

Electronic Supplementary Information (ESI)

**Two transition metal phosphonate
photocatalysts for H₂ evolution and CO₂
reduction**

Jiajia Wang, Ruoqian Zhang, Yuanyuan Liu, Zeyan Wang, Peng Wang,
Zhaoke Zheng, Xiaoyan Qin, Xiaoyang Zhang, Ying Dai and Baibao
Huang

Contents

I Experiment Section

II Characterizations

III Figures

I Experiment section

All chemicals used were of analytical grade, and were used without further purification.

Synthesis of CoPPA and NiPPA

Synthesis of CoPPA: $\text{Co}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (0.582 g, 2 mmol) and phenylphosphonic acid (PPA, 0.316 g, 2 mmol) were added in 60 mL N, N-Dimethylformamide (DMF) at room temperature. After being stirred for 30 min, the mixture was transferred into a 100mL Teflon-lined stainless autoclave and kept at 110 °C for 24 h. After being cooled naturally to room temperature, the obtained red purple product was collected by filtration and washed several times with deionized water and ethanol, and then dried at 60 °C for 12 h.

Synthesis of NiPPA: the same preparation conditions were used, except that different amounts of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.582 g, 2 mmol).

II Characterizations

The X-ray power diffraction (XRD) data of as-prepared samples

was collected on an X-ray powder diffraction (Bruker AXS D8). The UV-vis diffuse reflectance spectra were performed on a Shimadzu UV 2550 recording spectrophotometer, which was equipped with an integrating sphere and BaSO₄ was used as a reference. A Fourier transform infrared (FT-IR) spectra was performed on a Bruker ALPHA-T spectrometer using KBr pellets. The morphologies of as-prepared samples were obtained using scanning electron microscopy (SEM, Hitachi S4800). Electron paramagnetic resonance (EPR) spectra were obtained with a Bruker ESP A300 electron paramagnetic resonance spectrometer at room temperature. The Brunauer-Emmett-Teller (BET) surface areas of the samples were measured by a Micromeritics ASAP2020 analyzer at liquid nitrogen temperature. The XPS was characterized by using a Thermo Fisher Scientific (ESCALAB 250) X-ray photoelectron spectrometer and the results were charge corrected to the adventitious C 1s peak at 284.8 eV.

Photocatalytic reactions

Photocatalytic hydrogen evolution reactions were carried out in top-irradiation vessel connected to a glass-enclosed gas circulation system. In the procedure of hydrogen produce, 50 mg catalyst and 1 mL triethanolamine (TEOA) were mixed in 99 mL water with constant stirring. The temperature of reactions was kept at 15 °C. The amount of H₂ evolution was determined by a gas chromatograph

(TechcompGC7890 II).

The process of photocatalytic CO₂ reduction is as follows: 0.1 g sample and 1 mL TEOA were mixed into 99 mL deionized water with continuous stirring, and high purity CO₂ gas was continuously bubbled through the solution for 30 min before the lamp was turned on. The temperature of reactor of CO₂ reduction was controlled at 15 °C by using cooling water circulation. The determination of CO was performed with a chromatograph (Ceaulight GC-7920).

The ultraviolet lamp (Her aeus, GPH212T5VH/4) with wavelength of 254 nm was used as the light source for UV light photocatalytic process.

III Figures

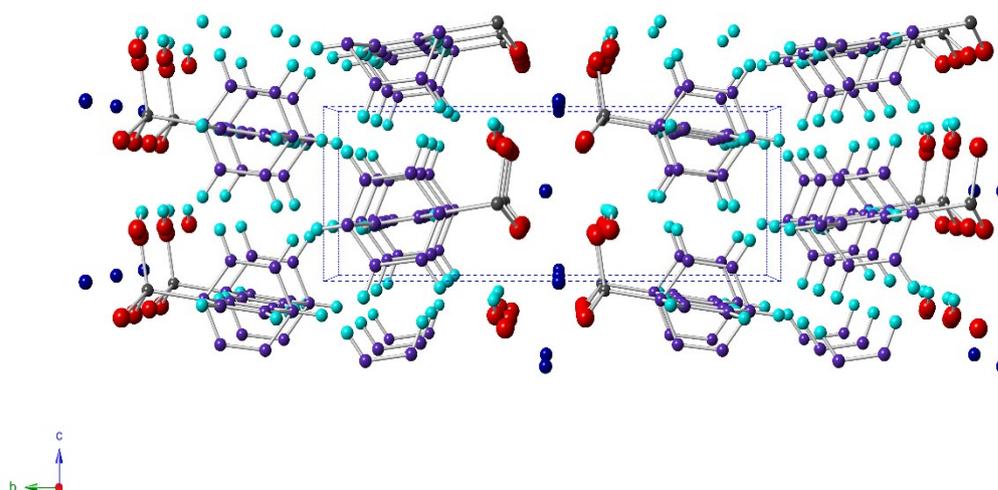


Fig. S1 schematic drawing for the structure of NiPPA (C: purple, O: red, P: grey, Ni: deep blue)

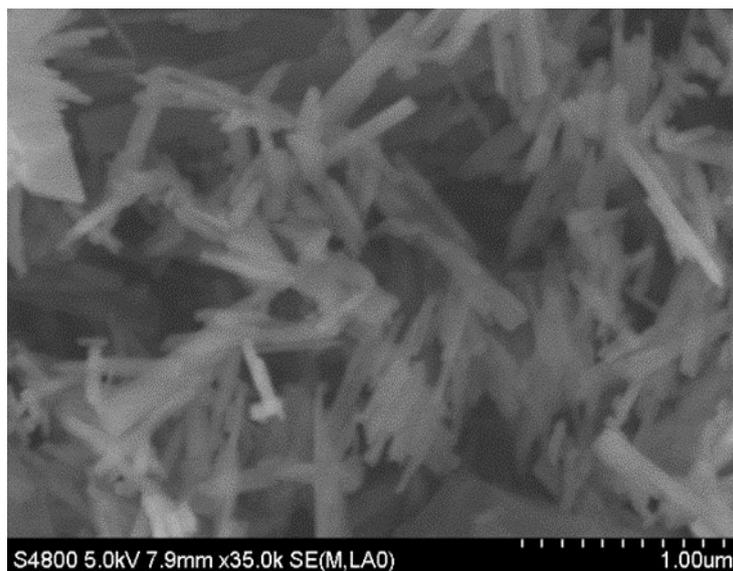


Fig. S2 SEM image of CoPPA

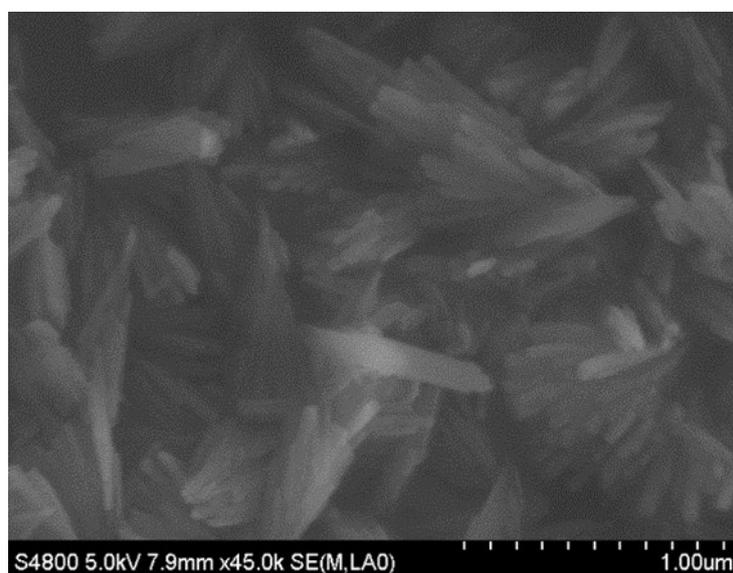


Fig. S3 SEM image of NiPPA

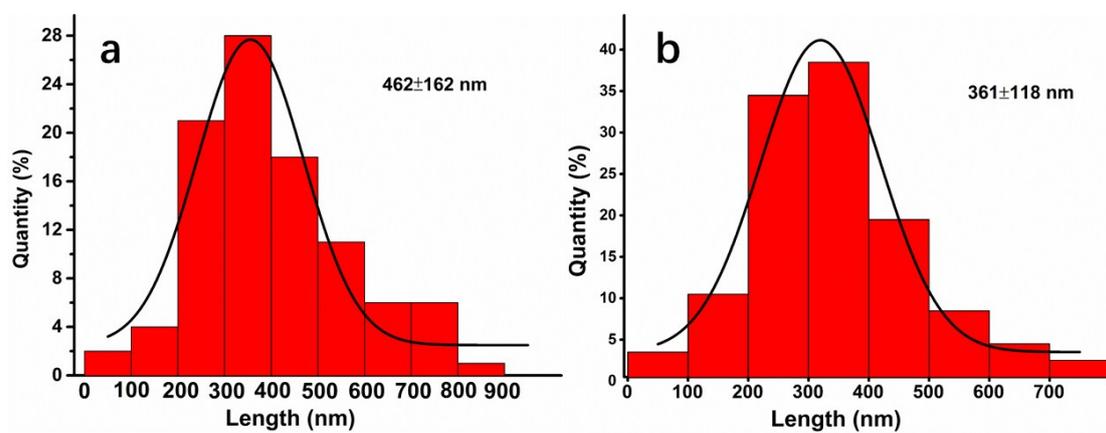


Fig. S4 the statistical length of CoPPA (a) and NiPPA (b) nanorod

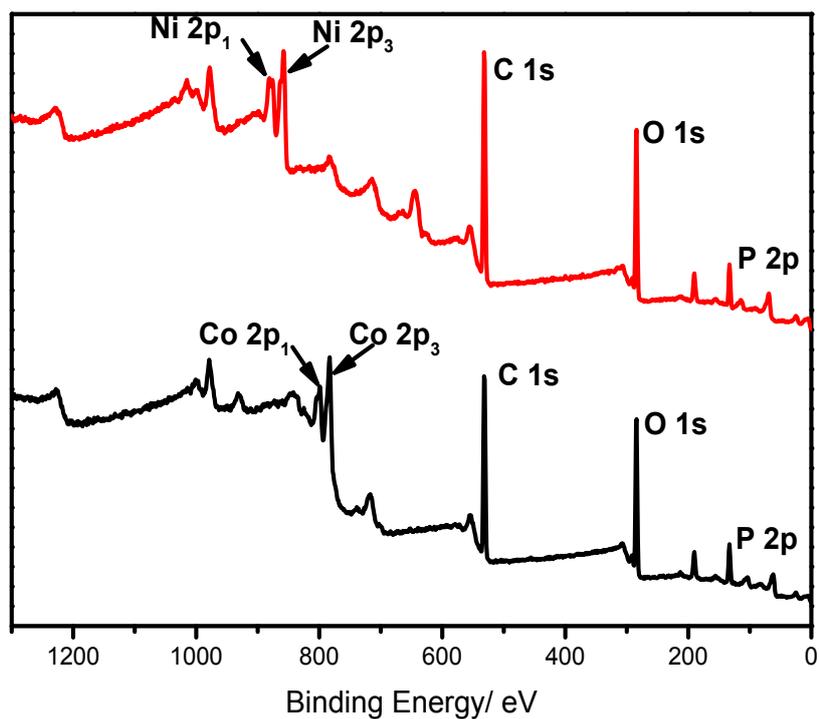


Fig. S5 a survey of XPS spectrum of CoPPA (black) and NiPPA (red)

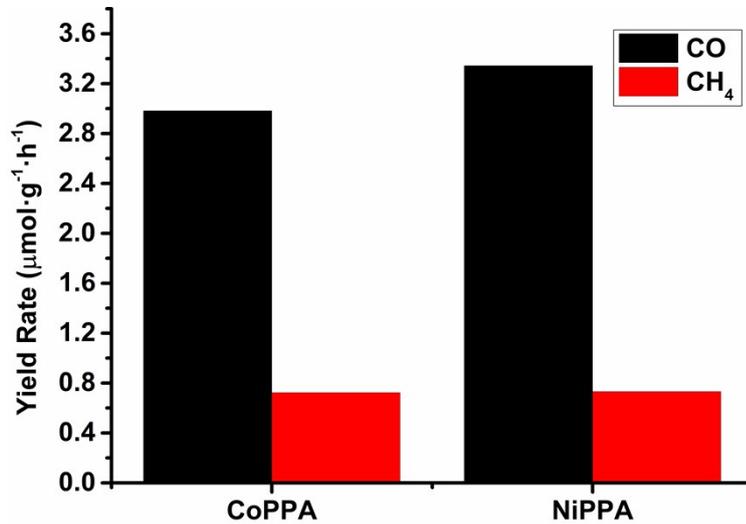


Fig. S6 yield rate of CO and CH₄ for corresponding samples

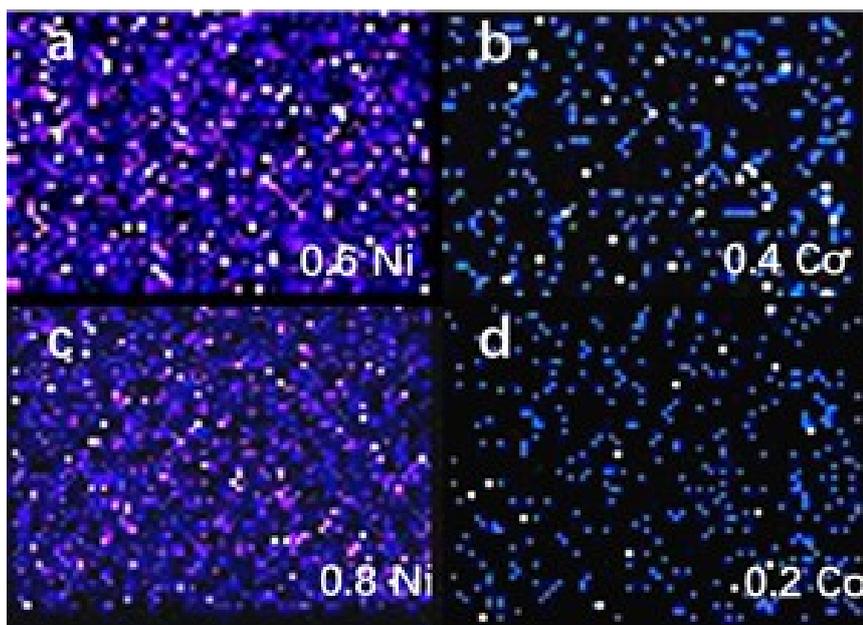


Fig. S7 EDX mapping images of Ni_xCo_{1-x}PPA with x=0.6 (a and b), x=0.8 (c and d)

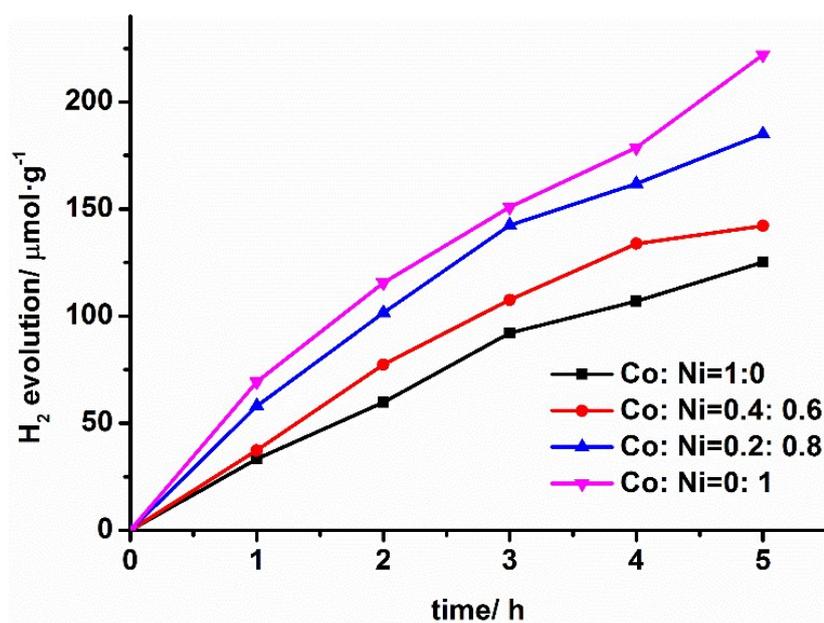


Fig. S8 photocatalytic H₂ production of Ni_xCo_{1-x}PPA (x=0, 0.6, 0.8, 1).

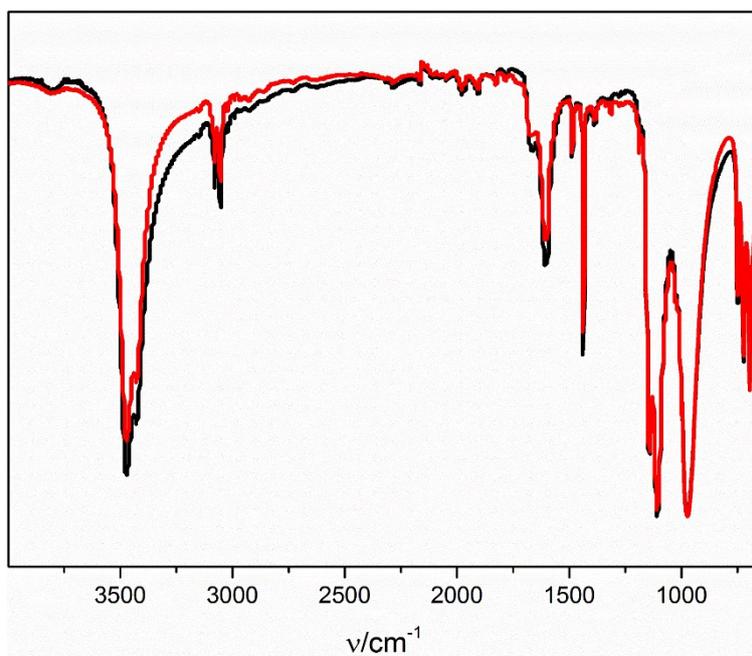


Fig. S9 FT-IR spectra of CoPPA before (black) and after (red) photocatalytic H₂ evolution under UV irradiation

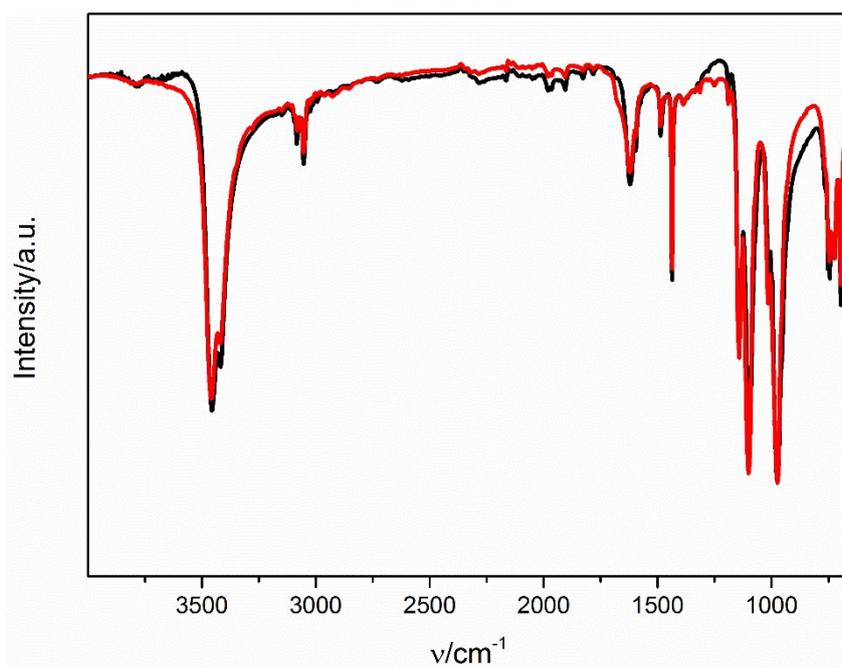


Fig. S10 FT- IR spectra of NiPPA before (black) and after (red) photocatalytic H₂ production under UV irradiation

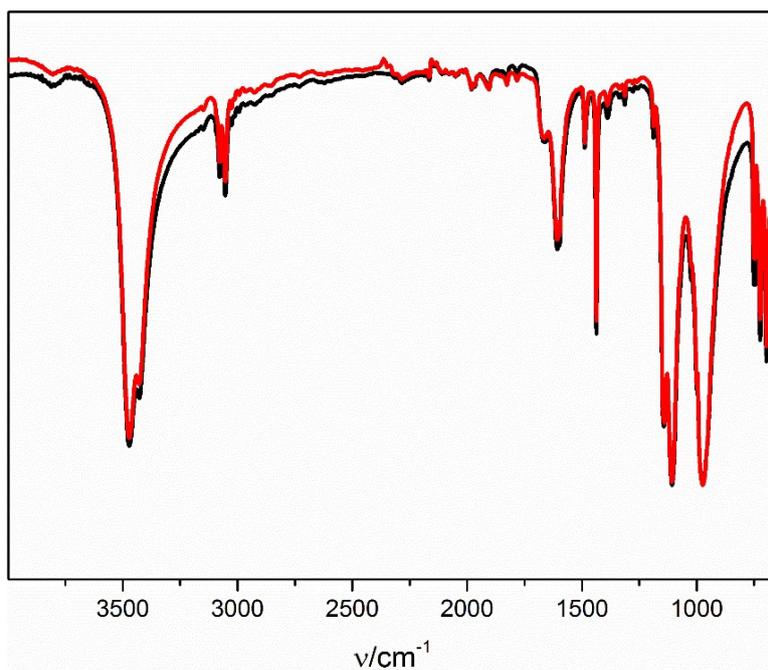
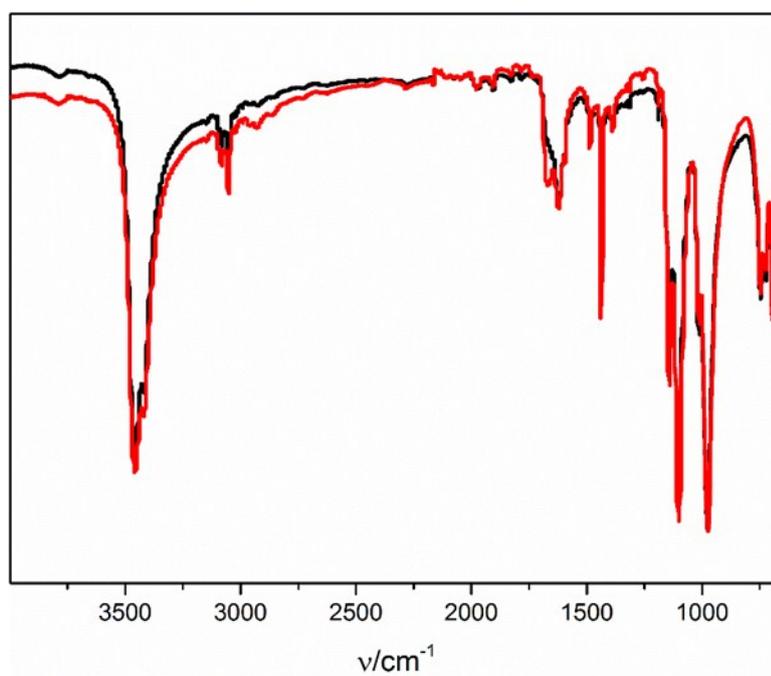


Fig. S11 FT-IR spectra of CoPPA before (black) and after (red)



photocatalytic CO_2 reduction

Fig. S12 FT-IR spectra of NiPPA before (black) and after (red)
photocatalytic CO_2 reduction

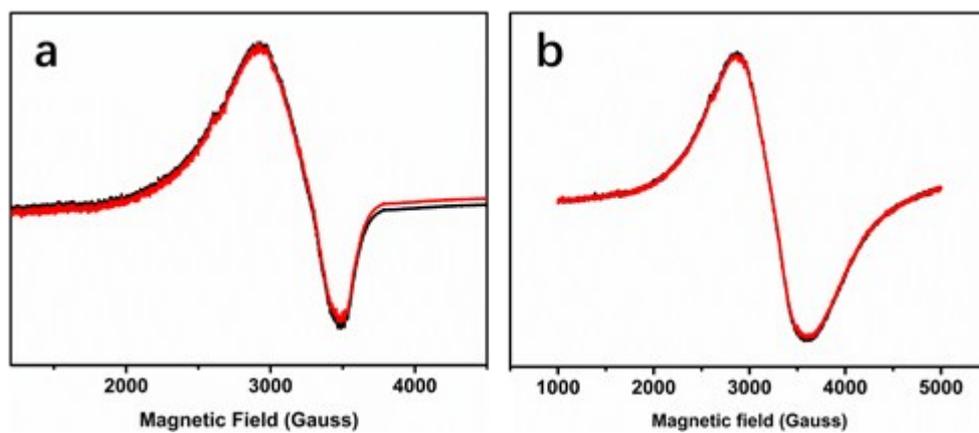
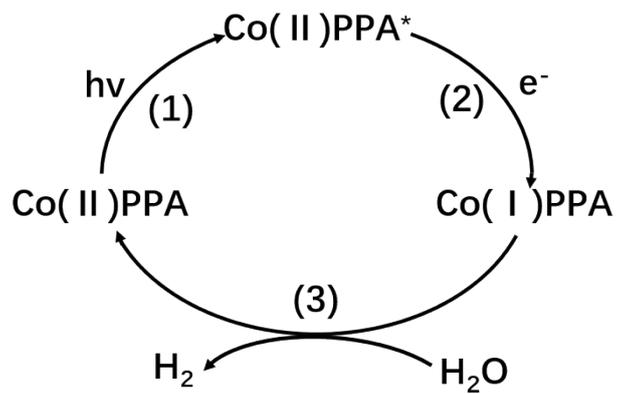


Fig. S13 EPR spectra of CoPPA (a) and NiPPA (b) before (black) and after (red) photocatalytic H₂ production



Scheme. 1 photocatalytic H₂ production mechanism of CoPPA.