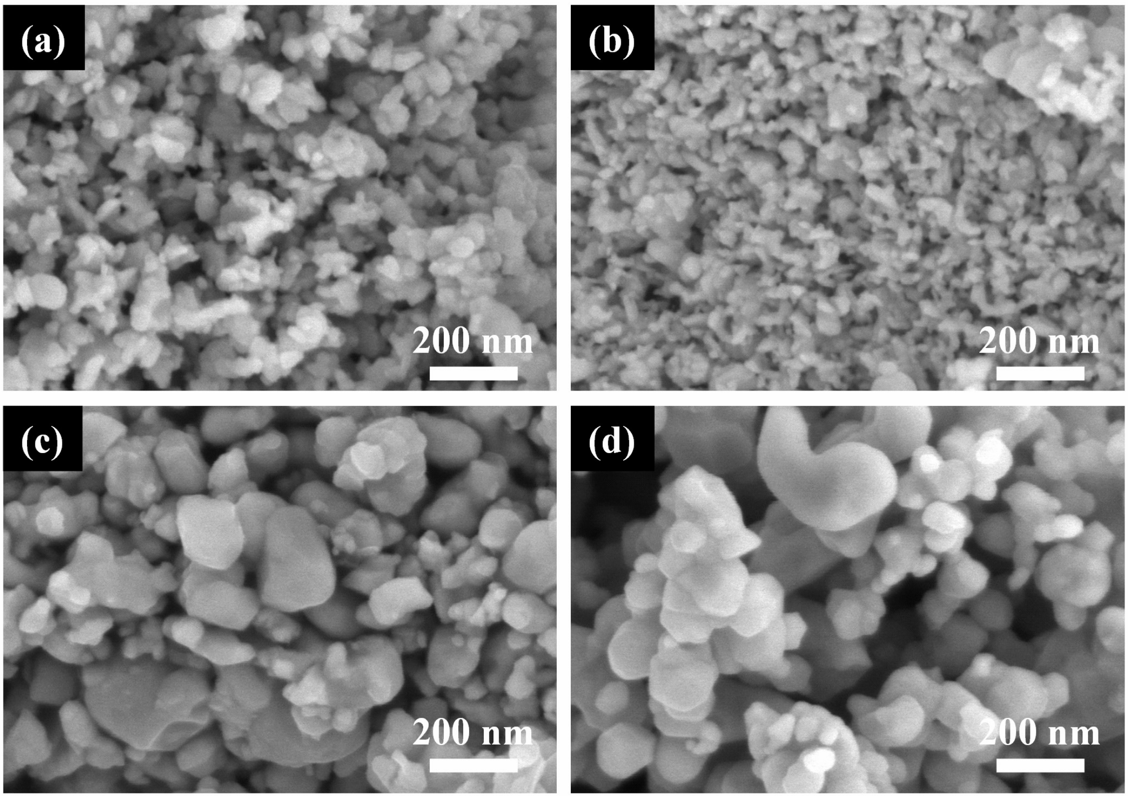

Fig. S10. SEM images of Ni-Mo_2C-0.063, Ni-Mo_2C-0.125, Ni-Mo_2C-0.25 and Ni-Mo_2C-0.5.

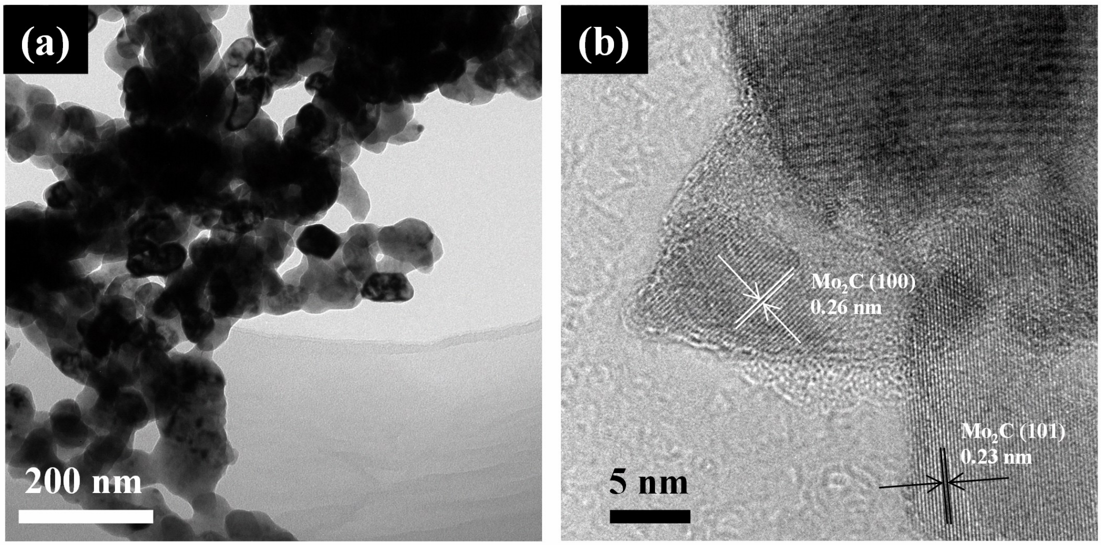

Fig. S11. (a) TEM and (b) HRTEM images of Ni-Mo_2C-0.125.

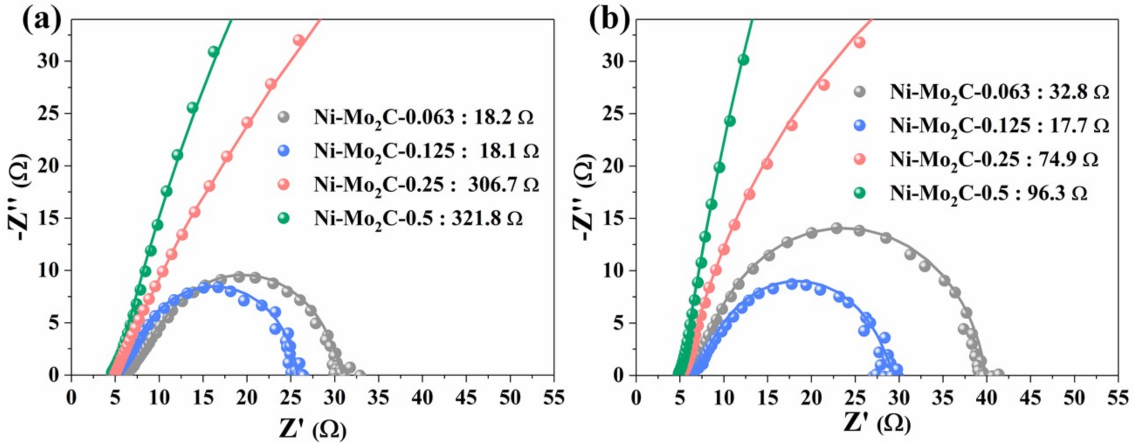

Fig. S12. (a) EIS Nyquist plots of Ni-Mo_2C-0.063, Ni-Mo_2C-0.125, Ni-Mo_2C-0.25 and Ni-Mo_2C-0.5 in 0.5 M H_2SO_4; (b) EIS Nyquist plots of Ni-Mo_2C-0.063, Ni-Mo_2C-0.125, Ni-Mo_2C-0.25 and Ni-Mo_2C-0.5 in 1 M KOH.

Table S2 Summary of the HER activity of Ni-Mo_2C-0.063, Ni-Mo_2C-0.125, Ni-Mo_2C-0.25 and Ni-Mo_2C-0.5 in 0.5 M H_2SO_4 and 1 M KOH.

Samples	**0.5 M H_2SO_4**			**1 M KOH**		
	η_{10} (mV)	**Tafel slopes (mV dec^{-1})**	**R_{ct} (Ω)**	**η_{10} (mV)**	**Tafel slopes (mV dec^{-1})**	**R_{ct} (Ω)**
Ni-Mo_2C-0.063	194	77.2	18.2	193	73.2	32.8
Ni-Mo_2C-0.125	185	70.8	18.1	172	68.3	17.7
Ni-Mo_2C-0.25	300	107.6	306.9	237	85.0	74.9
Ni-Mo_2C-0.5	386	199.5	321.8	280	86.2	96.3

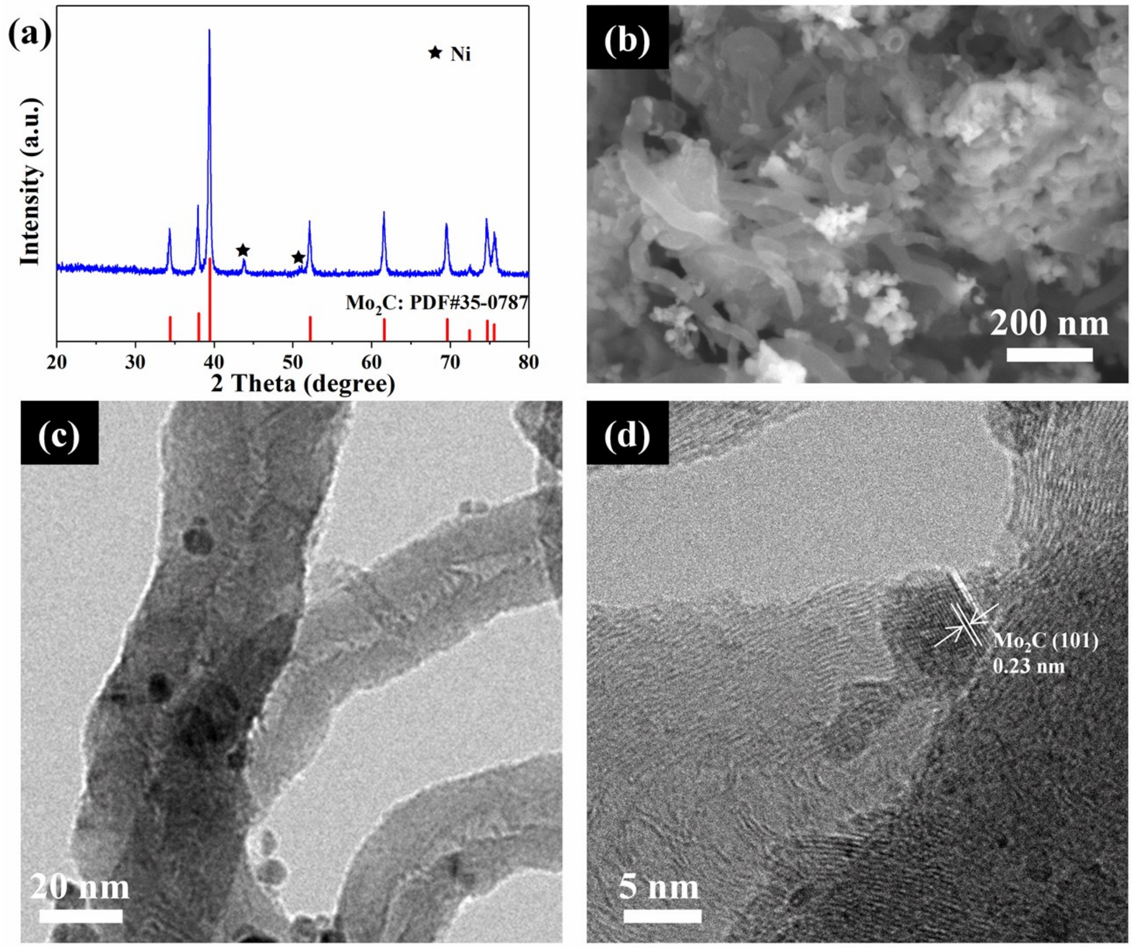

Fig. S13. (a) XRD pattern, (b) SEM, (c) TEM and (d) HRTEM images of Ni-Mo_2C/CNTs.

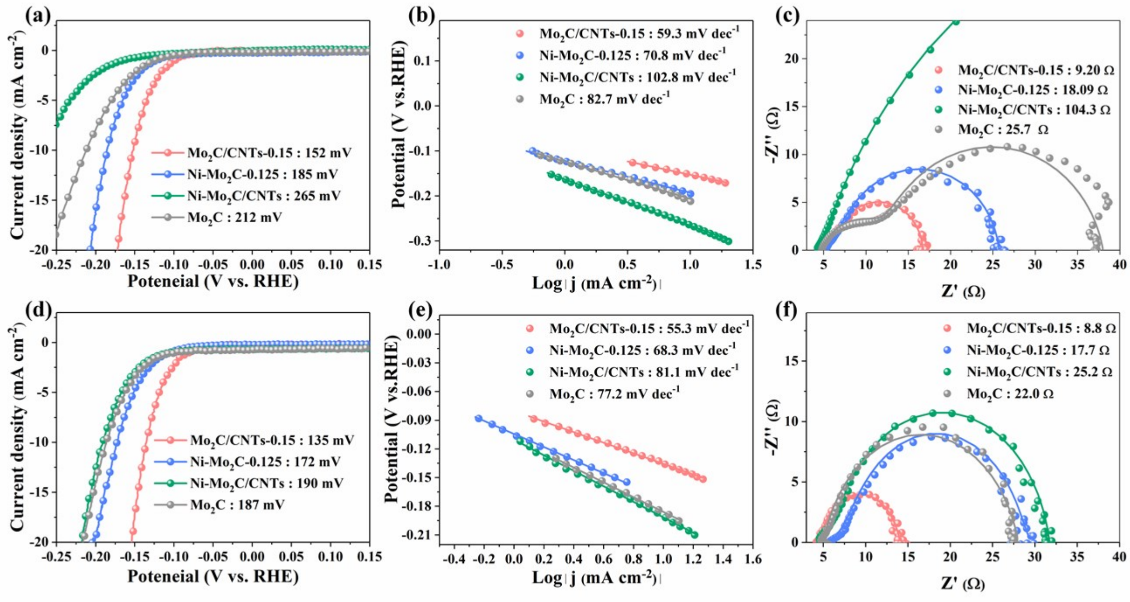

Fig. S14. HER performance of different samples. (a) Polarization curves, (b) Tafel plots and (c) Electrochemical impedance spectroscopy (EIS) Nyquist plots of Ni-Mo_2C-0.063, Ni-Mo_2C-0.125, Ni-Mo_2C-0.25 and Ni-Mo_2C-0.5 in 0.5 M H_2SO_4; (d) Polarization curves, (e) Tafel plots and (f) EIS Nyquist plots of Ni-Mo_2C-0.063, Ni-Mo_2C-0.125, Ni-Mo_2C-0.25 and Ni-Mo_2C-0.5 in 1 M KOH.

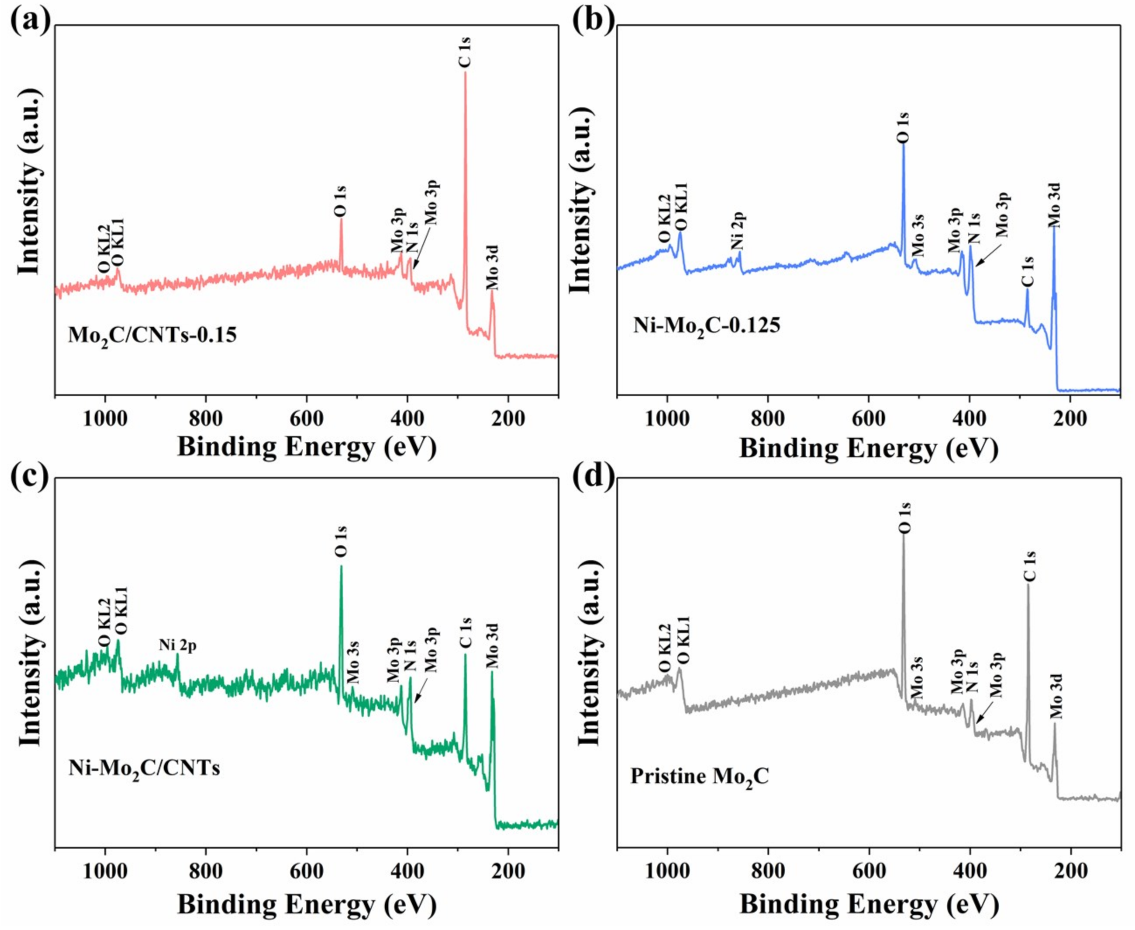

Fig. S15. Wide-scan survey XPS spectrums of Mo$_2$C/CNTs-0.15, Ni-Mo$_2$C-0.125, Ni-Mo$_2$C/CNTs and pristine Mo$_2$C.

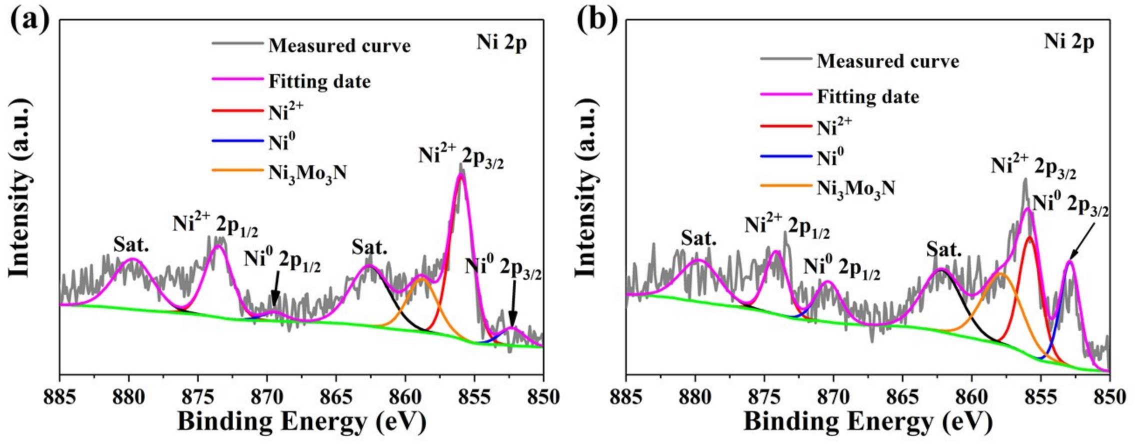

Fig. S16. The High-resolution XPS signals of Ni 2p for (a) Ni-Mo$_2$C-0.125 and (b) Ni-Mo$_2$C/CNTs.

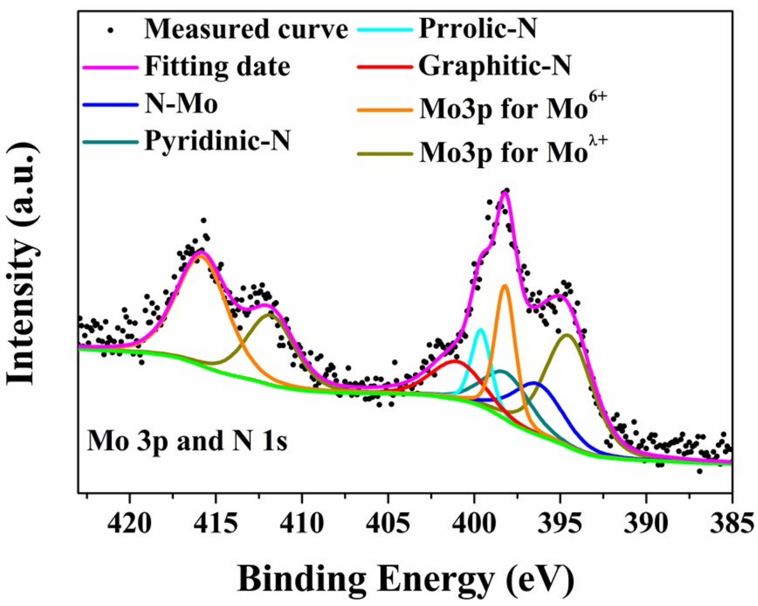

Fig. S17. The High-resolution XPS signals of Mo 3p and N 1s of Mo_2C/CNTs-0.15.

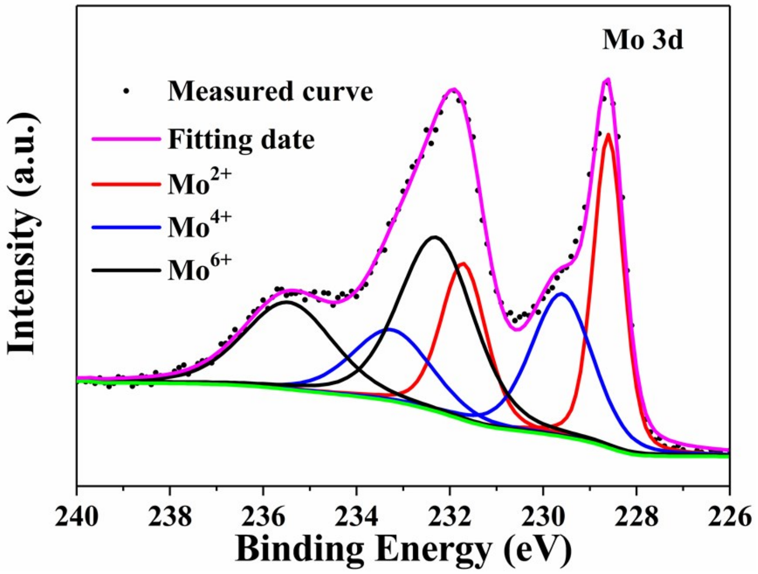

Fig. S18. The High-resolution XPS signals of Mo 3d of Mo_2C/CNTs-0.15.

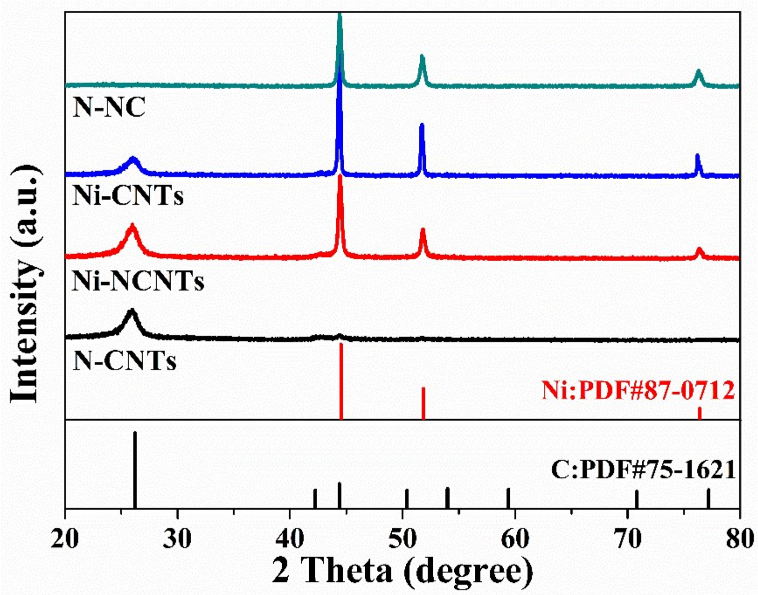

Fig. S19. The XRD patterns of N-CNTs, Ni-NCNTs, Ni-CNTs and Ni-NC.

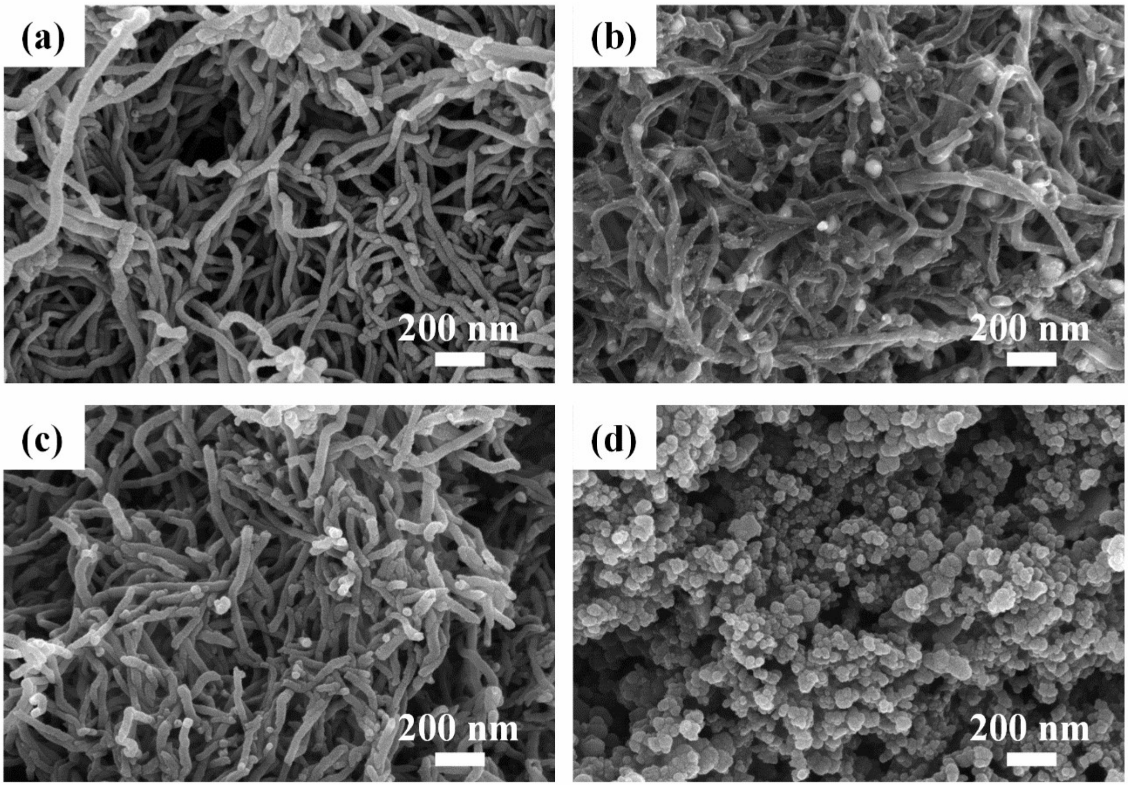

Fig. S20. The SEM images of N-CNTs, Ni-NCNTs, Ni-CNTs and Ni-NC.

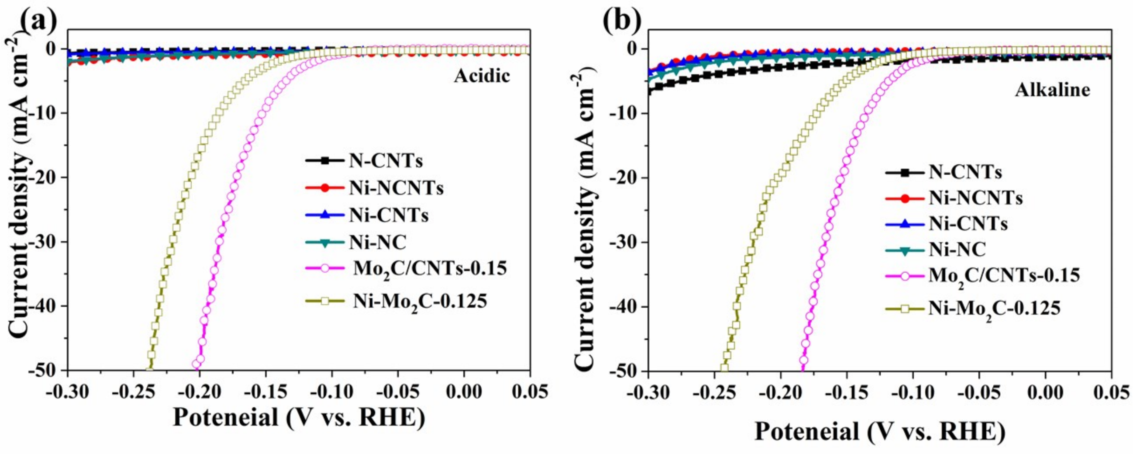

Fig. S21. The LSV curves of N-CNTs, Ni-NCNTs, Ni-CNTs and Ni-NC in (a) 0.5 M H_2SO_4 and (b) 1 M KOH (for comparison, the LSV curves of Mo_2C/CNTs and Ni-Mo_2C also were added).

Reference:

1. W. Wang, C. Liu, D. Zhou, L. Yang, J. Zhou and D. Yang, *J. Alloys. Compd.*, 2019, **792**, 230-239.