Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Electronic Supplementary Information

Black phosphorus synthesized by solvothermal reaction from red phosphorus and its catalytic activity for water splitting

Akiyo Ozawa, Muneaki Yamamoto, Tetsuo Tanabe, Saburo Hosokawa, Tomoko Yoshida

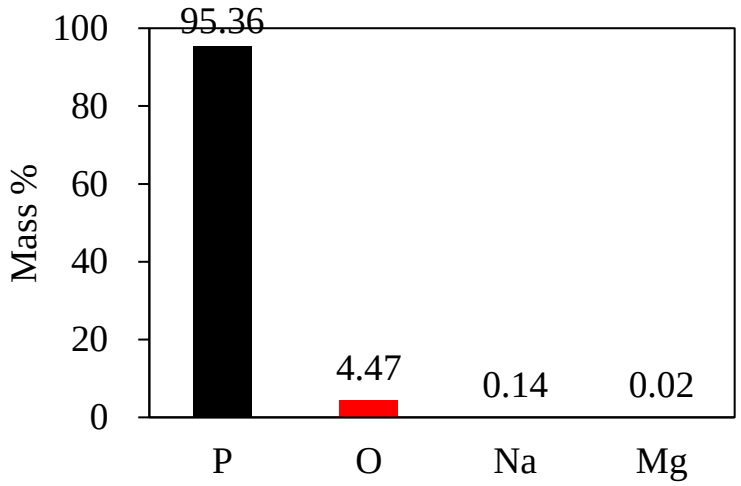

Fig. S1. Results of elemental analysis of sample 7 determined by X-ray fluorescence.

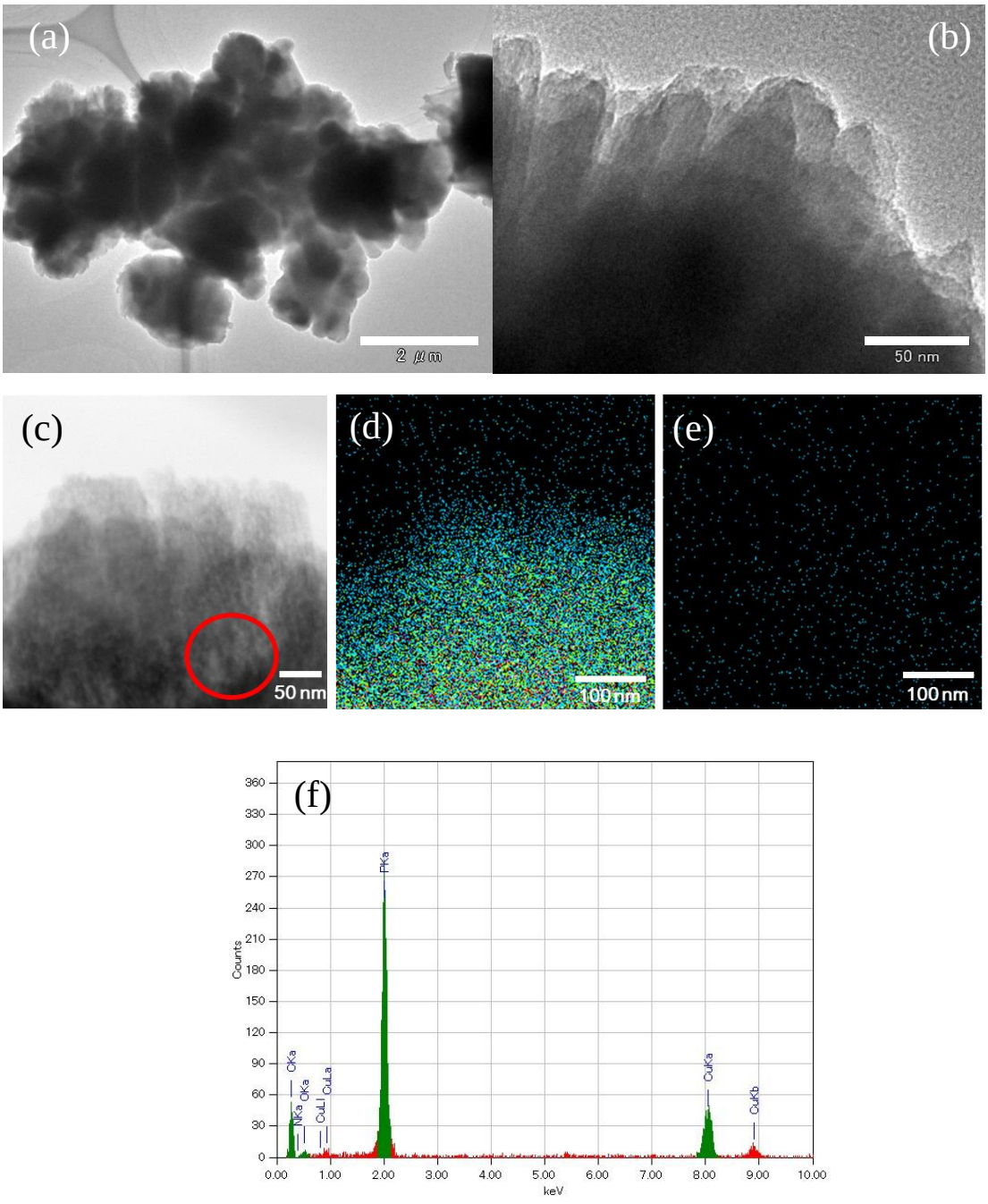

Fig. S2. (a), (b) Low resolution TEM images of sample 7, (c) STEM image corresponding to (b) with elemental mapping of P (d) and O (e) given by EDS analysis. (f) EDS spectrum take from the circled area in the STEM image. Scale bars from (a) to (e) were 2 μm, 50 nm, 50 nm, 100 nm, and 100 nm respectively. Cu detected in EDS spectrum was due to grid used for sample support.

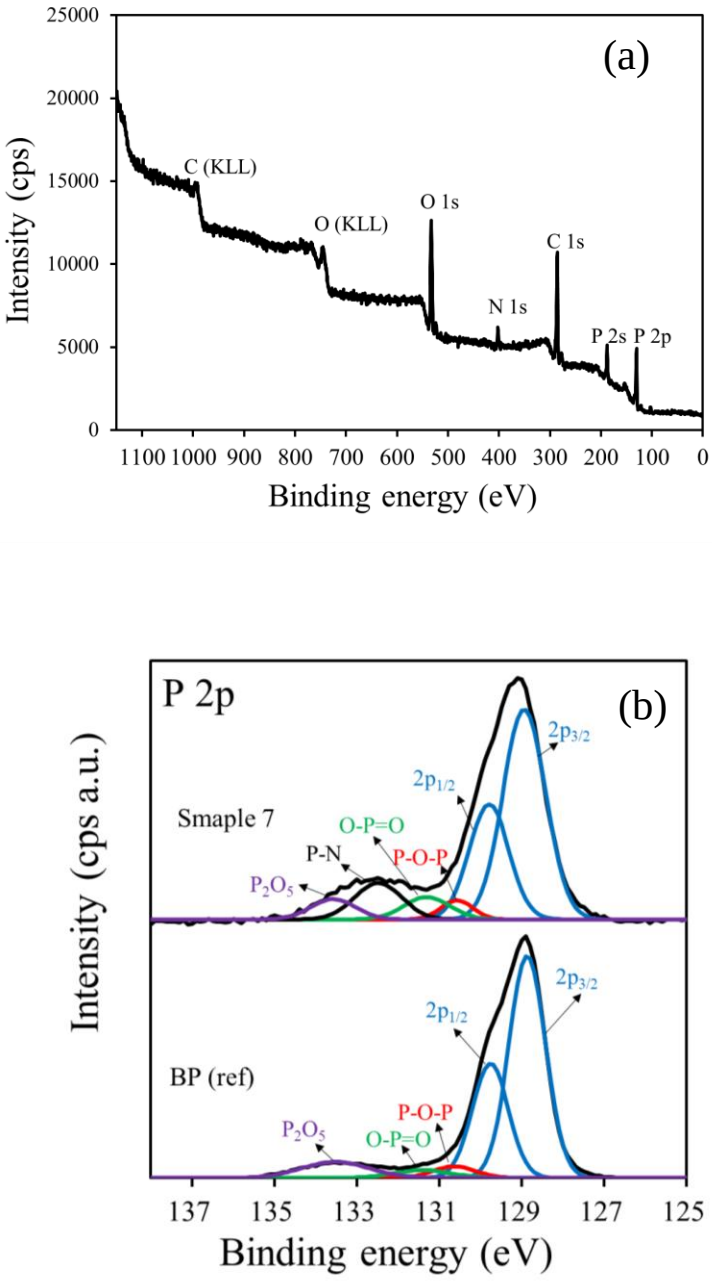

Fig. S3. XPS spectrum of sample 7, (a) wide range, and (b) focused to P 2p XPS range together with that of BP (ref) for comparison.

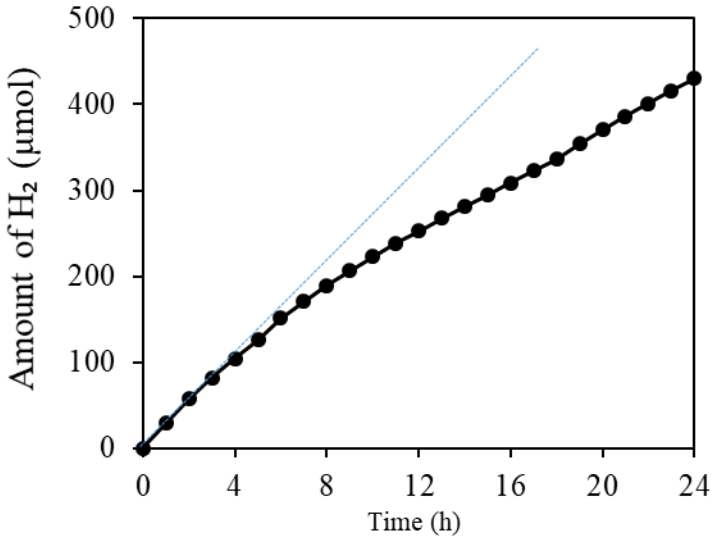

Fig. S4 Evolved hydrogen in a photocatalytic water splitting test with methanol aqueous solution under visible light irradiation using Co/sample 11 for 24 hours.

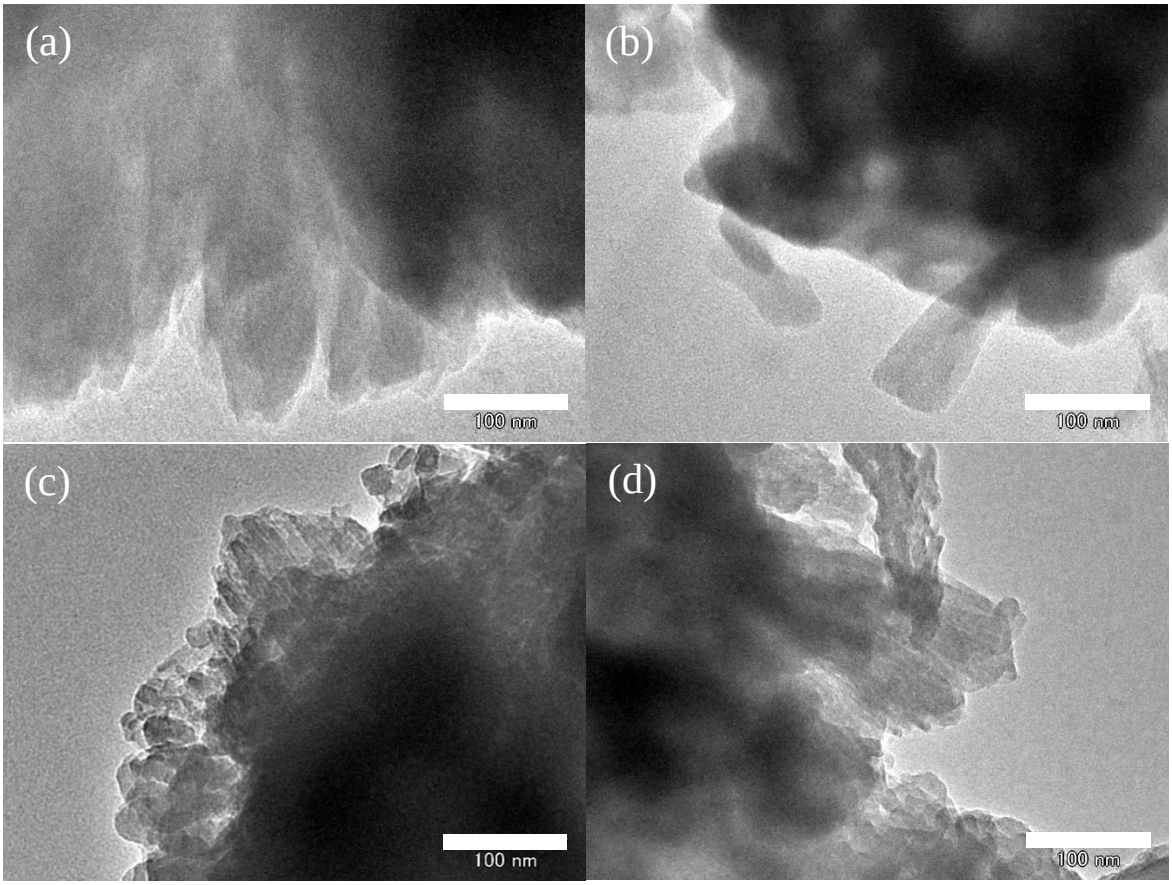

Fig. S5. TEM image of Co/sample 11. (a), (b) before and (c), (d) after photocatalytic reaction in Fig. S4.

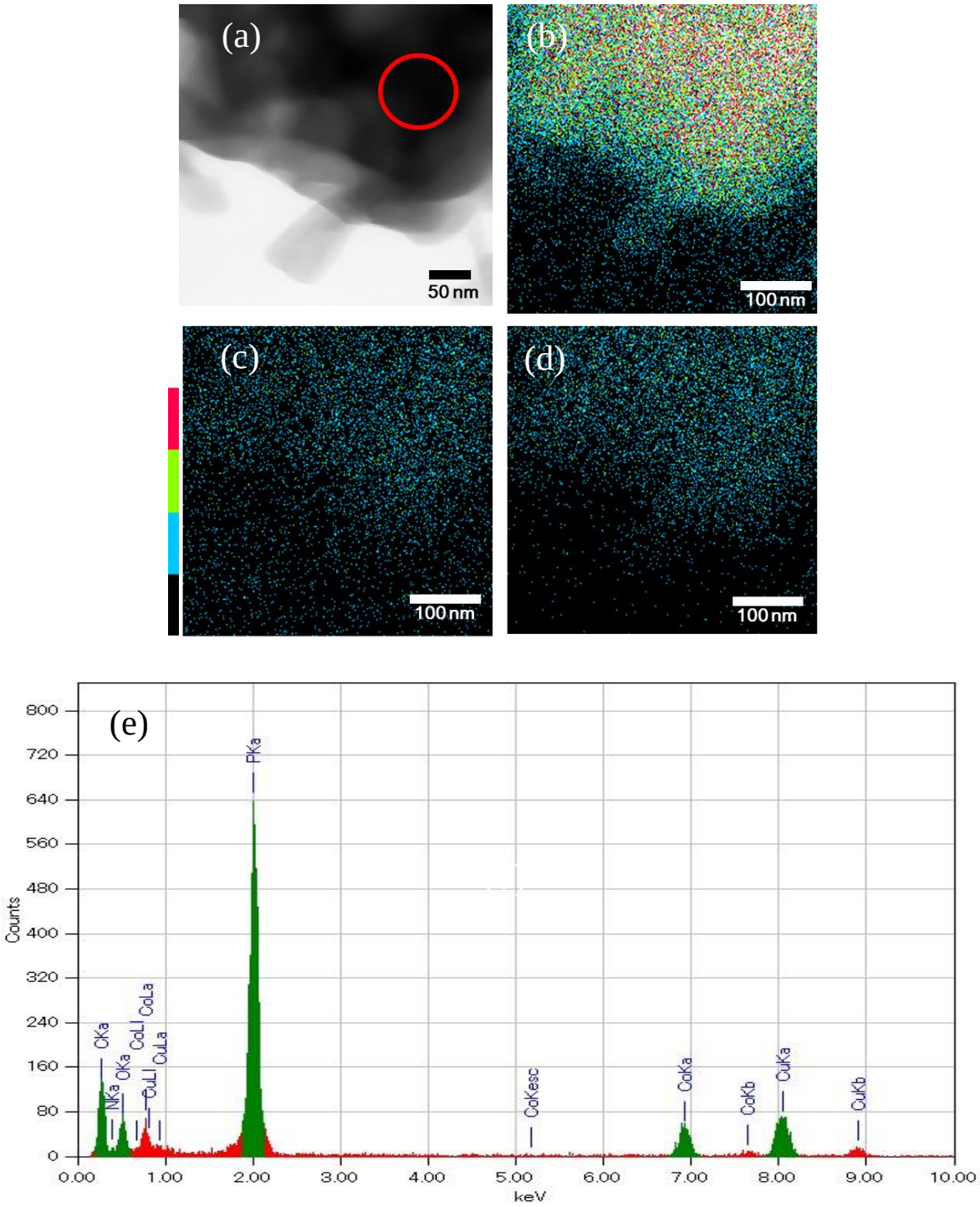

Fig. S6. Energy-dispersive X-ray spectroscopy (EDS) mapping of Co/sample 11 before photocatalytic reaction in Fig. S4, including STEM image (a), P element (b), O element (c), and Co element (d). (e) EDS spectrum in red frame of the STEM image. Cu detected in EDS spectrum was due to grid used for sample support.

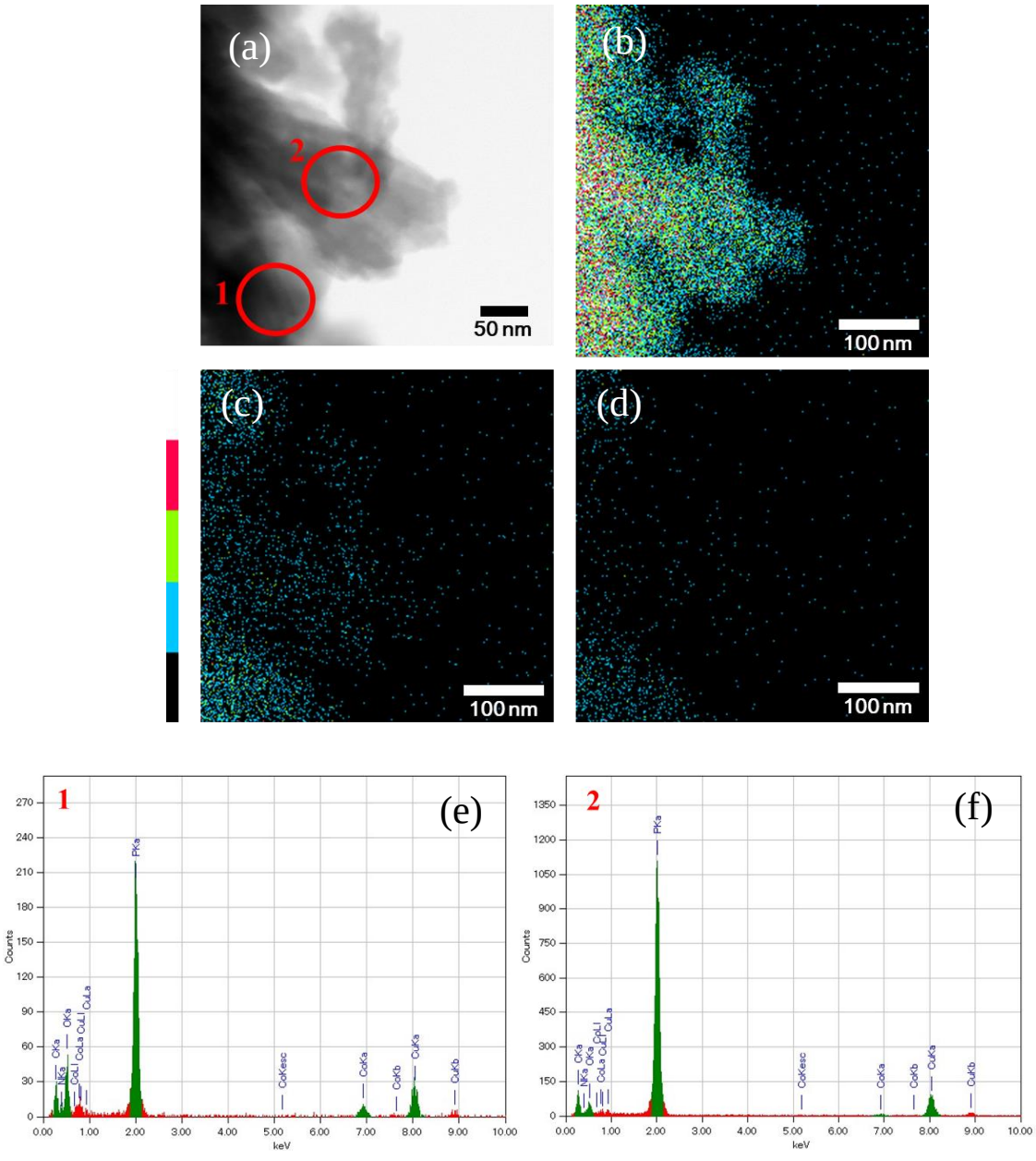

Fig. S7. Energy-dispersive X-ray spectroscopy (EDS) mapping of Co/sample 11 after photocatalytic reaction in Fig. S4, including STEM image (a), P element (b), O element (c), and Co element (d). (e) and (f) EDS spectrum in red frame 1 or 2 of the STEM image. Cu detected in EDS spectrum was due to grid used for sample support.

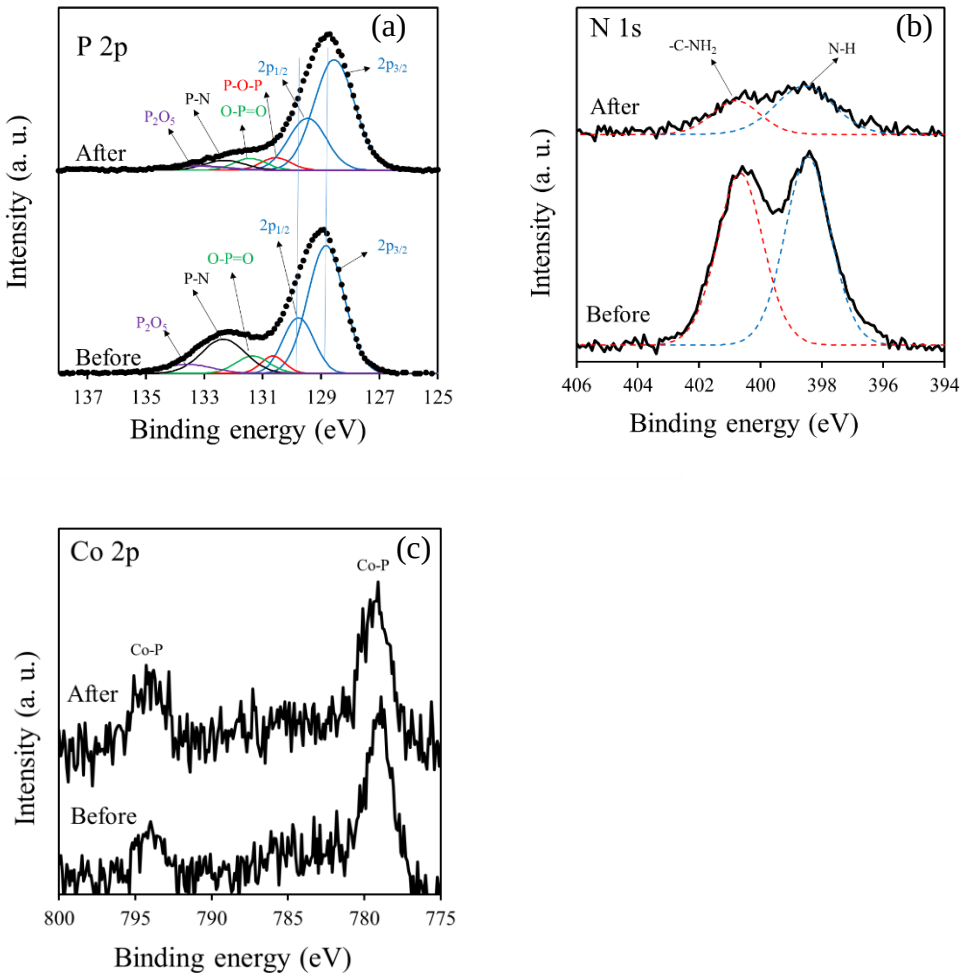

Fig. S8. (a) P 2p, (b) N 1s and (c) Co 2p XPS spectra of Co/sample 11 before and 24 hours after photocatalytic reaction in Fig. S4.

N 1s XPS spectra at 398.3 and 400.6 eV were due to absorbed ED and N-H bonding[1]. The two peaks were significantly changed during 24 hours under visible light irradiation. Decrease of -P-N bonding after the test was also observed in P 2p XPS spectra. As shown in Fig. S1, the amount of absorbed ED was slight. The absorbed ED would be no effect on the hydrogen evolution because the sample had been shown the hydrogen evolution even when the adsorbed ED almost disappeared.

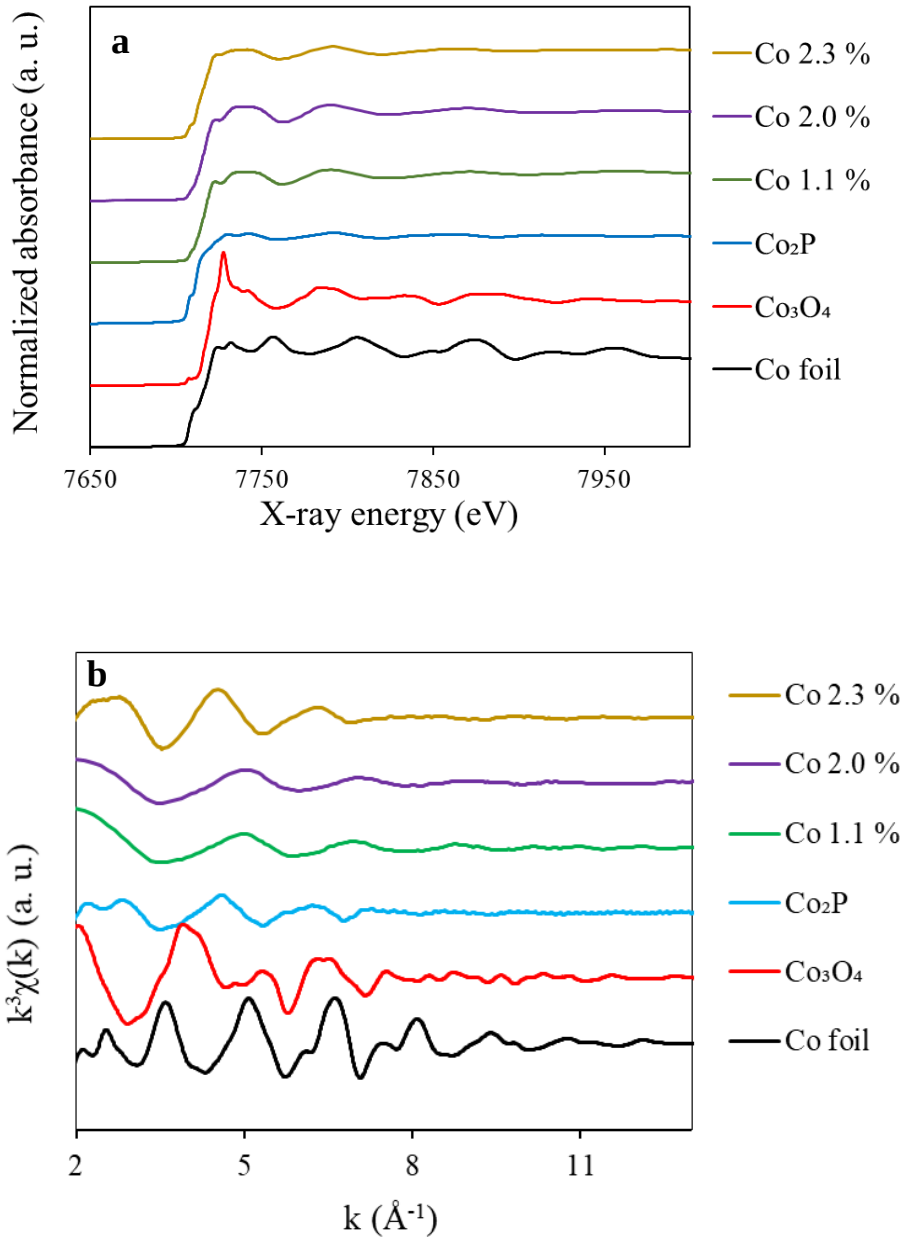

Fig. S9. (a) Co K-edge XANES and b) EXAFS spectra of the Co foil, Co_3O_4, Co_2P, 1.1, 2.0, and 2.3% Co/sample 11, respectively.

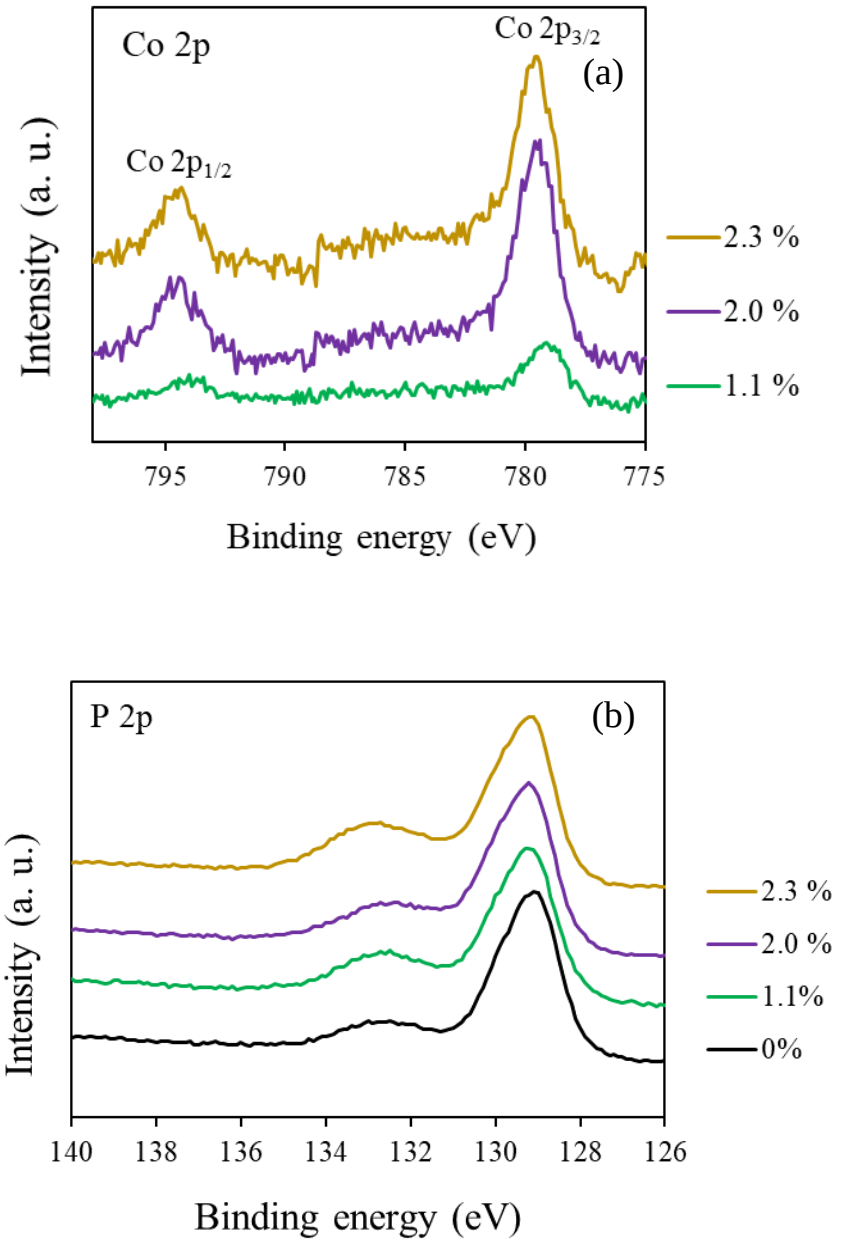

Fig. S10. (a) Co 2p XPS spectra of sample 11 depositing various amounts of Co. (b) P 2p XPS spectra corresponding to (a).

Reference

1. NIST X-ray Photoelectron Spectroscopy Database, NIST Standard Reference Database Number 20, National Institute of Standards and Technology, Gaithersburg MD, 20899 (2000)