

## Supporting Information

### Electron Transfer at the Heterojunction Interface of CoP/MoS<sub>2</sub> for Efficient Electrocatalytic Hydrogen Evolution Reaction

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**Materials.** Cobalt nitrate hexahydrate (Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, 99.0%), Sodium molybdate dihydrate (Na<sub>2</sub>MoO<sub>4</sub>·2H<sub>2</sub>O, 99.0%), Hexamethyl phosphoric triamide (HMTA, 99.0%) and Urea(99.5%) were purchased from Macklin. Molybdenum disulfide (MoS<sub>2</sub>, 99.0%), Sodium hypophosphite (NaH<sub>2</sub>PO<sub>2</sub>, 99.9%) and Ammonium fluoride (NH<sub>4</sub>F, 99.99%) were purchased from Aladdin. S powder(AR), Potassium hydroxide (KOH, 99.99%) and ethanol (C<sub>2</sub>H<sub>5</sub>OH, ≥99.7%) were purchased from Sinopharm Chemical Reagent Co., Ltd. Pt/C (20 wt%) was obtained from Alfa Aesar. Nafion (5 wt%) was purchased from Sigma-Aldrich.

**Synthesis of CoMo-LDH precursor.** The CoMo-LDH precursor was prepared via a straightforward one-step hydrothermal synthesis route. Initially, 2 mmol of Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, 3 mmol of Na<sub>2</sub>MoO<sub>4</sub>·2H<sub>2</sub>O, and 6 mmol of hexamethylenetetramine (HMTA) were dissolved in 60 mL of deionized water. Following complete dissolution through vigorous stirring, the resulting solution was transferred into a 100 mL reactor. Subsequently, the hydrothermal reaction was conducted for a duration of 6 hours at 90 °C. Upon cooling to ambient temperature, the resulting powder was subjected to sequential washing steps with deionized water and alcohol. Following this, centrifugation and drying procedures were employed to yield the CoMo-LDH precursor.

**Synthesis of CoP/MoS<sub>2</sub>.** The synthesized CoMo-LDH precursor was transferred to a tubular furnace for further processing. Upstream of the airflow, 250 mg of NaH<sub>2</sub>PO<sub>2</sub> and 250 mg of S powder were placed, while downstream, 50 mg of CoMo-LDH was positioned. The entire reaction procedure was carried out within an argon hydrogen (Ar/H<sub>2</sub>) atmosphere. CoP/MoS<sub>2</sub> samples were prepared at varying temperatures of 450, 550 and 650 °C (with a heating rate of 5 °C/min) for a duration of 2 hours each.

**Synthesis of CoP.** Initially, a solution comprising 2 mmol of  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , 10 mmol of urea and 5 mmol of  $\text{NH}_4\text{F}$  dissolved in 60 mL of deionized water was prepared. Following thorough stirring, this solution was subsequently transferred into a 100 mL reactor and maintained at 120 °C for a duration of 6 hours. Upon reaching room temperature after cooling, the resultant powder underwent multiple washes with deionized water and ethanol before being dried in an oven at 60 °C for 6 hours. The dried powder was then positioned downstream in the tubular furnace, while 1 g of  $\text{NaH}_2\text{PO}_2$  was placed upstream for phosphating. CoP samples were synthesized at a temperature of 300 °C for 2 hours, utilizing a heating rate of 2 °C/min.

### **Characterizations**

The crystal structures of the samples were characterized by X-ray diffraction (D/MAX 2500) with scanning speed of 5 °/min under  $\text{Cu K}\alpha$  radiation ( $\lambda=1.5406 \text{ \AA}$ ). The morphology characterizations and energy dispersive spectrometer (EDS) characterizations were conducted on a scanning electron microscopy (Hitachi S4800). The microstructure was determined by a high-resolution transmission electron microscopy (JEM-F200). X-ray photoelectron spectra were conducted with an  $\text{Al K}\alpha$  source on the apparatus of Thermo Scientific K-Alpha. Further, C1s at 284.8 eV was considered for data calibration.

### **Electrochemical measurements**

The electrochemical measurements were conducted on an electrochemical workstation (CHI 660E) based on the three-electrode system. A platinum electrode was used as the counter electrode. An  $\text{Ag}/\text{AgCl}$  (in saturated  $\text{KCl}$  solution) was chosen as the reference electrode. A glassy carbon electrode with the sample coated according to the following process was used as the working electrode. 5 mg electrocatalyst sample and 80 mL Nafion solution were uniformly dispersed in 1 mL ethanol. Then 5 mL electrocatalyst ink was dropped on the surface of the 3 mm diameter glassy carbon electrode. Finally, it was dried at 50 °C to obtain the required working electrode. 1 M  $\text{KOH}$  (PH = 13.8) was used as electrolytes. The linear sweep voltammetric (LSV) curves were tested at the scan rate of 5 mV/s (*iR*-corrected). Electrochemical impedance spectra Nyquist plots were measured at an overpotential of -400 mV (*vs*  $\text{Ag}/\text{AgCl}$ ) from 0.01 to  $10^5$  Hz. Cyclic voltammetry curves were measured at different scan rates (20 mV s<sup>-1</sup>, 40 mV s<sup>-1</sup>, 80 mV s<sup>-1</sup>, 120 mV s<sup>-1</sup>, 160 mV s<sup>-1</sup>, 200 mV s<sup>-1</sup>).

### **DFT Calculations**

The first principle calculations are performed to reveal the mechanism by using the Vienna ab initio simulation package.<sup>1-2</sup> The program has the projected enhancement wave pseudopotential<sup>3</sup> and the generalized gradient approximation of Perdew, Burke and Ernzerhof (PBE) exchange

correlation functional,<sup>4</sup> which is used to optimize the structure and obtain the free energy of all structures. The cutoff energy of the plane waves basis set is 500 eV and a Monkhorst-Pack mesh of  $2 \times 2 \times 1$  is used in K-sampling in the adsorption energy calculation. The electronic self-consistent iteration is set to  $10^{-5}$  eV, and the positions of all of the atoms are fully relaxed until the residual force on each atom is below  $0.02 \text{ eV \AA}^{-1}$ - $1.20 \text{ eV \AA}^{-1}$  of vacuum layer along the z-direction is applied to avoid periodic interactions. Spin polarization was included for the correct description of magnetic properties.

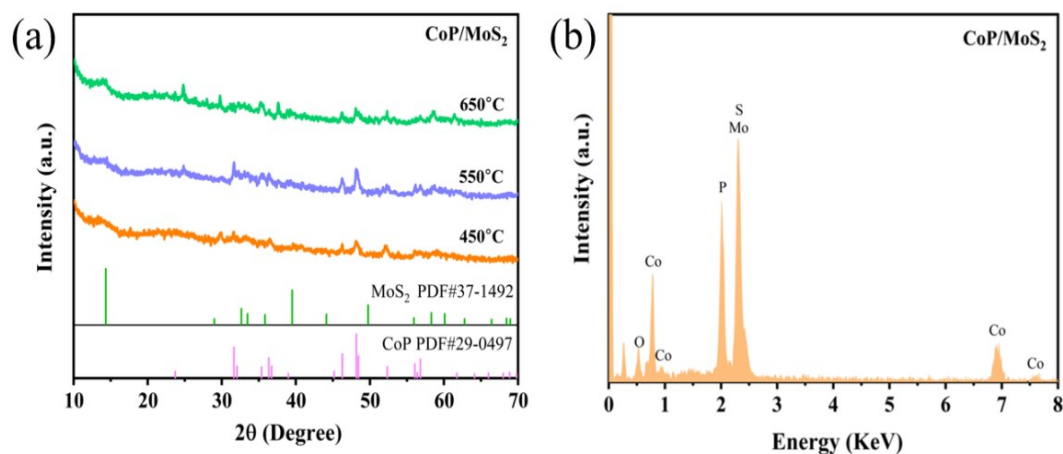


Figure S1. (a) Different temperatures of XRD patterns of CoP/MoS<sub>2</sub>, (b) EDS analysis of CoP/MoS<sub>2</sub>.

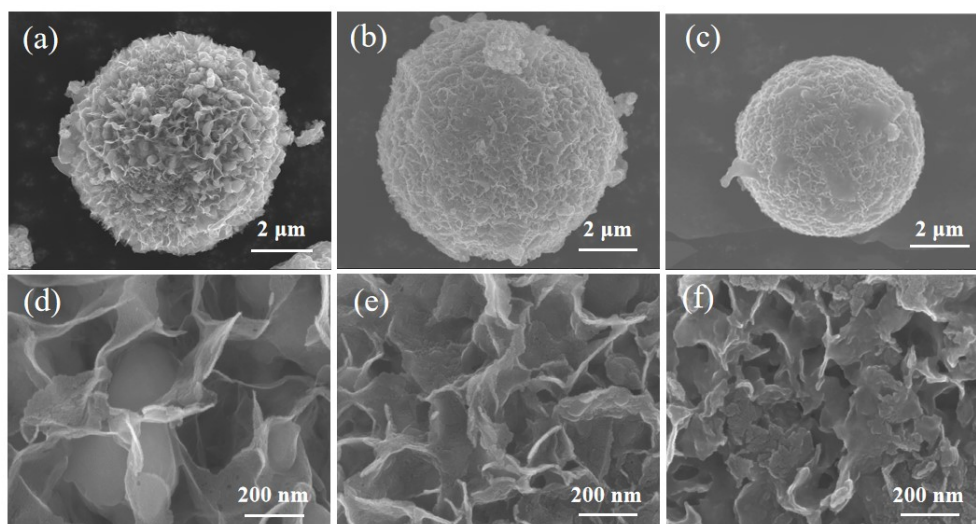


Figure S2. Different magnifications of SEM images for CoP/MoS<sub>2</sub> sample (a, d) 450 °C, (b, e) 550 °C, (c, f) 650 °C.

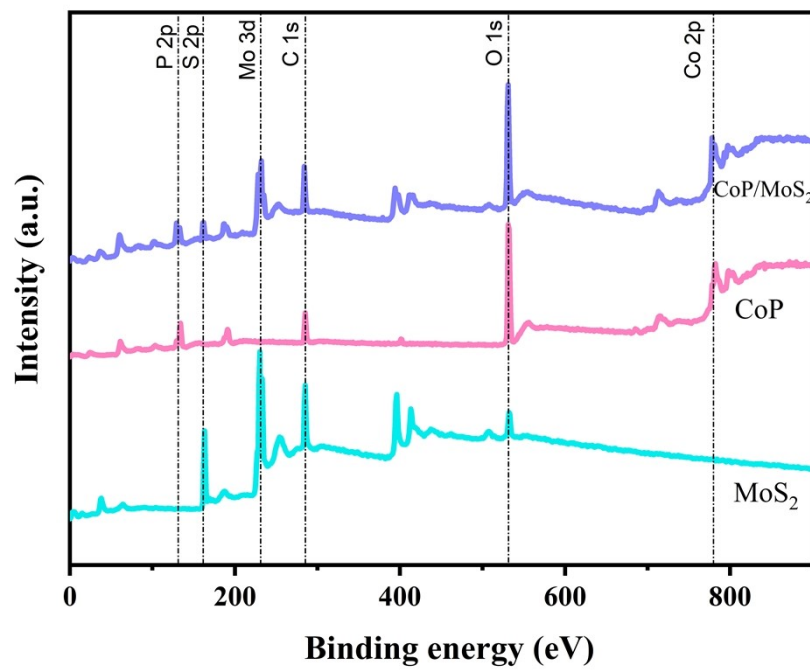


Figure S3. The full XPS survey for CoP/MoS<sub>2</sub>, CoP and MoS<sub>2</sub>.

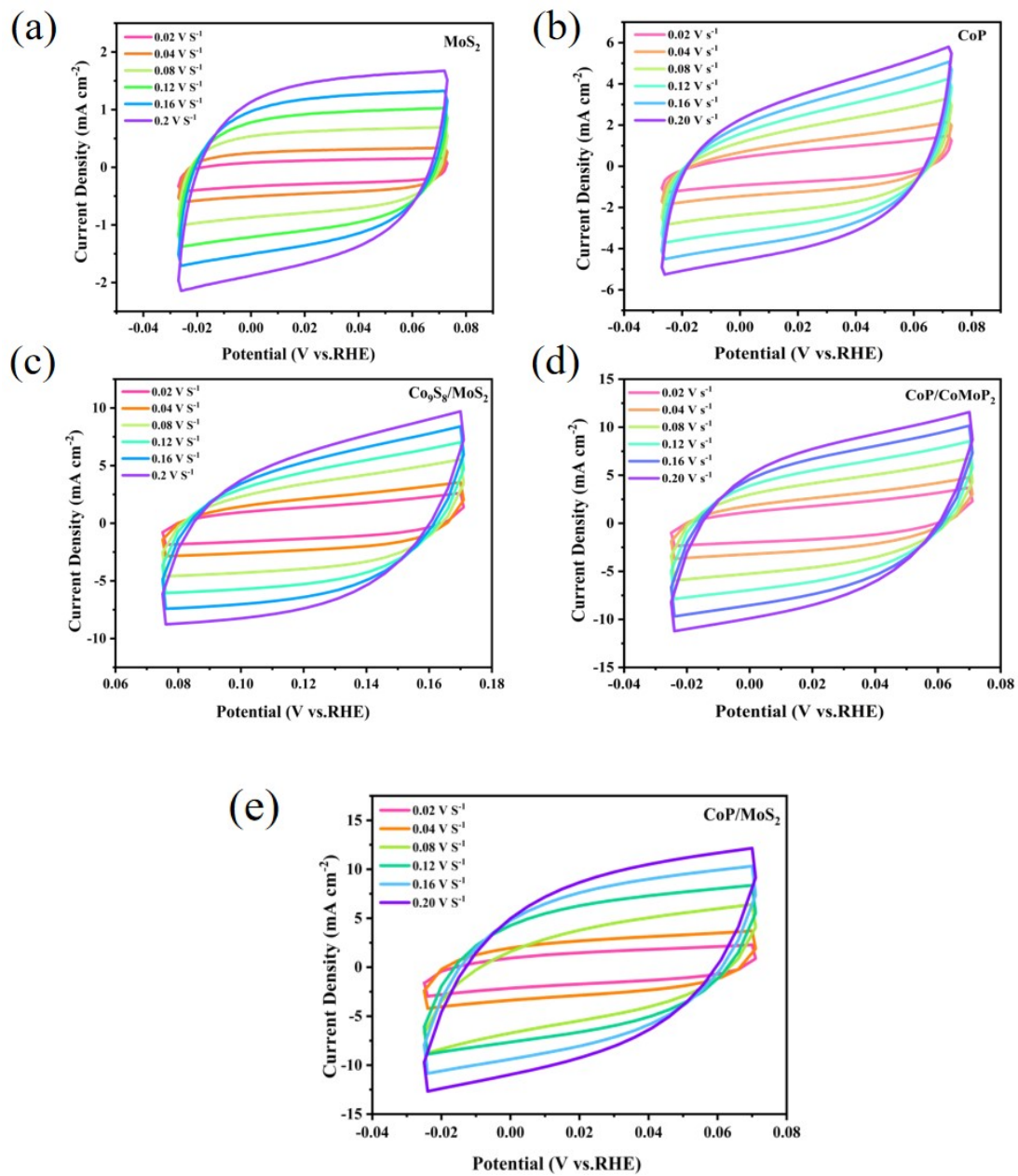


Figure S4. CV curves obtained with different scan rates from 0.02 to 0.20 V s<sup>-1</sup> in 1 M KOH for MoS<sub>2</sub>, CoP, Co<sub>9</sub>S<sub>8</sub>/MoS<sub>2</sub>, CoP/CoMoP<sub>2</sub> and CoP/MoS<sub>2</sub>.

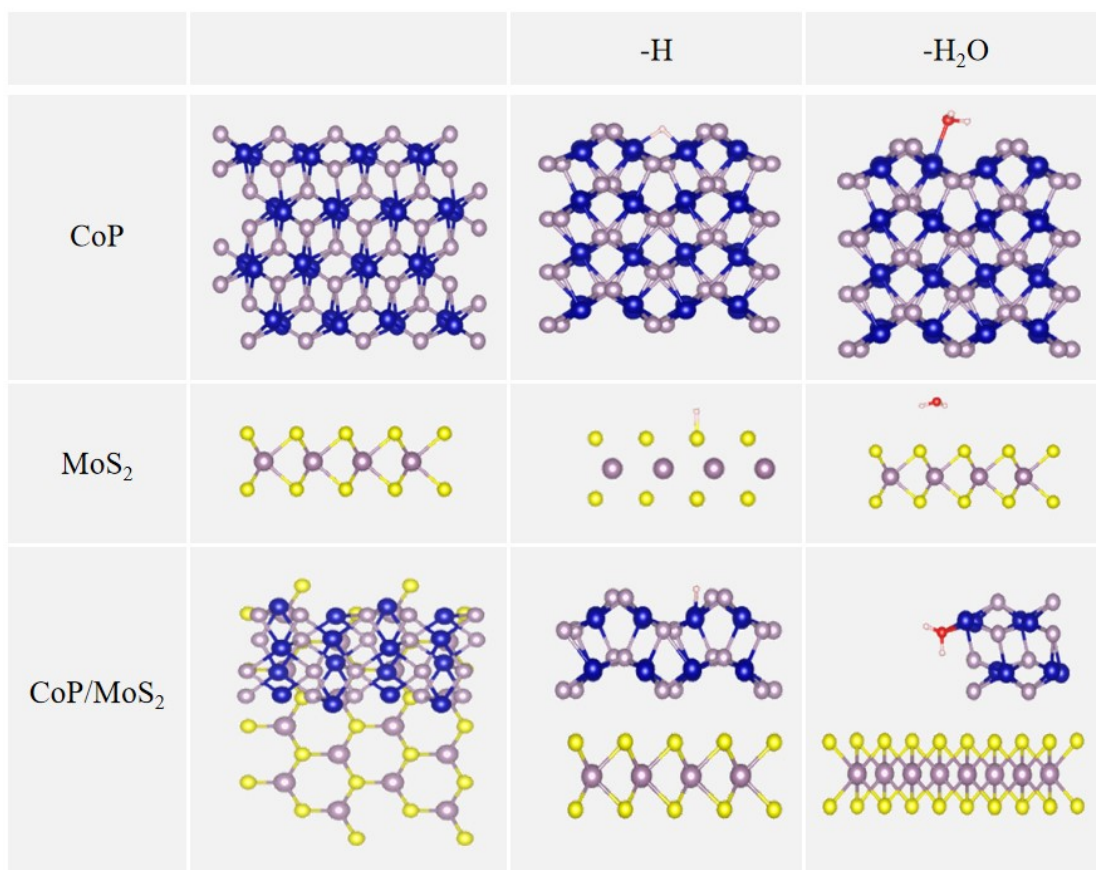


Figure S5. Optimized structures for (a) CoP, (b) MoS<sub>2</sub> and (c) CoP/MoS<sub>2</sub>.

Co: Blue, P: Purple(small), Mo: Purple(big), S:Yellow.

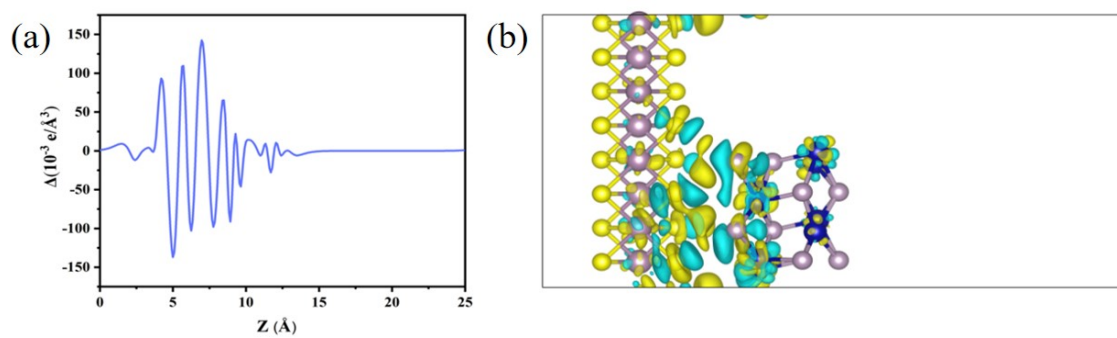


Figure S6. (a) Charge density difference curve for CoP/MoS<sub>2</sub>, (b) Charge density difference for CoP/MoS<sub>2</sub>.

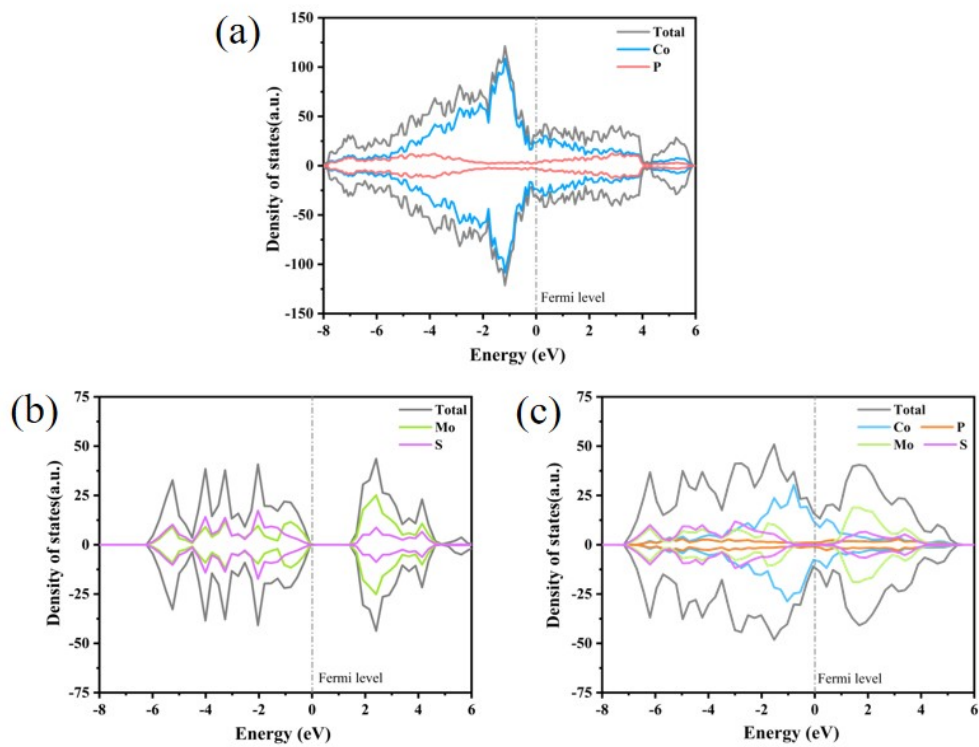


Figure S7. Calculate the density of three dimensional orbital states (a) CoP, (b) MoS<sub>2</sub> and (c) CoP/MoS<sub>2</sub>.

Table S1. Comparison of HER activity for CoP/MoS<sub>2</sub> in this work and other reported electrocatalysts (1 M KOH).

Catalysts	Potential (mV) @10 mA cm <sup>-2</sup>	Tafel slope (mV dec <sup>-1</sup> )	Reference
CoP/MoS <sub>2</sub>	88	87.5	This Work
CoP/MnO <sub>x</sub>	135	59.4	5
CoP/MoP@NPC	211	64.6	6
A-Fe-CoP/CPN	110	101	7
CoP/CeO <sub>x</sub>	118	77.26	8
CoP@CoB	135	80	9
Co <sub>2</sub> P/CoP@Co@NCNT	118	46	10
FeP/CoP@NPC	339	58.8	11
CoP-WP/rGO	96	36	12
CoP@FeCoP/NC	141	56.34	13
NCT@CoP@MoS <sub>2</sub>	195	74	14
R-Mn-CoP@Mn-CoOOH	110	45	15
CFC-CNT-CoO <sub>x</sub> /CoP	108	60	16
CoP/Ti <sub>3</sub> C <sub>2</sub>	102	68.7	17
CoP/CoCr <sub>2</sub> O <sub>4</sub>	212	90	18
Co/CeO <sub>2</sub> /Co <sub>2</sub> P/CoP@NC	195	66	19



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