Electronic Supplementary Material (ESI) for Faraday Discussions.

Supplementary Information

Visible Light-Driven Water Oxidation with a Ruthenium Sensitizer and a Cobalt-Based Catalyst Connected with a Polymeric Platform

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Figures

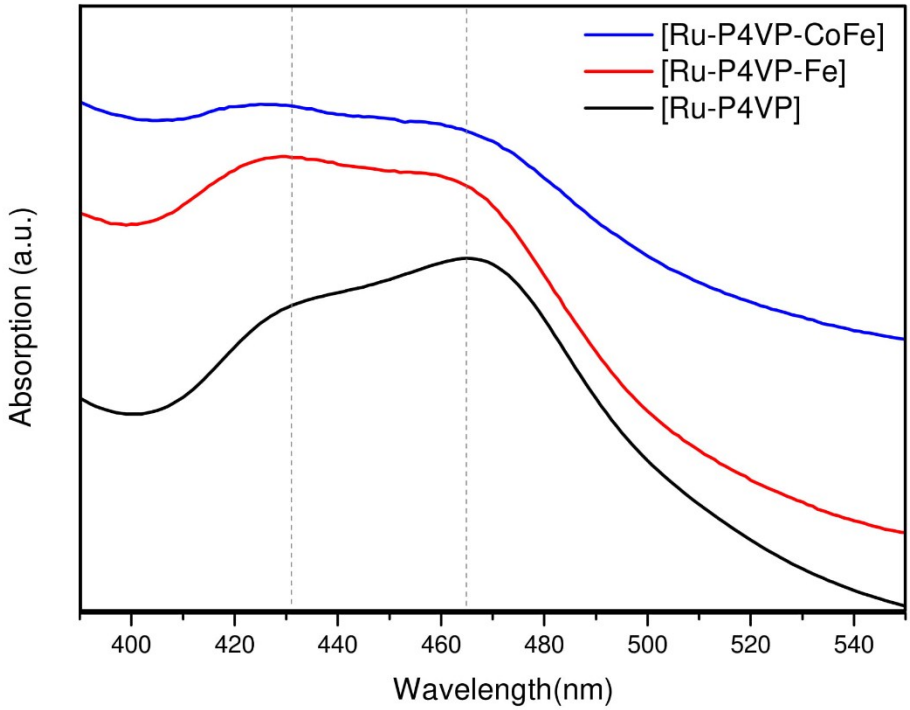

Fig. S1 UV-Vis spectra of [Ru-P4VP] (black line), [Ru-P4VP-Fe] (red line), and [Ru-P4VP-CoFe] (blue line).

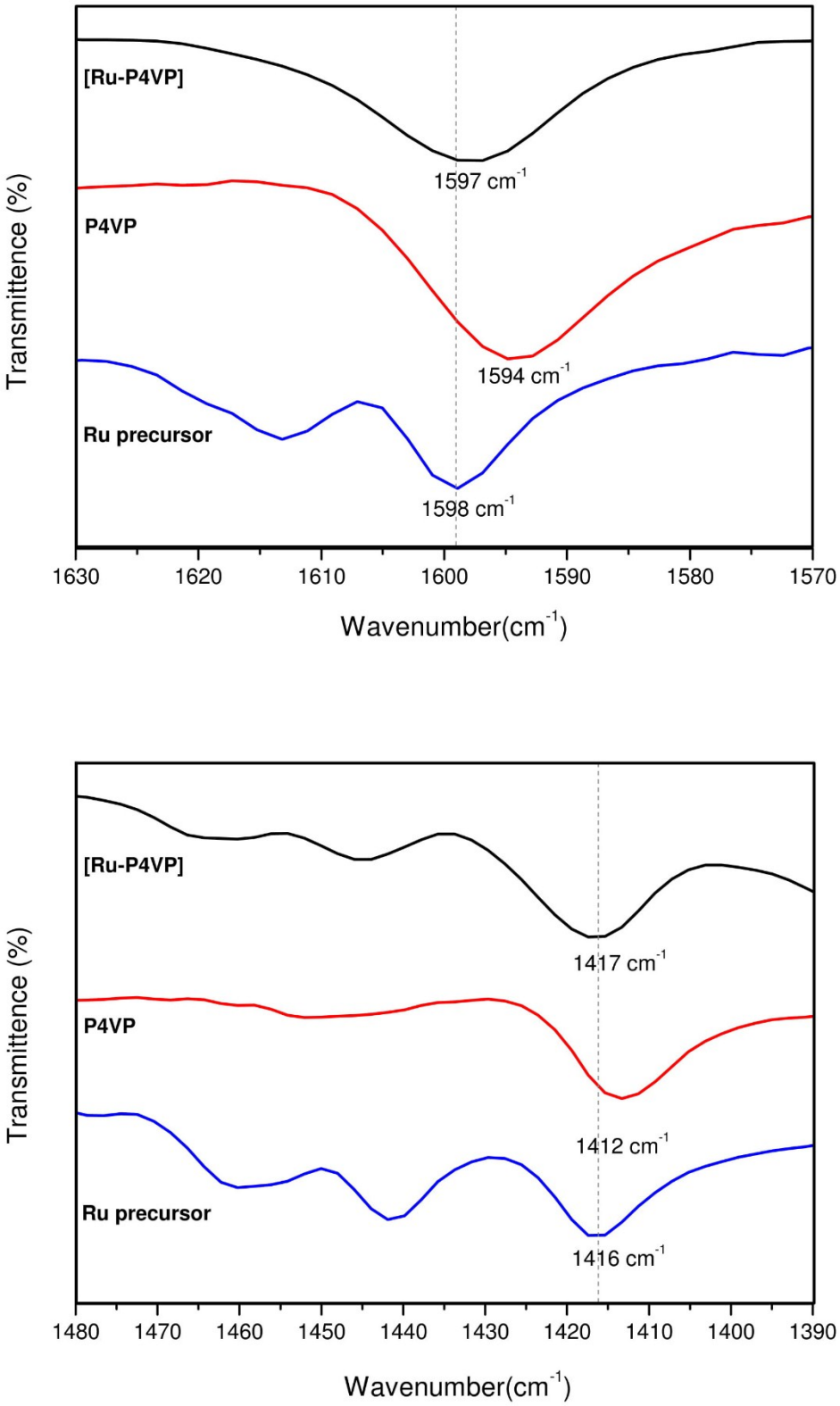

Fig. S2 FTIR spectra of Ru precursor, P4VP, and [Ru-P4VP].

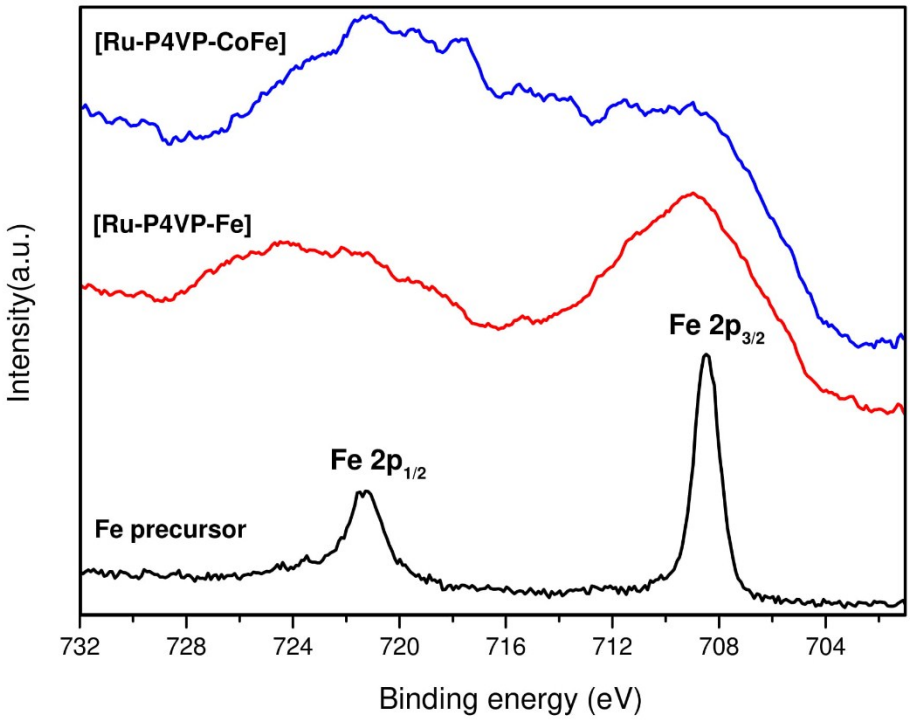

Fig. S3 XPS spectra of Fe 2p signals of Fe precursor, [Ru-P4VP-Fe], and [Ru-P4VP-CoFe].

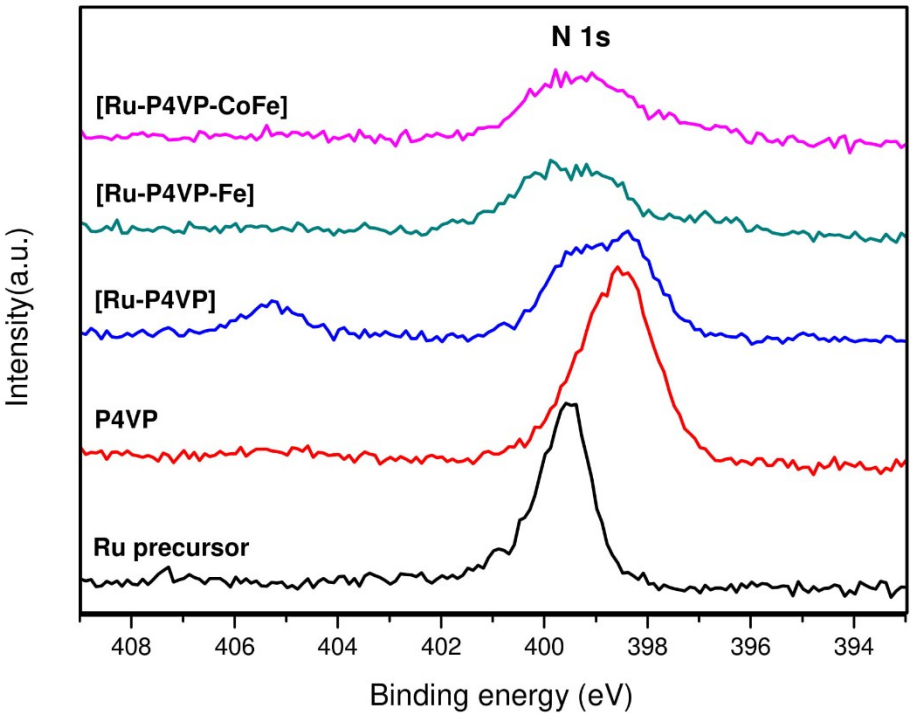

Fig. S4 XPS spectra of N 1s signals of Ru precursor, P4VP, [Ru-P4VP], [Ru-P4VP-Fe], and [Ru-P4VP-CoFe].

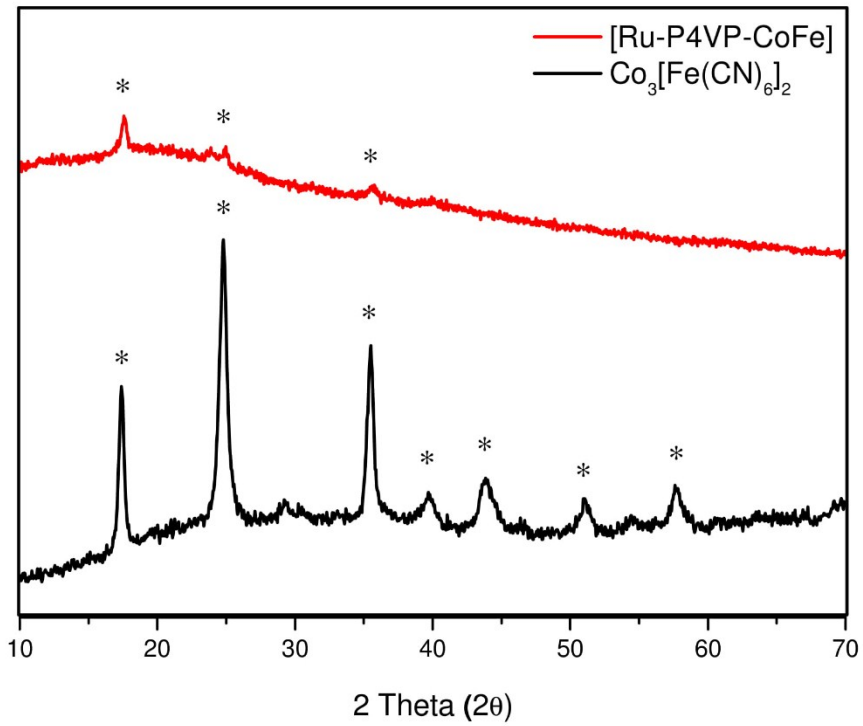

Fig. S5 GI-XRD patterns of $Co_3[Fe(CN)_6]_2$ (black line), and [Ru-P4VP-CoFe] (red line). The peaks that belong to Prussian Blue analogue are marked with asterisk (*).

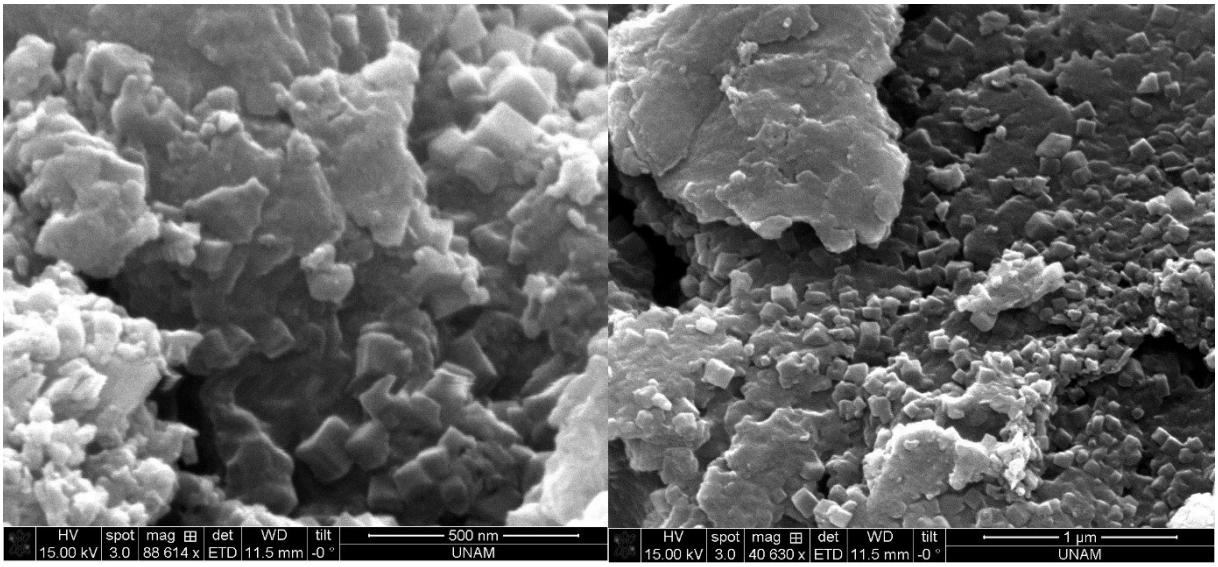

Fig. S6 SEM images of [Ru-P4VP-CoFe].

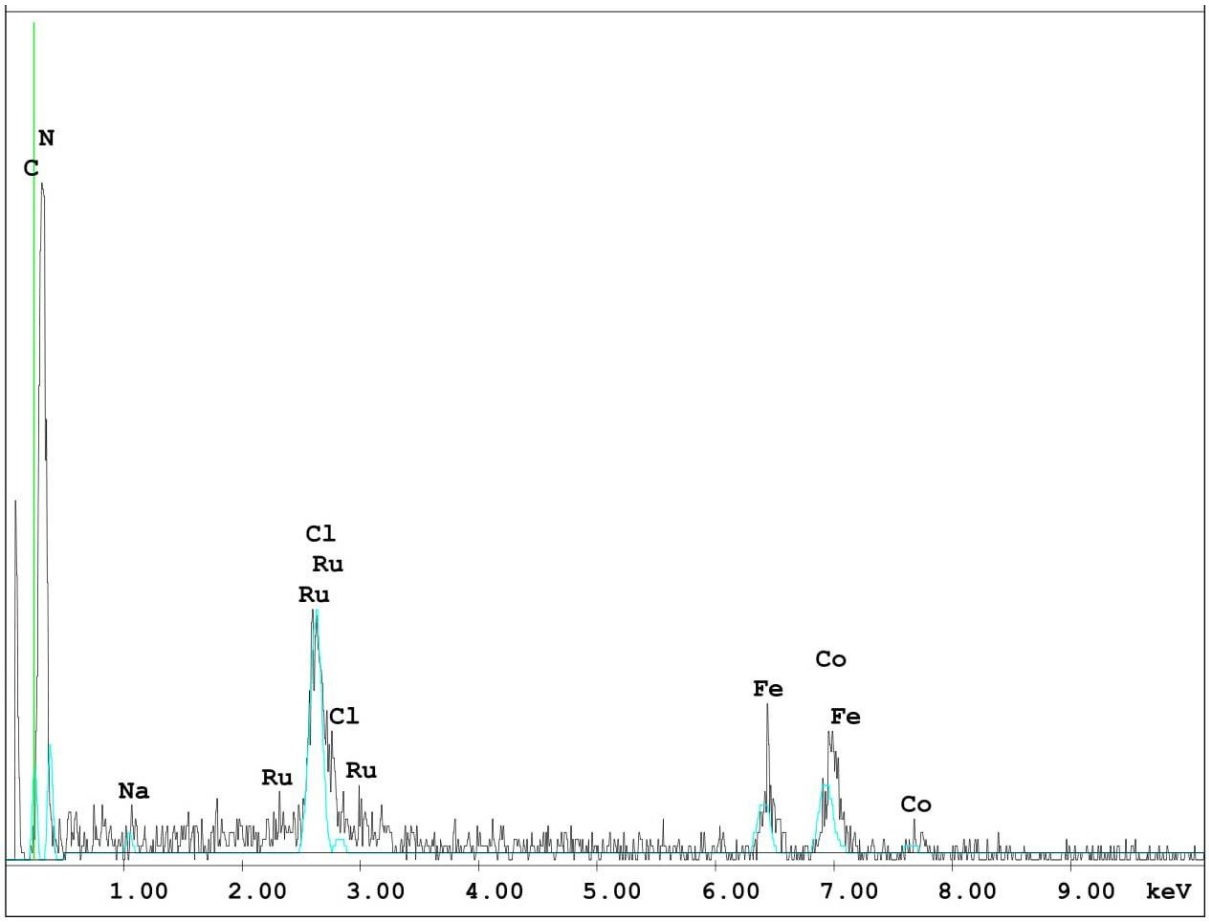

Fig. S7 EDX spectrum of [Ru-P4VP-CoFe].

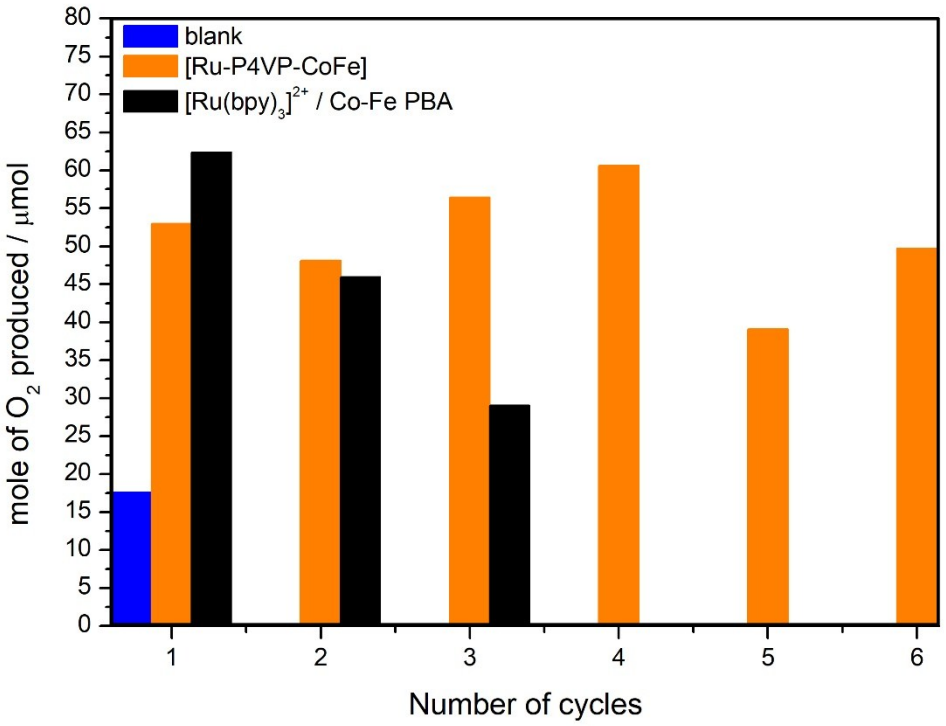

Fig. S8. Photocatalytic oxygen evolution by [Ru-P4VP-CoFe] (orange bar), $[Ru(bpy)_3]^{2+}$ / Co-Fe PBA system (black bar), and $[Ru(bpy)_3]^{2+}$ / Co-Fe PBA system without electron scavenger (blue bar). All experiments were performed in solution of 10 mL phosphate pH 7.0 buffer and 25 mg sodium persulfate.

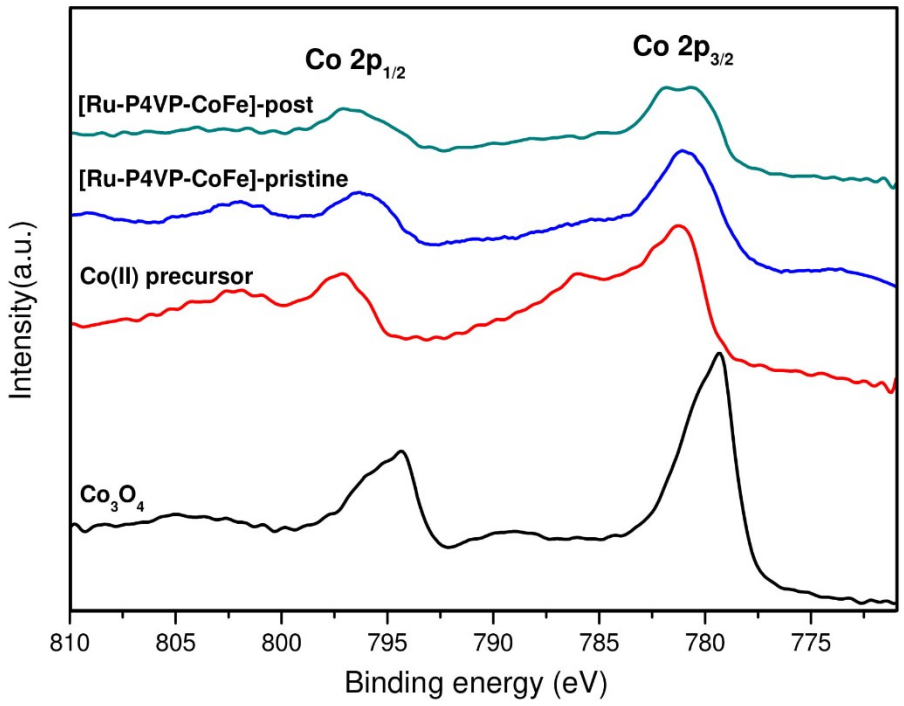

Fig. S9 XPS spectra of Co 2p signals of Co_3O_4, Co(II) precursor, [Ru-P4VP-CoFe], and [Ru-P4VP-CoFe] after six catalytic cycle.

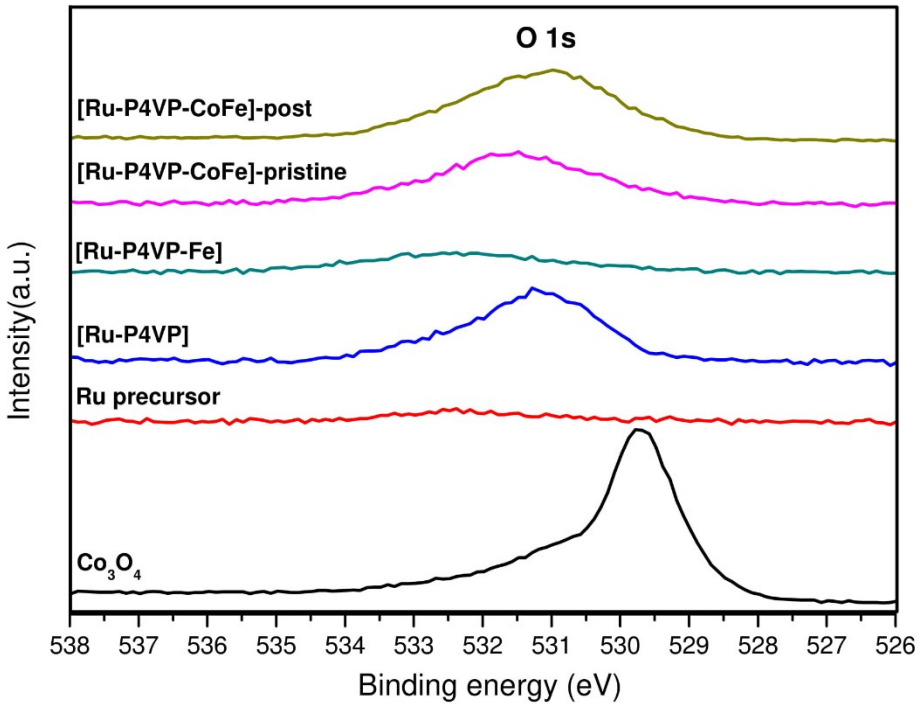

Fig. S10 XPS spectra of O 1s signals of Co_3O_4, Ru precursor, [Ru-P4VP], [Ru-P4VP-Fe], [Ru-P4VP-CoFe], and [Ru-P4VP-CoFe] after six catalytic cycle.

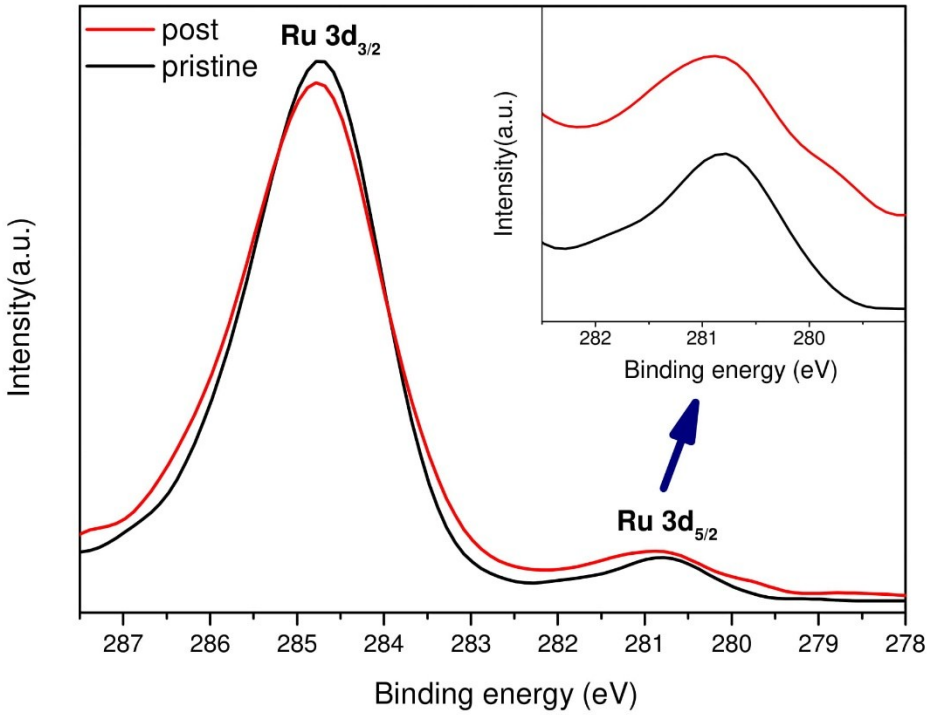

Fig. S11 XPS spectra of Ru $3d_{5/2}$ signals of pristine [Ru-P4VP-CoFe], and [Ru-P4VP-CoFe] after six catalytic cycles.

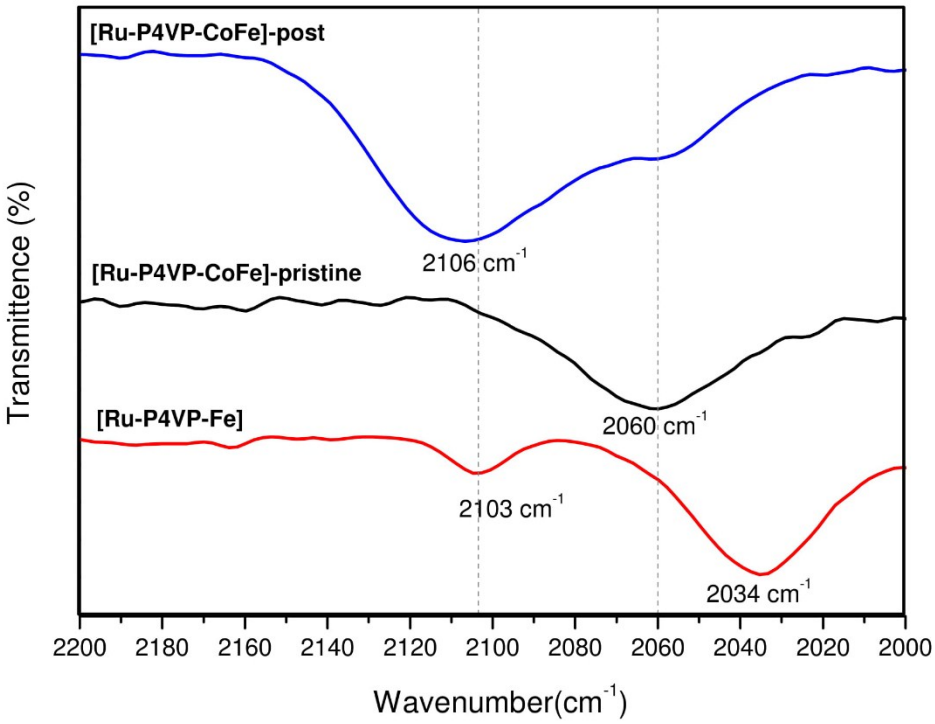

Fig. S12 FTIR spectra of [Ru-P4VP-Fe], [Ru-P4VP-CoFe], and [Ru-P4VP-CoFe] after six catalytic cycle.

Photocatalytic Studies

For each photocatalytic measurement, 10 mL phosphate pH 7.0 buffer was used, and 25 mg sodium persulfate was added as the electron scavenger. All measurements were done under constant stirring, and flask were covered with aluminum foil until the light was on. Pressure transducer was connected to two-neck round-bottom flask and one neck was covered with septa. Before light illumination, solution was purged with N_2 for 30 min, and two needles were used for N_2 in and out. When plateau was observed on pressure, 100 µL from the headspace of the cell was injected with gas-tight syringe into a gas chromatograph as an initial measurement. Pressure was allowed to reach plateau, and followingly light was on for 1 h. After 1 h of light illumination, light was off, and gas phase was analyzed by GC. During the process, pressure change was recorded versus time. Blank measurement was also taken according to the same procedure. Solution was consisted of 10 mL phosphate pH 7.0 buffer, and 25 mg sodium persulfate. TOF and TON were derived by using the data obtained from GC. O_2 to N_2 area ratio were calculated, and the value was multiplied with the headspace volume of the cell, then divided by injection volume of the gas tight syringe to obtain total O_2 amount in the cell. Subsequently, total O_2 amount of blank measurement and initial measurement were subtracted from the final experimental value.

Galan-Mascaros et al. reported that the TOF obtained was 4.5×10^{-4} s^{-1}, and it was used as a reference value. [1] 5 mg $[Ru(bpy)_3]^{2+}$, 5 mg Co-Fe PBA, and 25 mg sodium persulfate were dissolved in 10 mL phosphate pH 7.0 buffer, and photocatalytic experiment was conducted according to the above procedure.

After necessary subtractions, total amount of O_2 obtained was multiplied with a constant which will give TOF of 4.5×10^{-4} s^{-1} to obtain mole of O_2 produced. Mole of O_2 was used to calculate TOF, and equation is as follows:

$$\text{mole of } O_2 \text{ produced} = \text{total } O_2 \text{ amount} \times \text{constant}$$

$$\text{TOF} = \text{mole of } O_2 \text{ produced} / (\text{mole of catalyst} \times \text{time})$$

Constant derived according to the calculations were then used in [Ru-P4VP-CoFe] measurements to obtain mole of O_2, TOF, and TON values. For mole of catalyst value, it is assumed that all Co sides are active for water oxidation. TON equation is as follows:

$$\text{TON} = \text{TOF} \times \text{time}$$

After each photocatalytic experiment of [Ru-P4VP-CoFe] and $[Ru(bpy)_3]^{2+}$ and Co-Fe PBA systems, samples were kept in fridge for 1 day and re-used with the addition of 25 mg sodium persulfate.

Reference

[1] S. Goberna-Ferrón, W. Y. Hernández, B. Rodríguez-García and J. R. Galán-Mascarós, ACS Catal., 2014, 4, 1637–1641.