

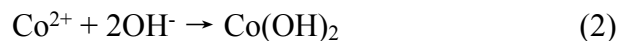
Electronic Supplementary Information

Experimental Section

Materials: $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and NaH_2PO_2 were purchased from Aladdin Ltd. (Shanghai, China). NaBH_4 was purchased from Tianjin Fuchen Chemical Reagent Factory. KOH , ethanol and HCl were purchased from Tianjin Chemical Corporation. Ti mesh was purchased from Phychemi Hong Kong Company Limited. CC and Ti plate were provided by Hongshan District, Wuhan Instrument Surgical Instruments business. SSM with 300 mesh sizes was purchased from Micro Mesh India Private Limited. NF was purchased from Shenzhen Green and Creative Environmental Science and Technology Co. Ltd. All the chemicals in the experiment were analytical grade and used without further treatments. The water use throughout all experiments was purified through a Millipore system.

Preparation of $\alpha\text{-Co}(\text{OH})_2/\text{Ti}$ mesh: Before electrodeposition, Ti mesh was firstly washed with HCl , ethanol, and water several times to remove the surface impurities. The electrodeposition solution contained 0.05 M $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. The deposition was carried out in a three-electrode cell configuration by a CHI 660E electrochemical analyzer (CH Instruments, Inc. Shanghai), using a graphite plate as the counter electrode, Ag/AgCl as the reference electrode, and the cleaned Ti mesh ($1 \times 2 \text{ cm}^2$) as the working electrode. The electrodeposition of $\alpha\text{-Co}(\text{OH})_2$ nanosheets film by cyclic voltammetry (CV) was performed within the potential range from -1.2 V to -0.8 V vs. Ag/AgCl at a scan rate of $50 \text{ mV} \cdot \text{s}^{-1}$. After deposition for 50 (30, 40, 60) scan cycles, the deposited electrode was rinsed first with deionized water, ethanol several times and then dried at $60 \text{ }^\circ\text{C}$ for 12 h in vacuum oven. The experiment was performed under N_2 blanket without stirring at different temperature for 50 scan cycles (293 K, 298 K, and 303 K) under otherwise identical preparation conditions. Note that different substrates (CC, NF, Ti plate, and SSM) are used as the working electrode deposition for 50 scan cycles at 298 K under otherwise identical preparation

conditions for hydroxide precursor. The possible electrodeposition mechanism for the formation of α -Co(OH)₂ is described by the following equations:



Preparation of CoP/Ti mesh: To synthesize CoP film, the as-prepared α -Co(OH)₂/Ti mesh and NaH₂PO₂ (0.05 g) were placed at two separate positions in a porcelain boat with NaH₂PO₂ at the upstream side of the furnace. Subsequently, the sample was heated at 300 °C for 120 min in Ar atmosphere, and then cooled to ambient temperature under Ar. After that, a black film was observed on Ti mesh. The loading for CoP on Ti mesh was determined to be ~0.60 (0.32, 0.48, 0.71) mg cm⁻².

Characterizations: XRD measurements were performed using a RigakuD/MAX 2550 diffractometer with Cu K α radiation ($\lambda=1.5418$ Å). SEM images were collected on a XL30 ESEM FEG scanning electron microscope at an accelerating voltage of 20 kV. TEM measurements were made on a HITACHI H-8100 electron microscopy (Hitachi, Tokyo, Japan) with an accelerating voltage of 200 kV. XPS measurements were performed on an ESCALABMK II X-ray photoelectron spectrometer using Mg as the exciting source. ICP-AES analysis was performed on Model ARCOS FHS12 (SPECTRO Analytical Instruments Inc., Germany).

Hydrogen evolution: The hydrogen generation experiments were performed in a 25 mL two-necked round-bottom flask, one neck was connected to a gas burette and the other was sealed with a rubber cap. The temperature of the reaction was maintained at the desired value by using a constant temperature bath. Catalyst concentration was determined by a certain area. When catalyst was placed in the two-necked round-bottom flask, then the alkaline NaBH₄ (3 mL) solution was quickly injected by a syringe. The hydrogen generated by the systems was identified using a mass flow meter whose output was continuously recorded by a computer. Electronic balance was connected to a computer. The weight data were automatically recorded by a data

acquisition software modified by us. The systematic error and personal error can be substantially reduced in such a way.

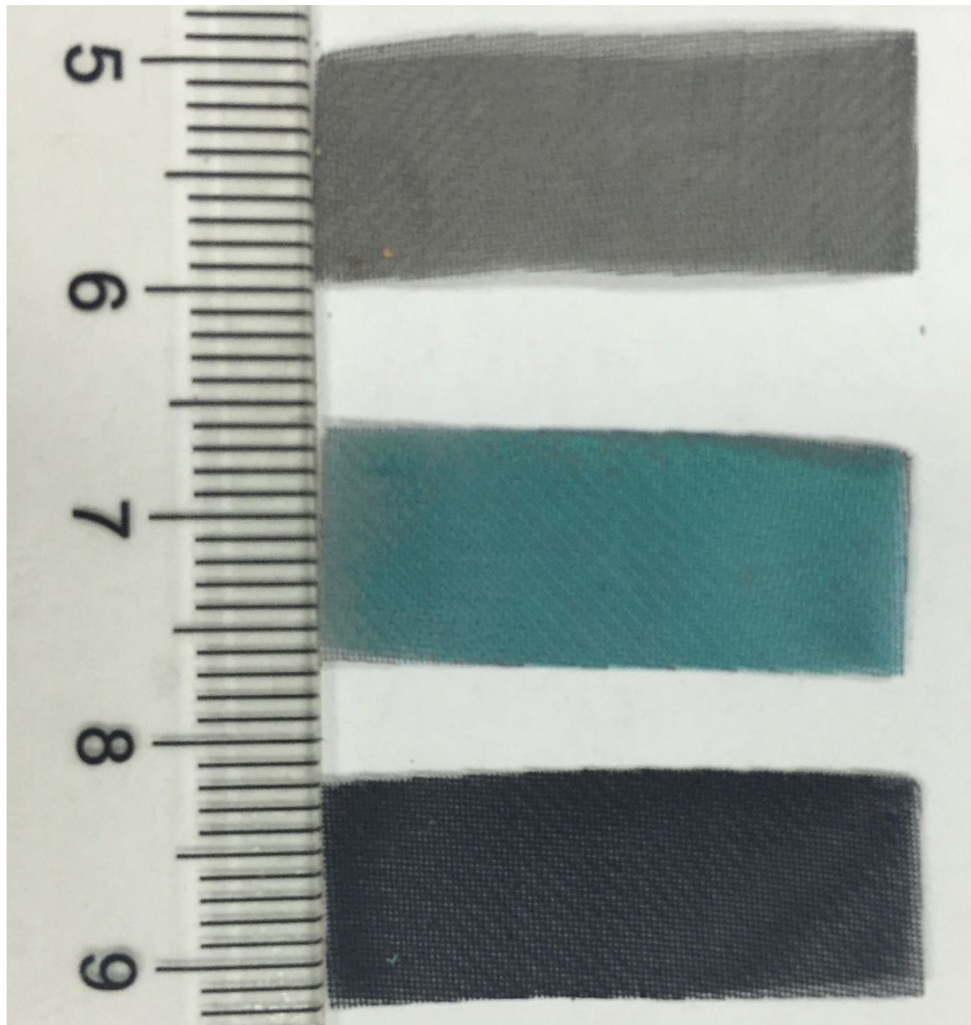


Fig. S1. Optical photograph of (from up to down) bare Ti mesh, α -Co(OH)₂/Ti mesh, and CoP/Ti mesh.

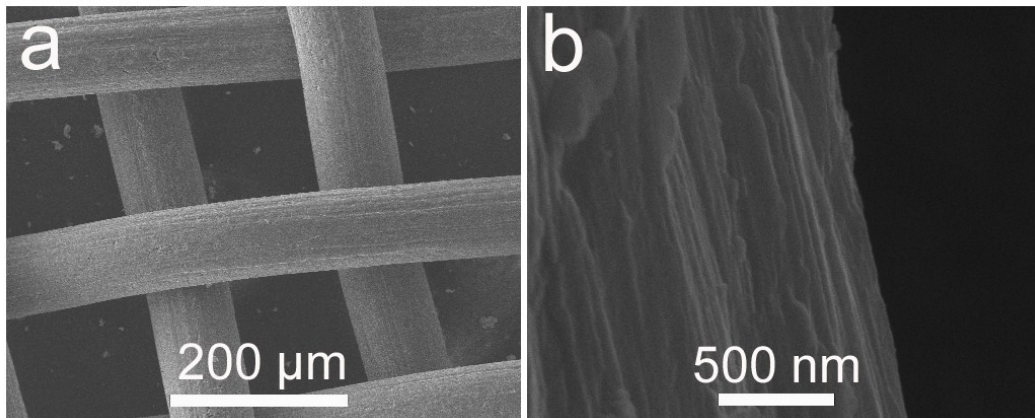


Fig. S2. SEM images of Ti mesh.

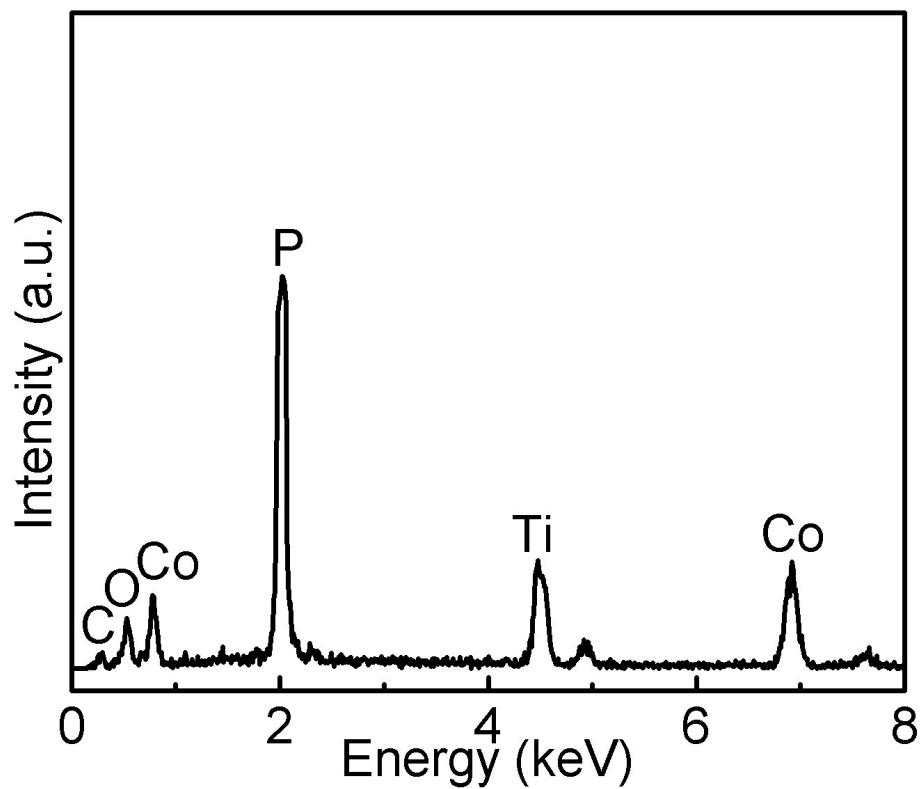


Fig. S3. EDX spectrum of CoP/Ti mesh.

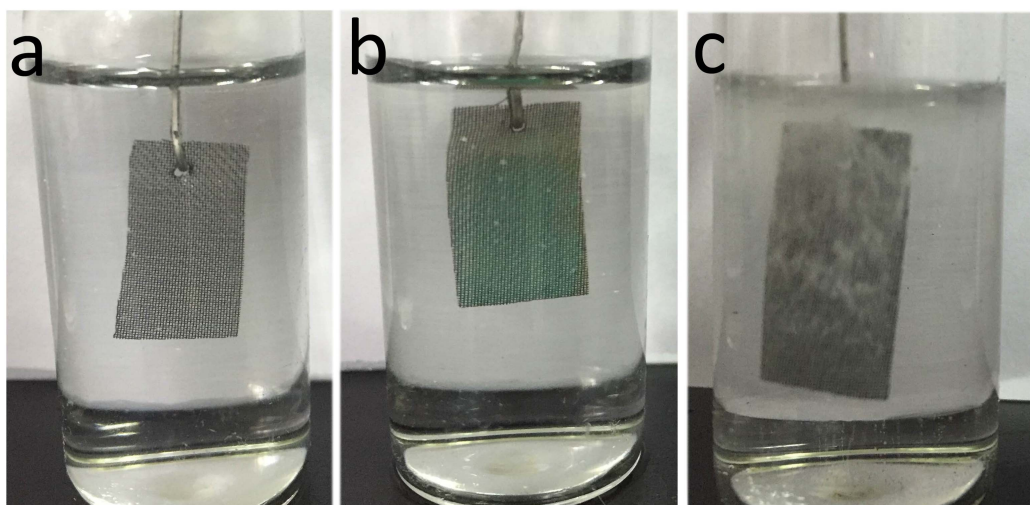


Fig. S4. Optical photographs for the hydrolysis of alkaline NaBH_4 solutions catalyzed by (a) Ti mesh, (b) $\alpha\text{-Co(OH)}_2/\text{Ti}$ mesh, and (c) CoP/Ti mesh.

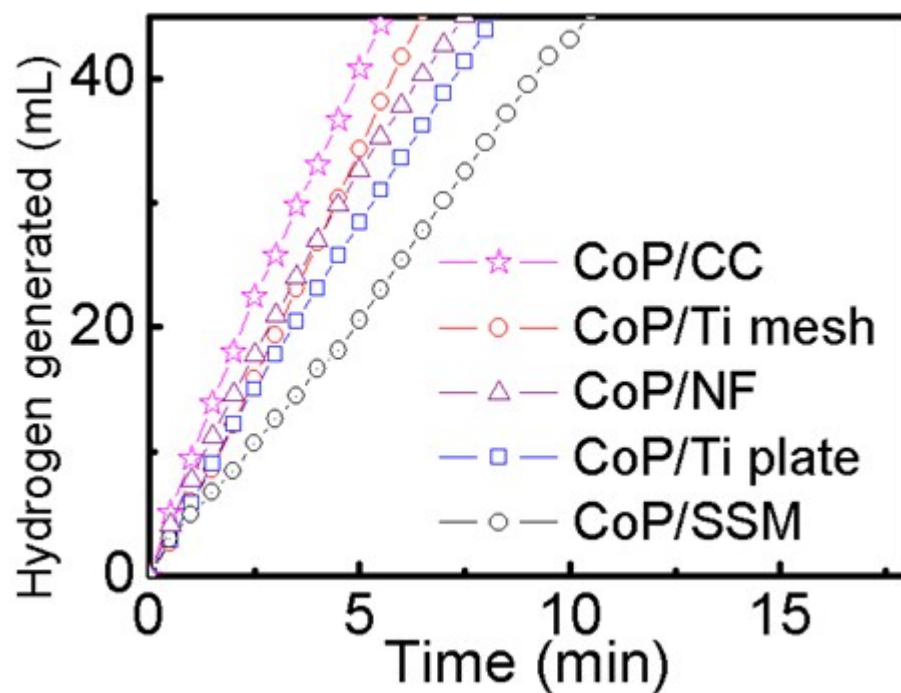


Fig. S5. Plots of the volume of hydrogen vs. time from NaBH_4 hydrolysis catalyzed by CoP on different substrates in aqueous solution (3 mL) containing NaBH_4 (1.0 wt%) and NaOH (2.0 wt%) at 298 K.

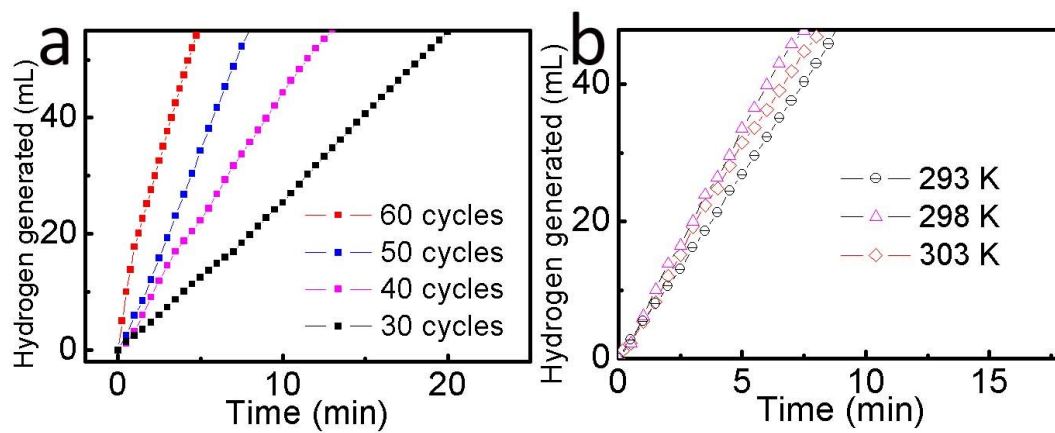


Fig. S6. Plots of the volume of hydrogen vs. time from NaBH₄ hydrolysis (3 mL) at 298 K catalyzed by CoP/Ti mesh prepared under different deposition conditions for precursor: (a) cycle number; (b) temperature.

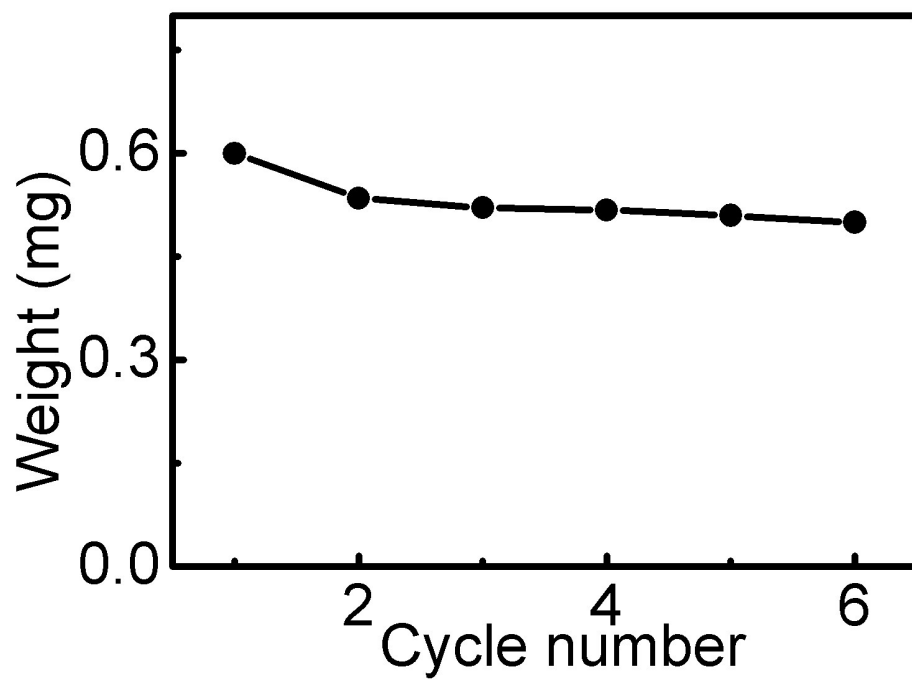


Fig. S7. Effect of cycling number on the weight of CoP in aqueous solution (3 mL) containing NaBH_4 (1.0 wt%) and NaOH (2.0 wt%) at 298 K.

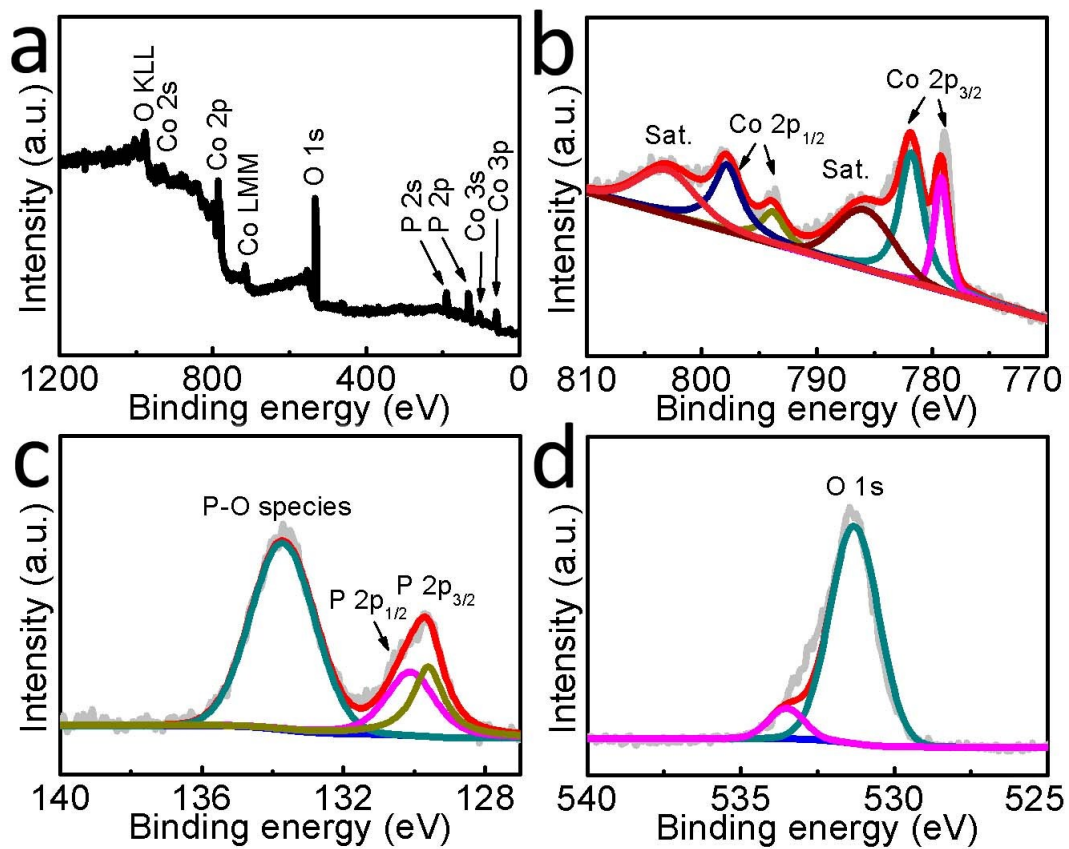


Fig. S8. (a) XPS survey spectrum for CoP after hydrolysis. XPS spectra in the (b) Co 2p, (c) P 2p, and (d) O 1s regions for CoP after hydrolysis.

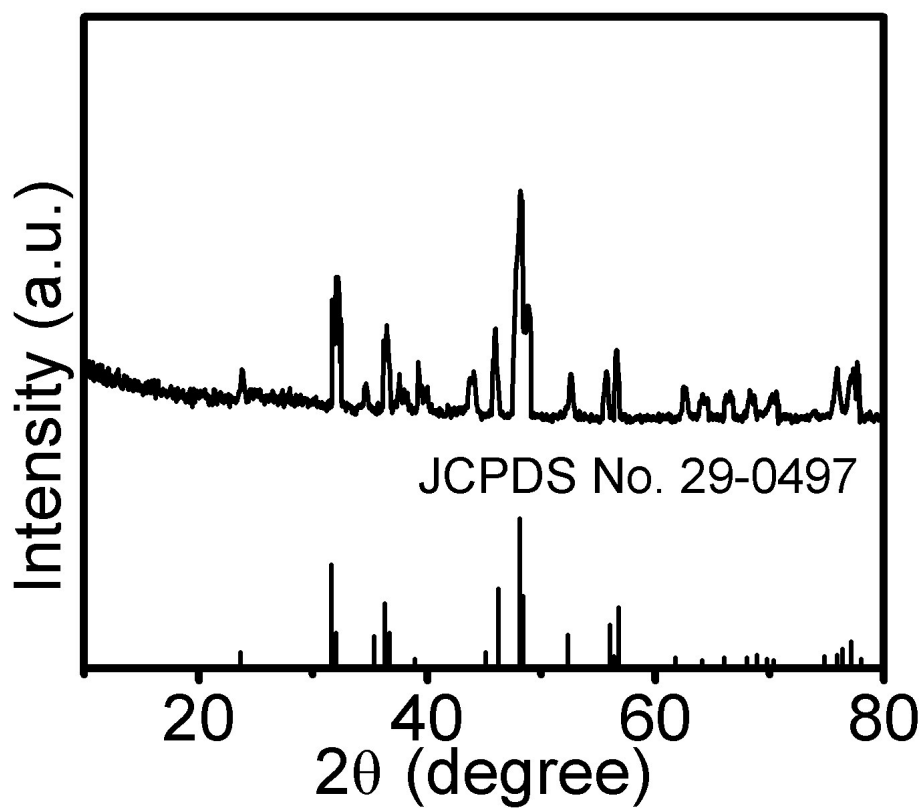


Fig. S9. XRD pattern of the CoP after catalytic reaction.