Electronic Supplementary Information

Coordination Polymers for Catalysis: Enhancement of Catalytic Activity through Hierarchical Structuring

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Synthesis of hierarchical Prussian white (PW):

In a typical procedure, 10 mmol benzoic acid and 2.8 mmol $K_4Fe(CN)_6$ were dissolved into 45 mL water and 30 mL ethanol mixed solvents. The obtained solution were transferred into a 90 mL Teflon-lined stainless-steel autoclave, sealed and maintained at 120 ^oC for 24 h. After the solution was cooled to room temperature, the obtained deep blue solid was collected by centrifugation, washed several times with water and ethanol, and then dried in a vacuum oven at 40 ^oC for 12 h. For the fabrication of cubic PW, ethanol was replaced by glycol while other parameters were kept the same as those of hierarchical PW.

Activation of PW crystals:

Due to strong reducibility, Fe^{II} exposed on the surface of the PW crystals was partly oxidized. Thus, the PW crystals were activated by hydrazine hydrate as they were used for the first time catalysis, then they were re-activated by hydrazine hydrate before each catalytic test. In a typical run, 20 mg PW and 1 mL hydrazine hydrate (80 wt%) was added into 20 mL H_2O. Afterwards, the PW suspension was ultrasound for 5 min and shaked for 20 min in a constant temperature incubator shaker at 40 ^oC. At last, the PW solid was collected by centrifugation, washed several times with water and ethanol, and then dried in a vacuum oven at 40 ^oC for 12 h.

Degradation of methylene blue (MB)

In a typical procedure, 4 mg of hydrazine hydrate treated PW were added to 20 mL 40 mg/L MB solution and then shaked in the dark for 30 min in a constant temperature incubator shaker at 25 ^oC, which ensured the adsorption-desorption equilibrium of MB on the sample. Then the degradation reaction was initiated by adding 2 mL H_2O_2 (30 wt%) into the mixed solution. Every 5 min, 1 mL of solution was taken from the conical flask and diluted to 8 mL, and then centrifuged. The concentration of MB in the supernatant was analyzed using a UV-2802S Spectrophotometer made by UNIC at a wavelength of 665 nm. Controlled experiment was carried out with Cubic PW. In order to reuse the hierarchical PW, they were also treated with hydrazine hydrate water solution

before each cyclic experiment.

Characterization:

The phase compositions of the prepared samples were monitored by X-ray diffraction (XRD) using a Rigaku RINT 2500X diffractometer with Cu-Kα radiation and conventional θ-2θ geometry. The morphologies of the products were determined on a field emission scanning electron microscope (FESEM, Hitachi S-4800), and a transmission electron microscope (TEM, JEOL JEM--2100F). Fourier-transform infrared (FT-IR) spectra were measured in wavenumber ranging from 400 to 4000 cm^{-1} using Nicolet Nexus 670 FT-IR spectrophotometer. The Mössbauer spectrum was measured using a Mössbauer spectrometer in a consultant acceleration mode with a 25 mCi ^{57}Co(Pd) source, and the spectrum was calibrated by a 25μm α-Fe foil at room temperature. The Mössbauer parameters were fitted by a standard least-squares fitting program. UV-Vis absorption spectrums were measured on UV-2802S Spectrophotometer. Nitrogen sorption measurements were carried out by using an ASAP-2000 surface area analyzer at 77 K.

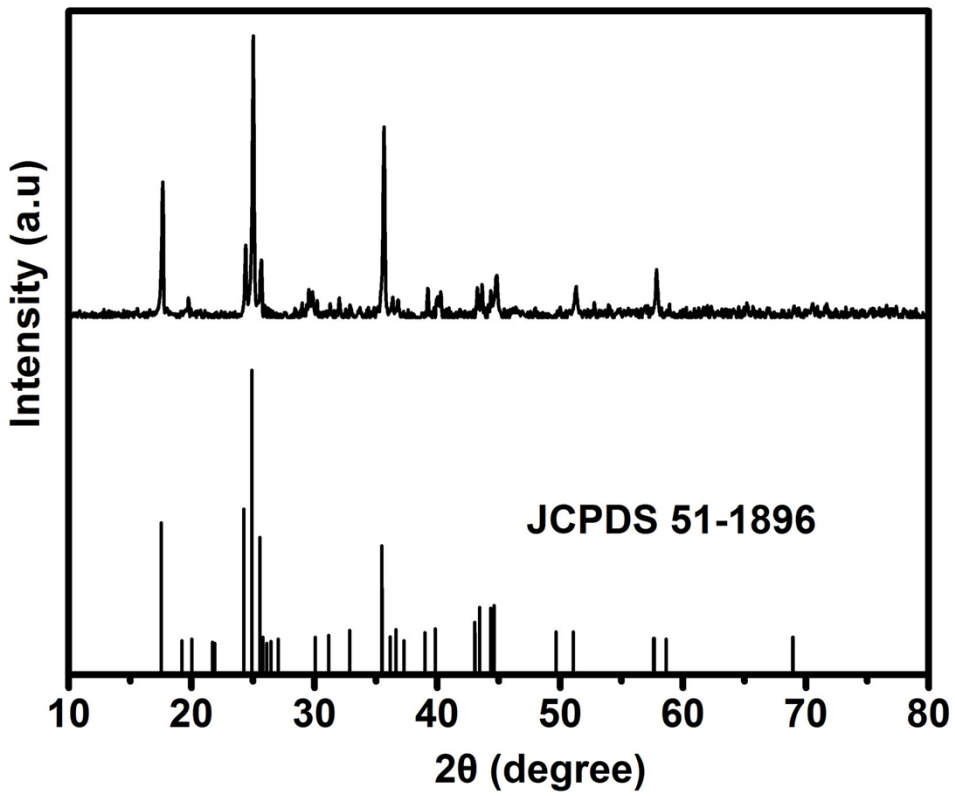

Fig. S1 XRD pattern of the hierarchical PW crystals prepared following a typical procedure.

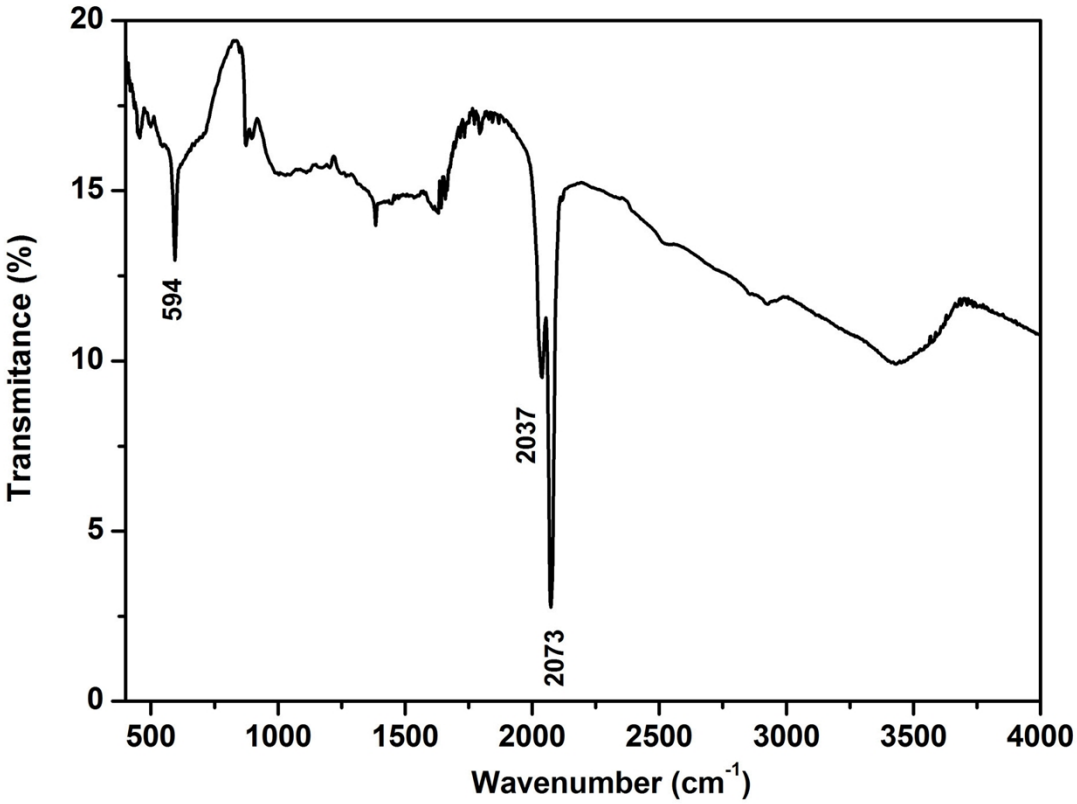

Fig. S2 FTIR spectrum of the hierarchical PW crystals.

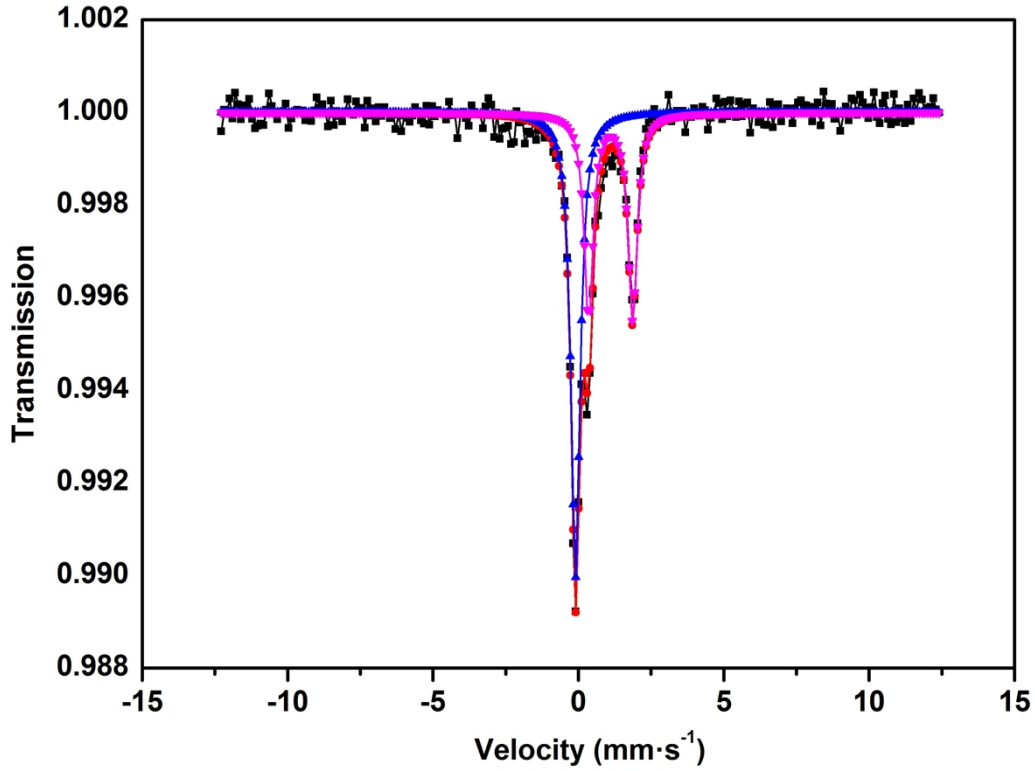

Fig. S3 Mössbauer spectrum of hierarchical PW crystals.

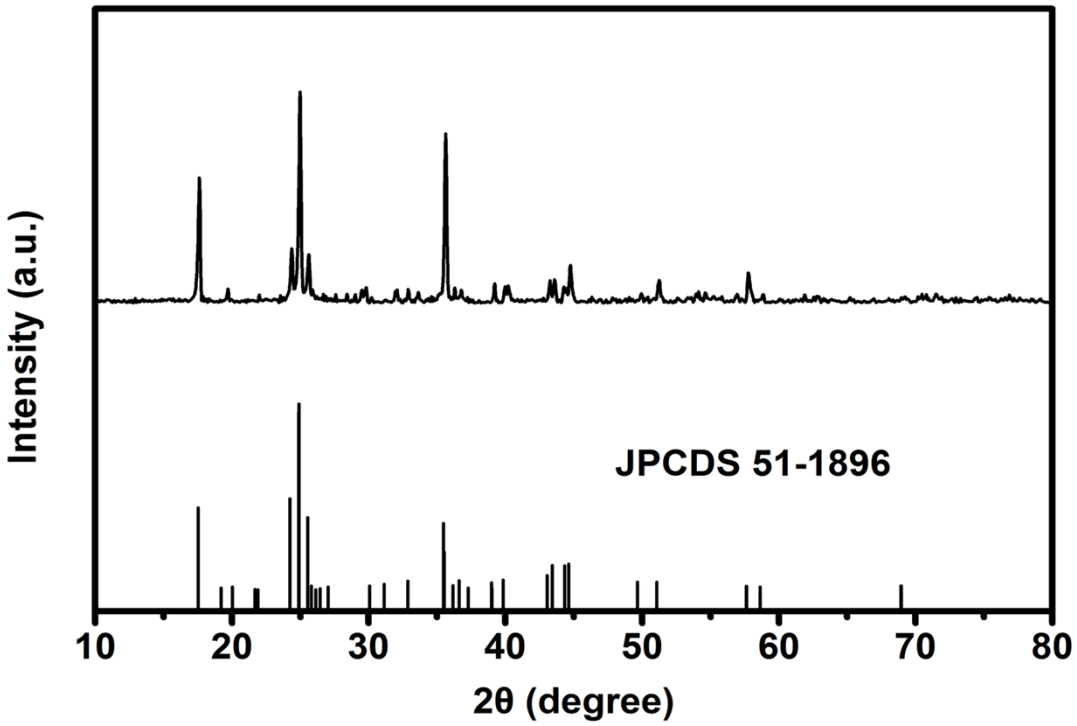

Fig. S4 XRD pattern of the hierarchical PW crystals exposed in air for four months.

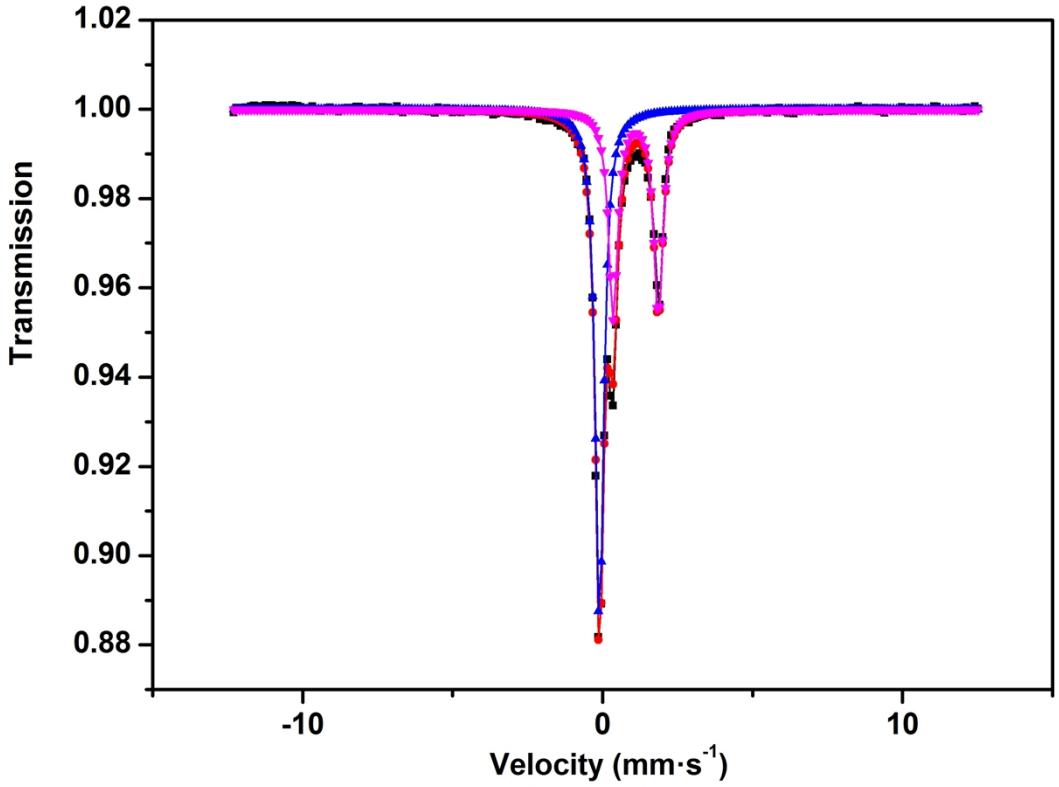

Fig. S5 Mössbauer spectrum of hierarchical PW crystals exposed in air for four months.

The spectrum has the same absorption peaks as the peaks shown in Fig. S3. Only low spin Fe^{II} (the isomer shift is - 0.1 mm/s) and high spin Fe^{2+} (the isomer shift is 1.11 mm/s and the quadrupole splitting is 1.51 mm/s) can be detected, which indicates the hierarchical PW crystals has excellent stability in air.

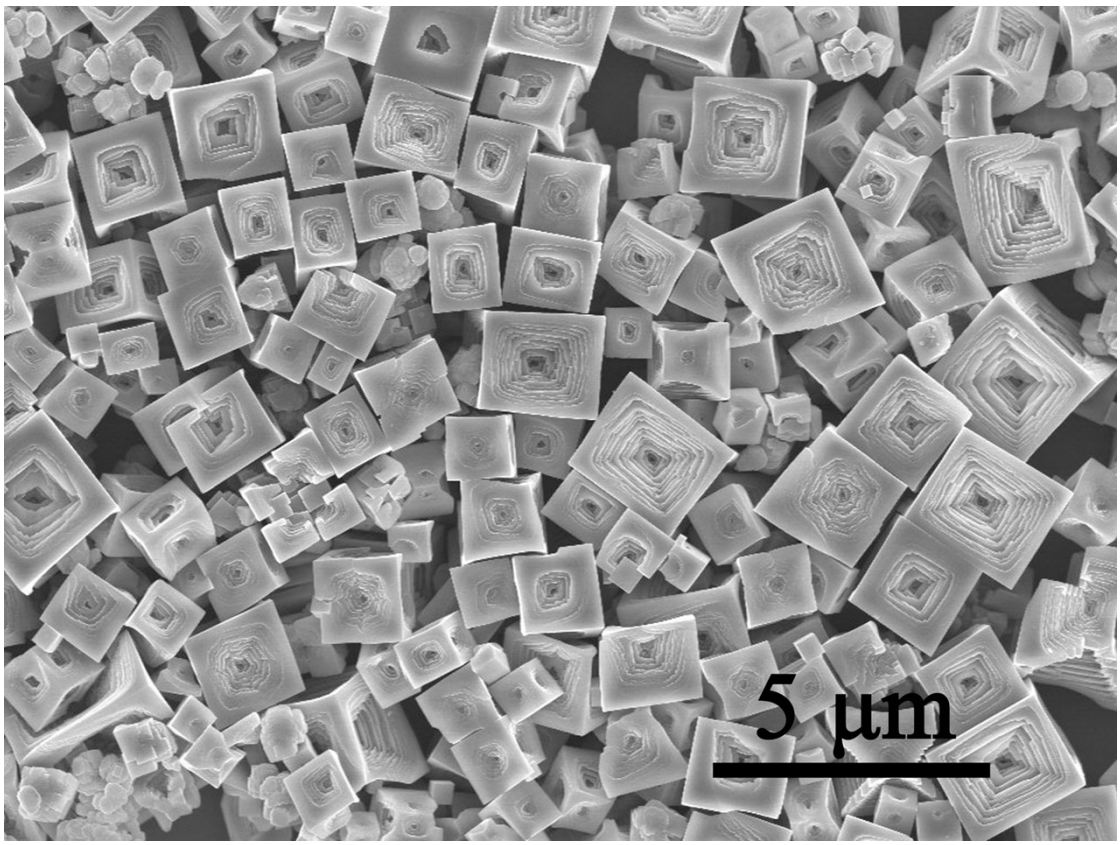

Fig. S6 Low magnification FESEM image of these as-prepared products.

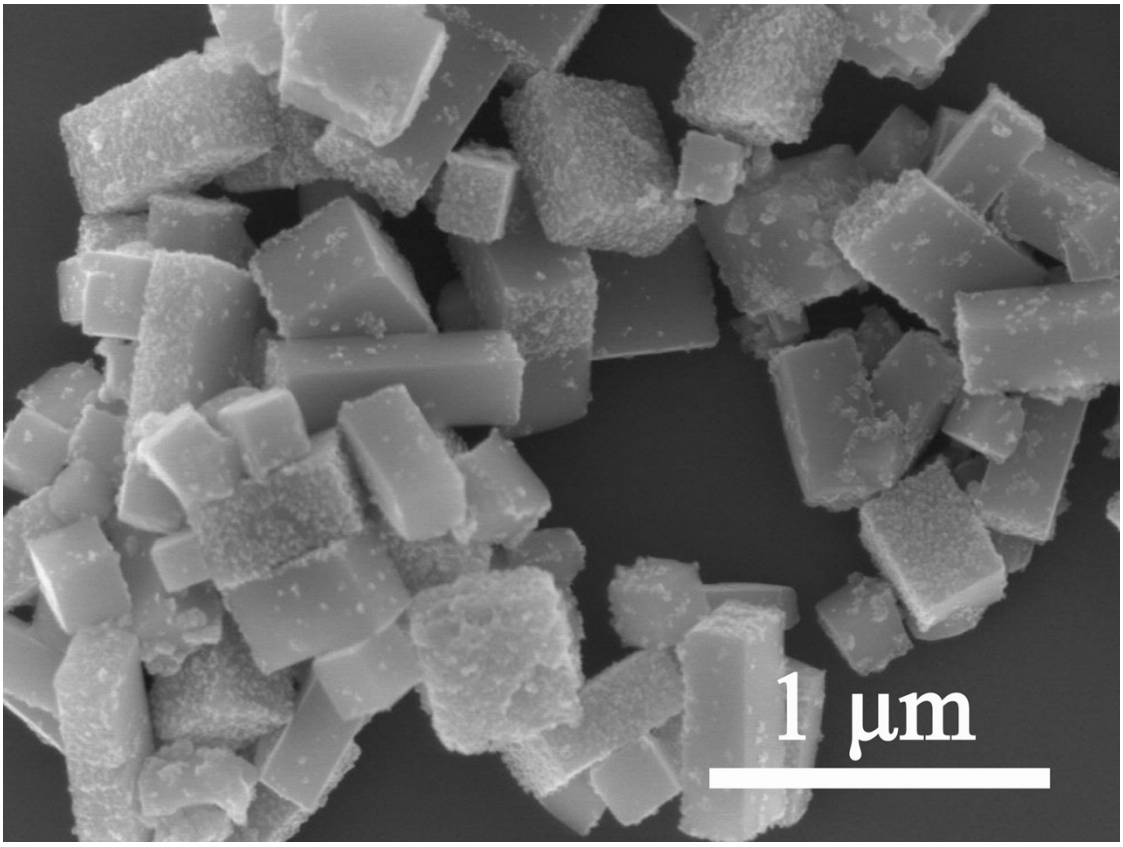

Fig. S7 FESEM picture of the products obtained at 0.2 mmol potassium ferrocyanide while other reaction conditions were kept constant.

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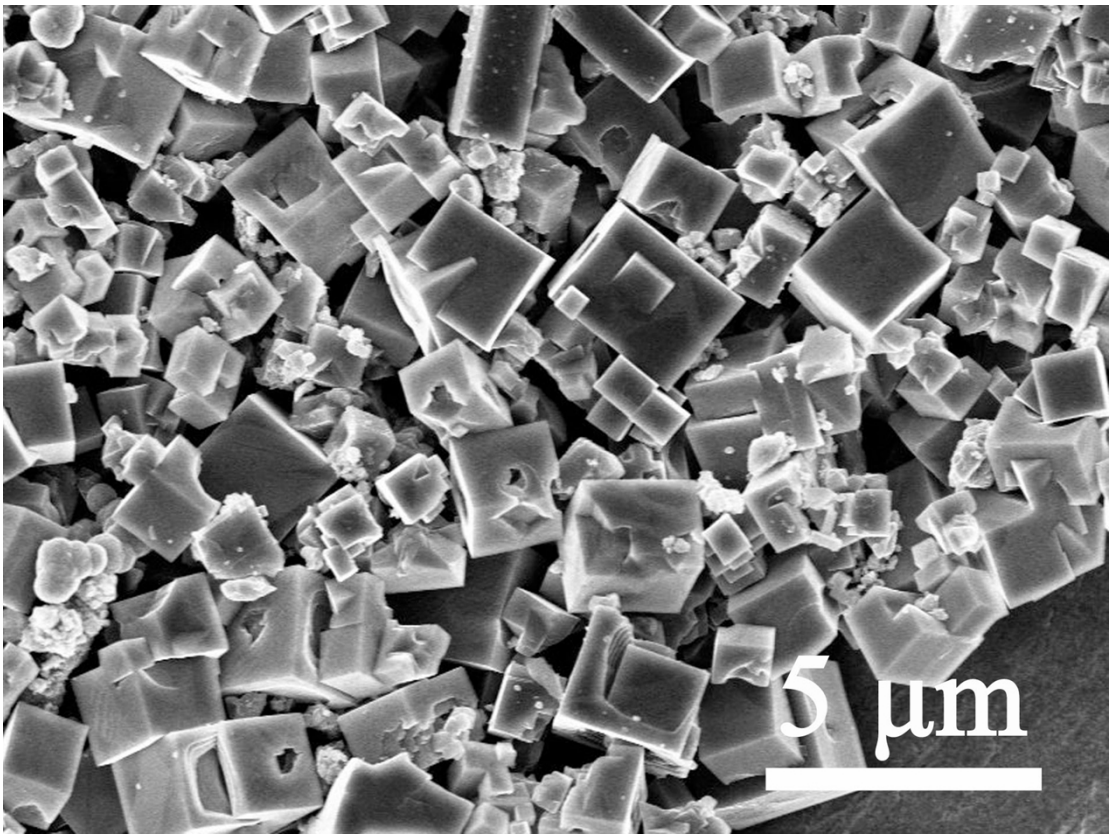

Fig. S8 FESEM picture of the products obtained at 55 mL water/ 20 mL ethanol mixed solvents while other experimental parameters were kept constant.

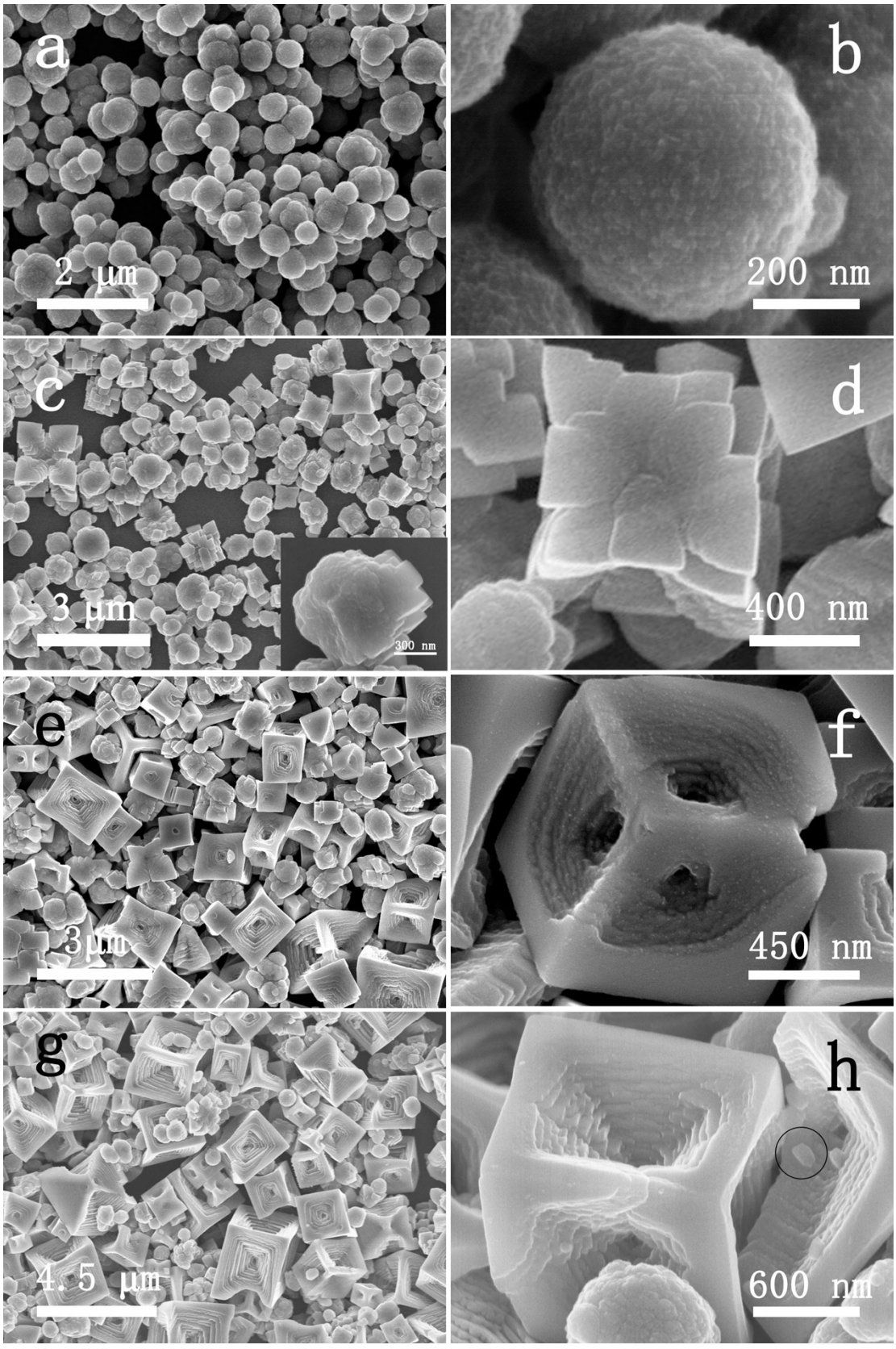

Fig. S9 Low- and high- magnification FESEM images of products obtained at different reaction times (a) and (b) 30 min, (c) and (d) 1 h (inset : FESEM of a broken particles), (e) and (f) 2 h, (g) and (h) 3 h.

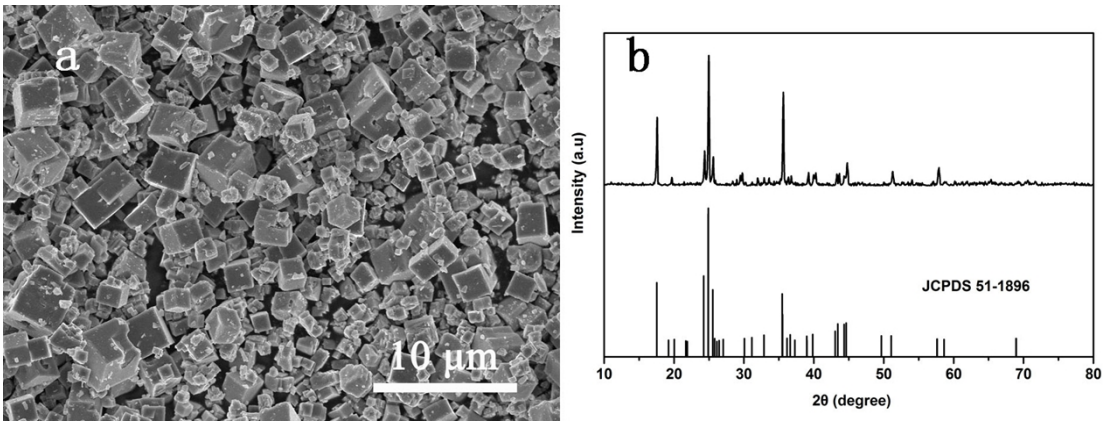

Fig. S10 (a) FESEM image and (b) XRD pattern of the cubic PW crystals obtained by using 45 mL water/ 30 mL glycol mixed solvents while other reaction conditions were kept constant.

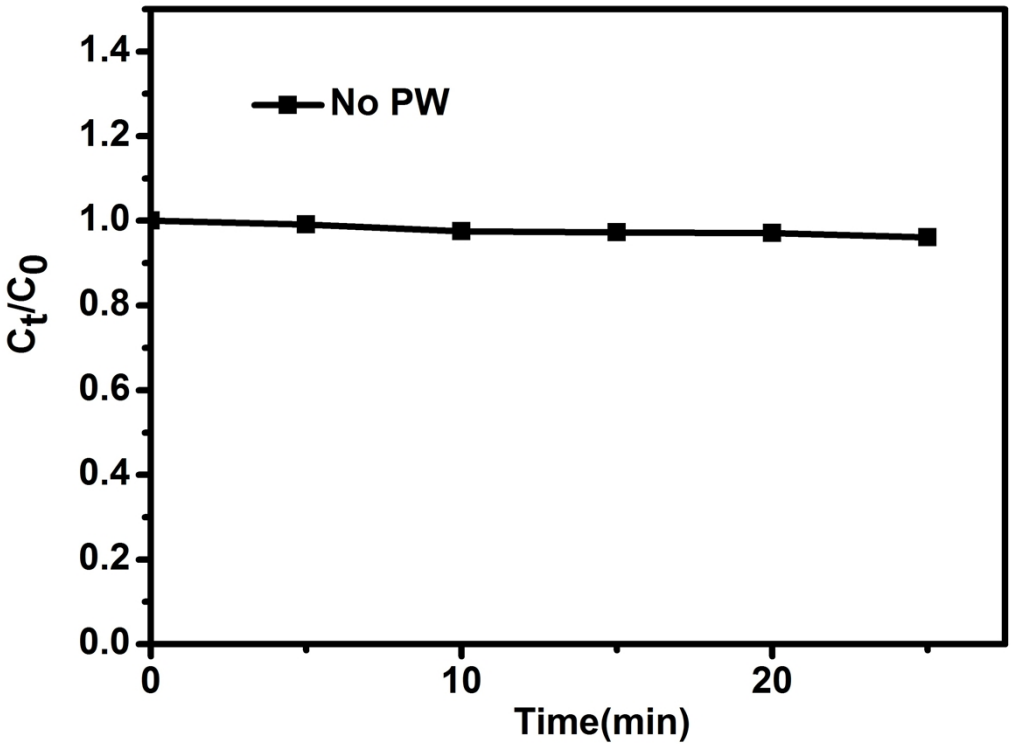

Fig. S11 The time-dependent degradation curve of MB in the absence of PW

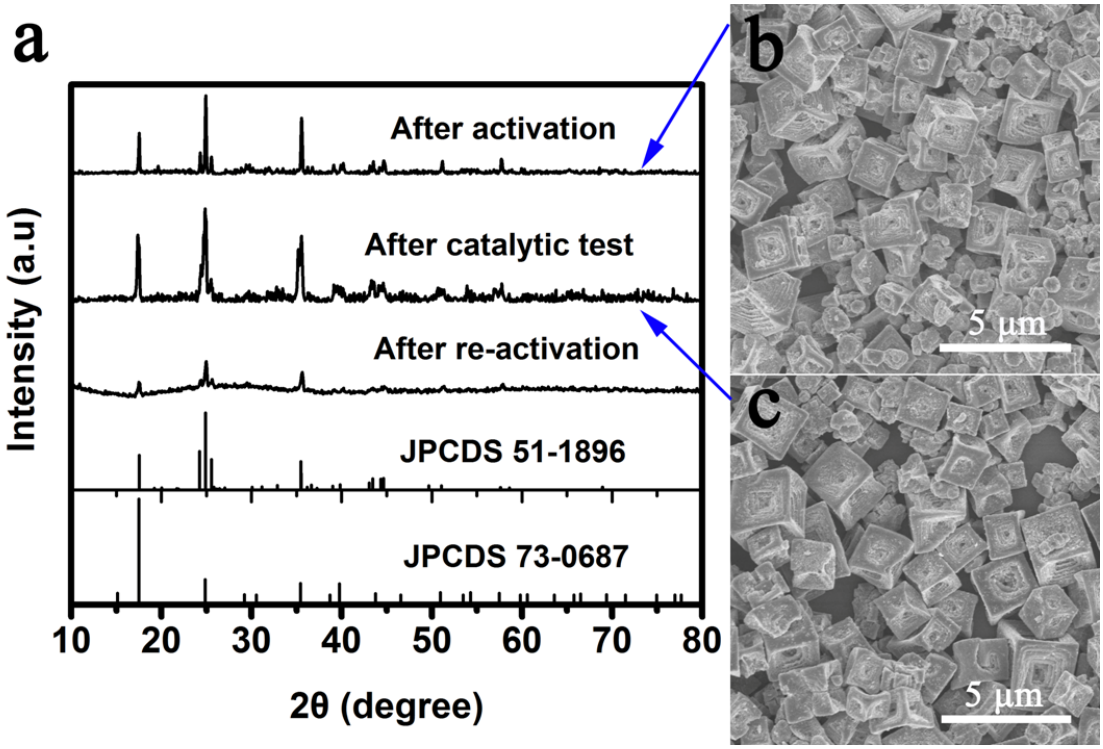

Fig. S12 (a) XRD patterns of the samples during one catalysis cycle. (b) and (c) FESEM images of the samples after the activation and catalytic test, respectively.