

Supplementary Materials

Boosted catalytic activity toward the hydrolysis of ammonia borane by mixing Co- and Cu-based catalysts

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Experimental Section

Preparation of Co₃(PO₄)₂ microsphere. A mixture solution of 1.5 mmol CoSO₄·7H₂O (Aladdin, ≥99%) was prepared in 2.7 mL of deionized water with stirring. Next, 135 μL of a H₃PO₄ (Aladdin, ≥85%) solution (30%) was dropwise added to the CoSO₄ solution. Then, the obtained solution is poured into a mixture solution (61.3 mL) containing 0.67 mmol sodium dodecyl sulfate (SDS, Tianjin Baishi Chemical Reagent Co. Ltd., AR) and 67 mmol urea (Tianjin Yongda Chemical Reagent Co. Ltd., ≥99%). The obtained solution was hydrothermally heated at 120 °C for 2 h. Subsequently, the resultant sample was rinsed with ethanol and deionized water. Then, the product was dried in oven at 80 °C for 6 h.

Preparation of flower-like Cu₃(PO₄)₂·3H₂O. A mixture solution of 0.9 mmol SDS (Tianjin Baishi Chemical Reagent Co. Ltd., AR) and 100 mmol urea (Tianjin Yongda Chemical Reagent Co. Ltd., ≥99%) was mixed with a mixture solution of 24 mL deionized water and 40 mL isopropyl alcohol (IPA, Taishan Yueqiao Reagent Plastic Co. Ltd., >99.7%) with stirring. Then, 8 mL of a 0.063 M CuSO₄·5H₂O (Tianjin Baishi

Chemical Co. Ltd., $\geq 99\%$) solution was added into the above solution. After stirring for 30 min, 135 μL of a H_3PO_4 (Aladdin, $\geq 85\%$) solution (30%) was slowly added into the mixed solution. Then, after stirring for another 30 min, the final mixture solution was hydrothermally heated at 100 $^\circ\text{C}$ for 2 h. After the reaction, the final product was thoroughly rinsed with deionized water and ethanol. Then, the product was dried in an oven at 60 $^\circ\text{C}$ for 24 h.

Preparation of rod-shape CuO. A solution of 3 mmol CuCl_2 (Taishan Yueqiao Reagent Plastic Co. Ltd., Jiangmen, China, $>99.0\%$) was prepared in 20 mL of deionized water with stirring. Then, 20 mL of a 0.1 M Na_3PO_4 (Taishan Yueqiao Reagent Plastic Co. Ltd., Jiangmen, China, $>98.0\%$) solution was added dropwise into the above solution with stirring for 30 min. Subsequently, 20 mL of a mixture solution of 0.1 M SDS (Tianjin Baishi Chemical Reagent Co. Ltd., Tianjin, China, AR) and 0.3 M sodium salicylate ($\text{C}_7\text{H}_5\text{NaO}_3$, Tianjin Damao Chemical Reagent Co. Ltd., Tianjin, China, $>99.5\%$) was added into the above mixture solution. After stirring for another 30 min, 20 mL of 5 M NaOH (Taishan Yueqiao Reagent Plastic Co. Ltd., Jiangmen, China, $>96.0\%$) solution was slowly added into the mixed solution. Eventually, after stirring for another 30 min, the mixture solution was hydrothermally heated at 150 $^\circ\text{C}$ for 8 h. After the reaction, the final product was rinsed with deionized water and ethanol. Then, the product was dried in an oven at 80 $^\circ\text{C}$ for 6 h.

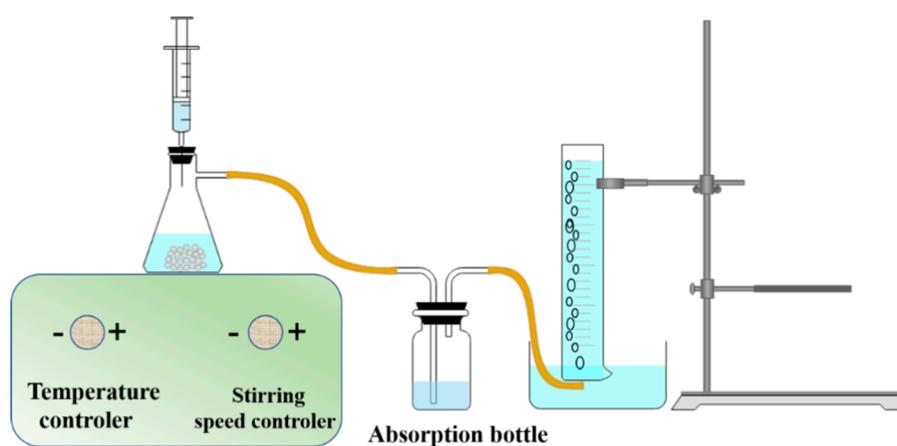


Figure S1 Illustration of the set-up for the hydrolysis experiments.

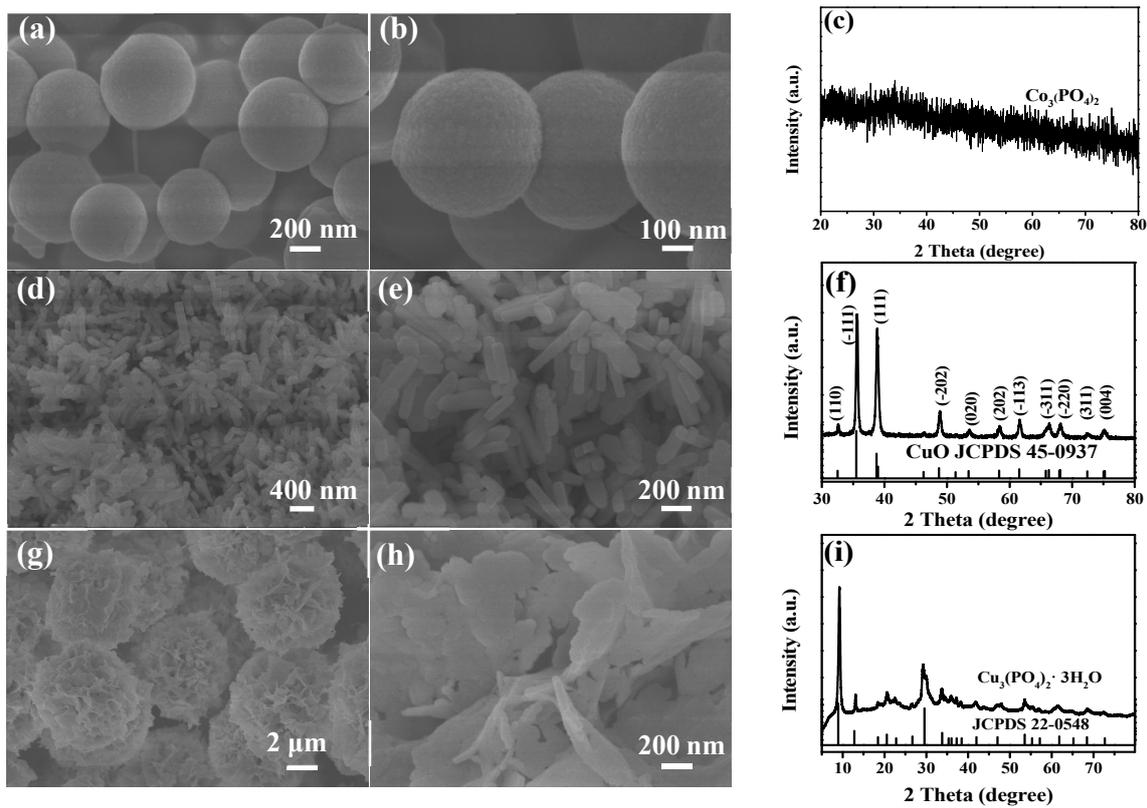


Figure S2 SEM images of $\text{Co}_3(\text{PO}_4)_2$ (a, b), CuO (d, e) and $\text{Cu}_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$ (g, h), and XRD patterns of $\text{Co}_3(\text{PO}_4)_2$ (c), CuO (f) and $\text{Cu}_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$ (i).

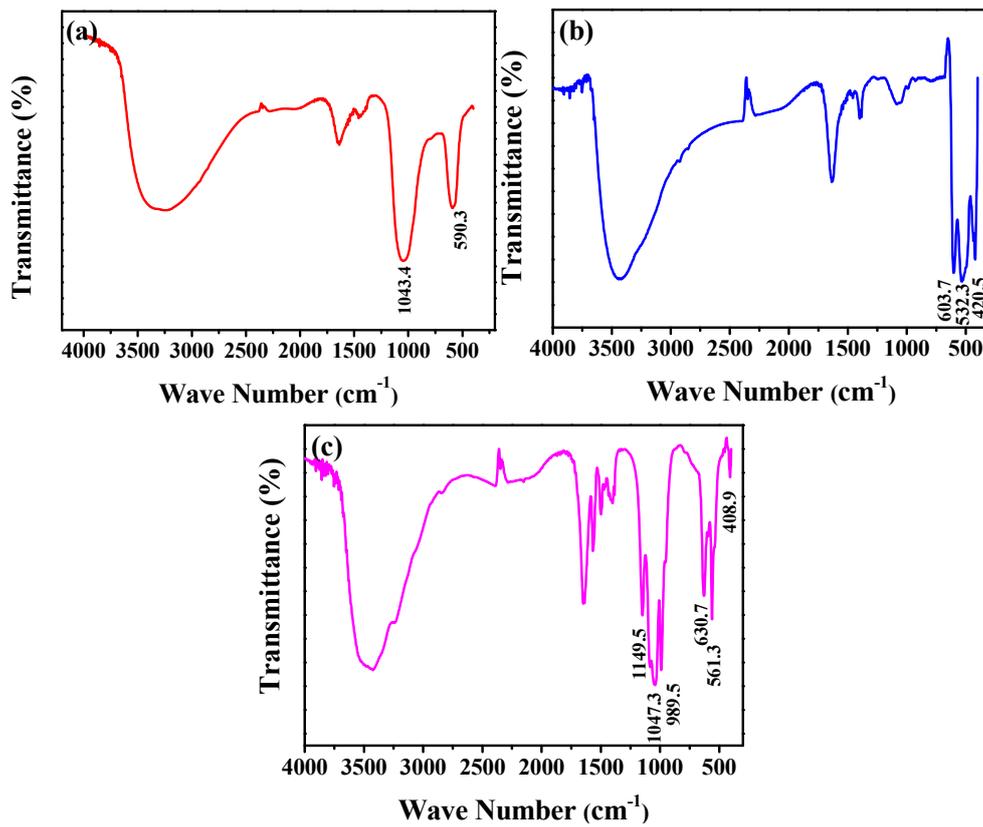


Figure S3. FT-IR spectrum of $\text{Co}_3(\text{PO}_4)_2$ (a), CuO (b) and $\text{Cu}_3(\text{PO}_4)_2$ (c).

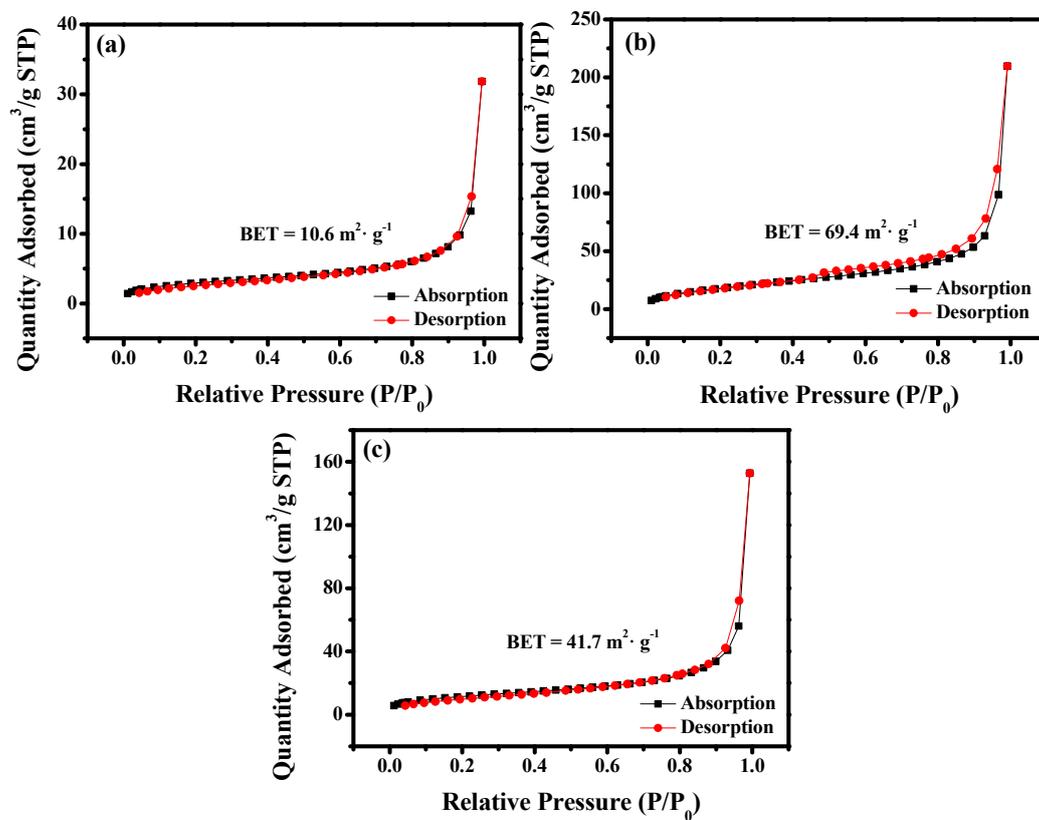


Figure S4. N_2 adsorption-desorption isotherms of CuO (a), $\text{Co}_3(\text{PO}_4)_2$ (b) and $\text{Cu}_3(\text{PO}_4)_2$ (c).

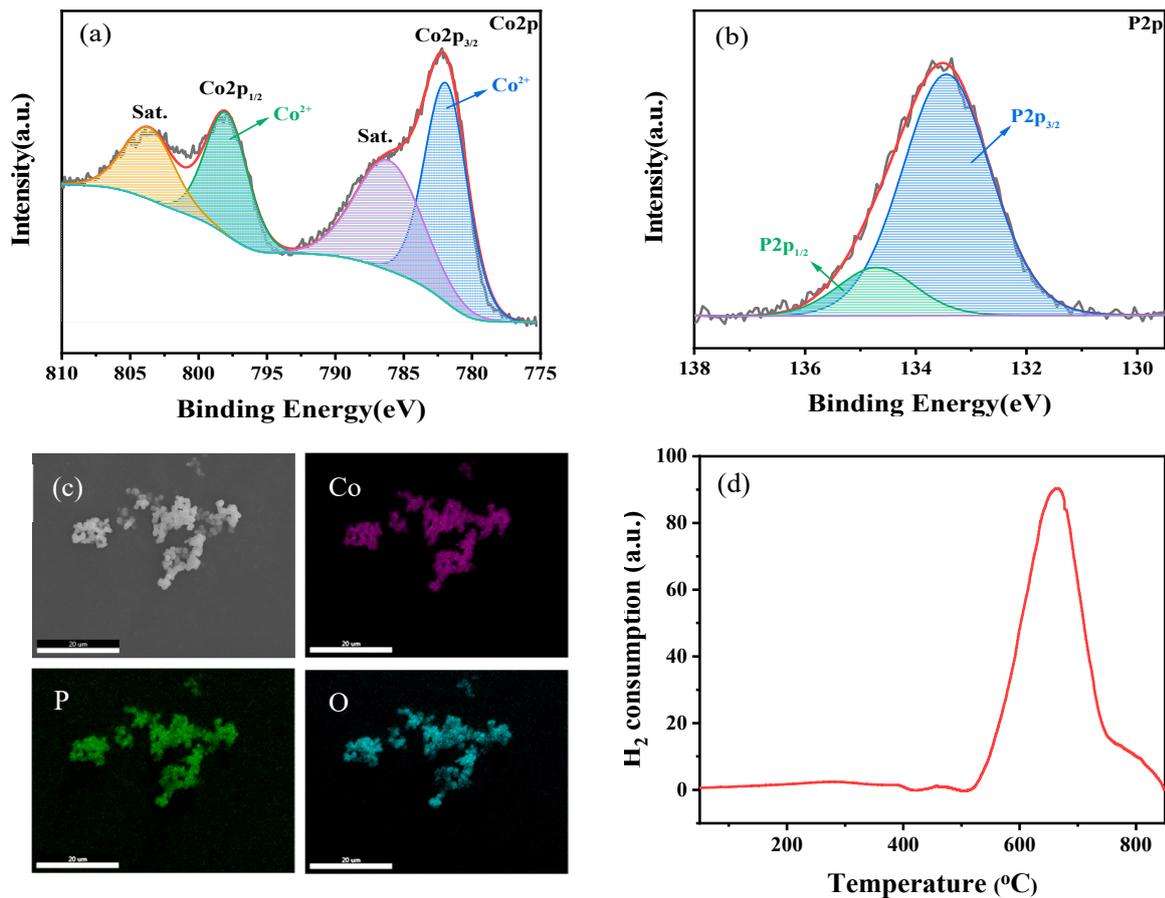


Figure S5. XPS spectra in Co 2p and P 2p regions (a, b), elemental mapping (c) and H₂-TPR profile (d) of Co₃(PO₄)₂.

In Figure S5a and 4b, the peaks at 798.1 and 782.0 eV are attributed to the Co2p 1/2 and Co2p 3/2 states of Co 2p, respectively. The peaks at 134.2 and 133.3 eV are indexed to P2p 1/2 and P2p 3/2 of the phosphorus atom in the phosphate group (Feng et al. International Journal of Hydrogen Energy 2020, 45: 17444-17452.). In Figure S5c, the elemental mapping verifies that the elements of Co, P and O are uniformly distributed in the sample. H₂-TPR profile in Figure S5d shows a peak centered at 660 °C, which corresponds to the reduction of Co³⁺ in Co₃(PO₄)₂ to metallic Co. This result is similar to that in the previous report (Feng et al. International Journal of Hydrogen Energy 2020, 45: 17444-17452.).

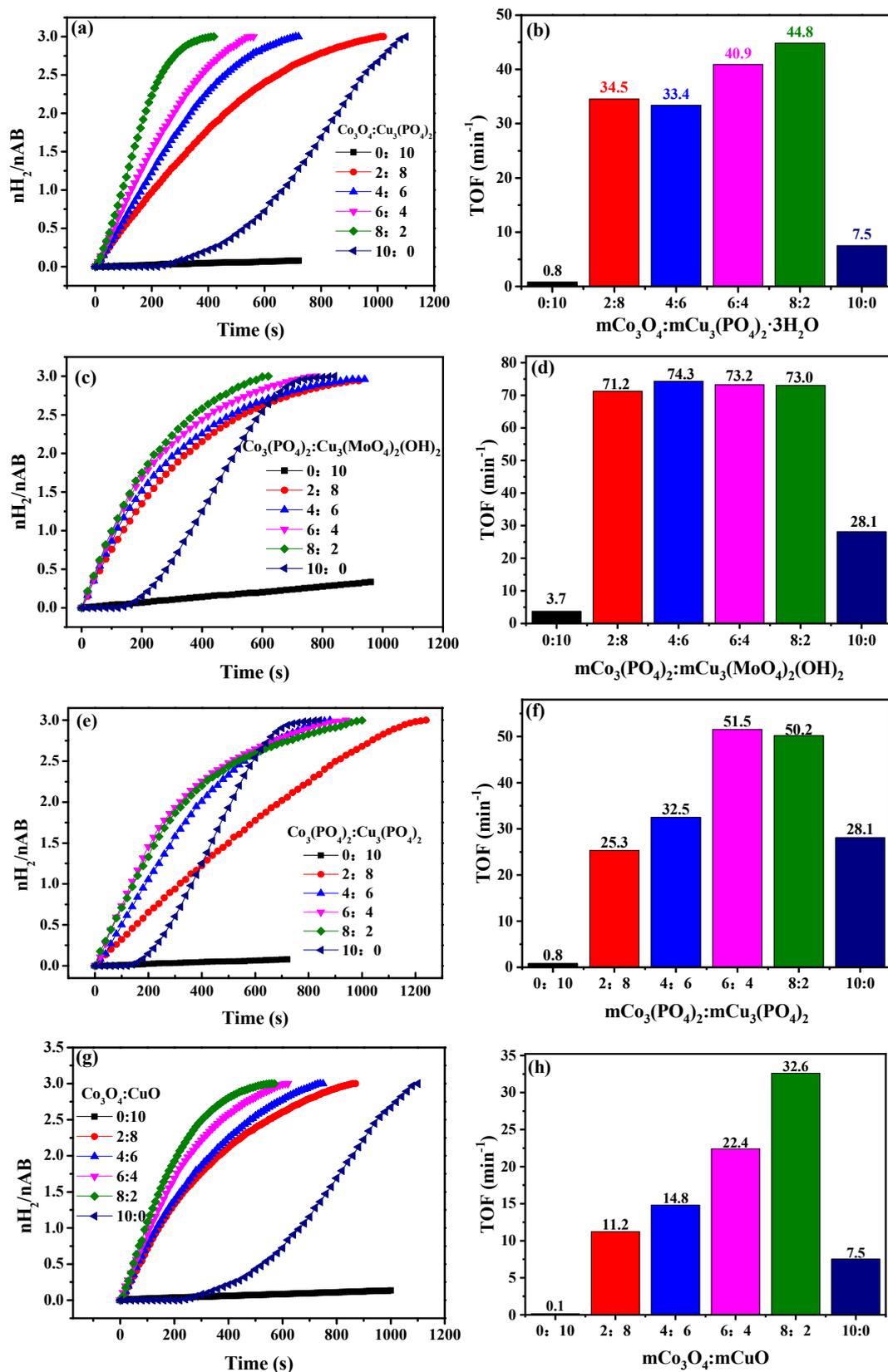


Figure S6. Catalytic performance of mixture of Co- and Cu-based catalyst with various mass ratio and the comparison of their TOF Value: Co_3O_4 and $\text{Cu}_3(\text{PO}_4)_2$ (a, b), $\text{Co}_3(\text{PO}_4)_2$ and $\text{Cu}_3(\text{MoO}_4)_2(\text{OH})_2$ (c, d), $\text{Co}_3(\text{PO}_4)_2$ and $\text{Cu}_3(\text{PO}_4)_2$ (e, f), Co_3O_4 and CuO (g, h).

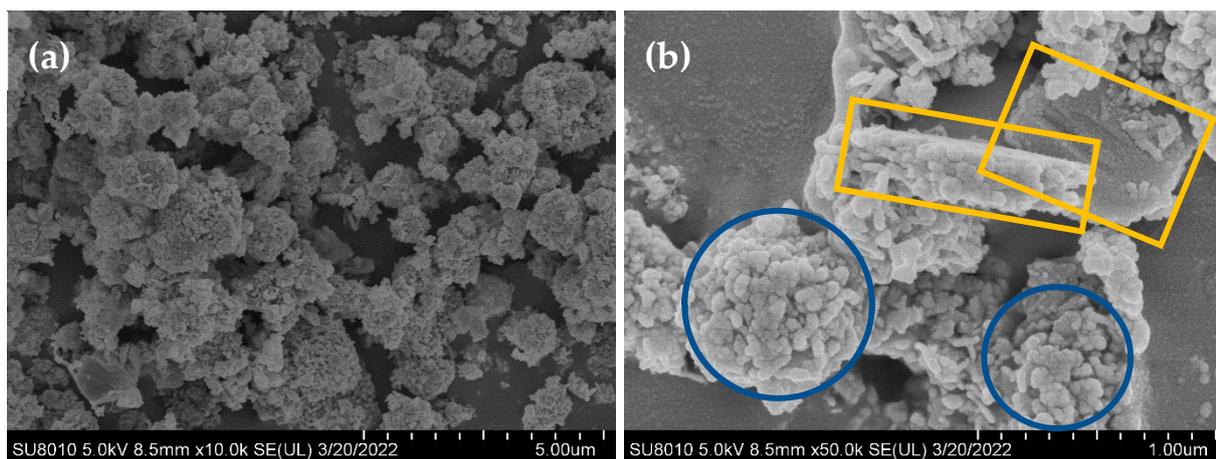


Figure S7. Low-magnification (a) and high-magnification (b) SEM images of the catalysts after 5th catalytic run. The Co_3O_4 microspheres and $\text{Cu}_3(\text{MoO}_4)_2(\text{OH})_2$ nanoplates in Figure S7b are marked with blue circles and yellow rectangles, respectively.