

**In-situ self-assembly of Zirconium metal–organic
framework onto ultrathin carbon nitride for enhanced
visible-light-driven conversion of CO₂ to CO**

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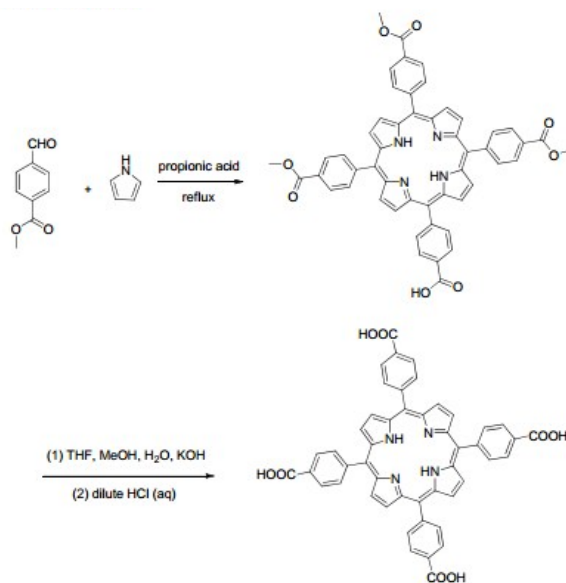
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Experimental

Preparation of ultrathin $g\text{-C}_3\text{N}_4$ (UCN)

All the raw materials purchased were used without further purification. The UCN was synthesized by the polycondensation of cyanuric acid (C), melamine (M), and 2,4-diamino-6-methyl-1,3,5-triazine as starting materials (Mm). Typically, 20 mmol 2,4-diamino-6-methyl-1,3,5-triazine and 10 mmol cyanuric acid were dissolved in 200 ml deionized water. After stirring vigorously for 48 h, the white solid was obtained by centrifugation and then dried at 60 °C for 24 h in a vacuum oven. Finally, the resulting powder was calcined in Ar atmosphere at 550 °C for 4 h with a heating rate of 2 °C min^{-1} . For comparison, bulk $g\text{-C}_3\text{N}_4$ (BCN) was prepared by heating melamine in a chamber furnace to 550 °C for 4 h with a heating rate of 2 °C min^{-1} under air.

2.2. Preparation of H_2TCPP



2.3. Preparation of Zr-PMOFs

20 mg (0.085 mmol) $\text{ZrCl}_4 \cdot 6\text{H}_2\text{O}$, 500 mg benzoic acid and 400 μL H_2O were introduced into 5 mL of DMF. The suspension was stirred for 10 minutes at room temperature, then 20 mg (0.026 mmol) TCPP added and stirring was continued for another 10 min. The mixture was introduced into a 25 mL Teflon lined autoclave and heated at 120°C for 24 hours. The solid was recovered by centrifugation, washed 3

times with DMF and CH₃OH, subsequently, dried at 60 °C for 24 h under vacuum.

2.4. Preparation of Zr-PMOFs/g-C₃N₄

A series of Zr-PMOFs/UCN (ZPUCN) hybrid photocatalysts were obtained by an in-situ solvothermal reaction. In brief, a certain of UCN powder was dispersed in DMF, ultrasonication was carried out for 30 min. Subsequently, 20 mg ZrCl₄·6H₂O, 500 mg benzoic acid and 400 μL H₂O were introduced into 5 mL of DMF. Then, 20 mg H₂TCPP was added and stirring was continued for another 10 min. The mixture was introduced into a 25 mL Teflon lined autoclave and heated at 120°C for 24 hours. After centrifugation, the solid was obtained after drying at 80 °C under vacuum. The obtained sample was denoted as ZPUCN-x, where x is the actual mass of the addition of UCN during the solvothermal reaction (x= 1.5, 3.0, 4.5 mg). If mark it as a mass ration, it's about 5%, 10%, 15%. The Zr-PMOFs/BCN (ZPBCN) composite was prepared in a similar way expect that UCN was used instead BCN

2.5. Characterization

The as-synthesized samples were characterized by X-ray diffraction (Bruker D8 advance system), a field-emission scanning electron microscopy (FESEM, FEI Quanta 250F) attached energy-dispersive spectroscopy (EDS), X-ray photoelectron spectroscopy (XPS) measurements were conducted on a Kratos AXIS Supra system. The C 1s peak at 284.6 eV was used as the reference to calibrate the XPS spectra. UV-vis diffuse reflectance spectra (DRS, a Shimadzu UV-2600 spectrometer). Photoluminescence (PL) emission spectra were measured at room temperature on a Cary Eclipse Fluorescence Spectrophotometer (Agilent).

2.6. Electrochemical measurements

Electrochemical impedance spectra (EIS) and photocurrent density were carried out using a CHI-770 (Shanghai Chenhua) workstation with a three-electrode system in 0.5 M Na₂SO₄ solution. The counter and reference electrodes were Pt plate and Ag/AgCl electrode, respectively. The working electrode was prepared as followed: 10 mg as-obtained samples was dispersed in mixed solution with 150 μL isopropyl alcohol,

30 μL naphthol and 820 μL deionized water. Then the solution was coated on a piece of FTO glass (1 cm \times 2 cm) and then dried at 180 $^{\circ}\text{C}$ for 12 h in a vacuum oven. Prior to and during all measurements, the electrolyte was purged with nitrogen.

2.7. Photocatalytic performance

The photoreduction test was conducted at room temperature in a glass device (Aulight) shown in Fig. S2 at a pressure of 0.8 atm. A 300 W Xe arc lamp (Aulight CEL-HXF300, Beijing) equipped with a 400 nm cutoff filter was used as the light source, which was placed at the top of the optical window (light intensity $I = 70 \text{ mW}\cdot\text{cm}^{-2}$). Photocatalyst (10 mg) was added into a mixed solution composed 0.3 mL of H_2O and 30 mL acetonitrile. Then, the gas-closed glass reactor filled with the above mixture solution was bubbled with the high purity CO_2 gas for 60 min to remove the air inside before illumination. During the photocatalytic process, the produced gas at different reaction time was detected and quantified online by a gas chromatography (Hope GC 9860) with both TCD and FID detectors. The liquid products were analyzed separately at the end of the photoreaction by a HS-GC and GC-MS (Agilent 7890B-Agilent 5977B)

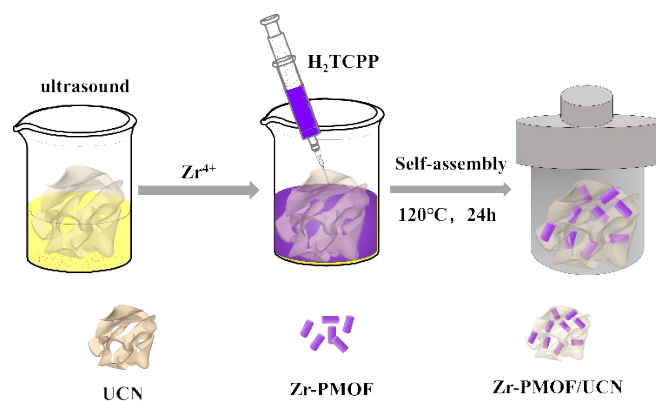


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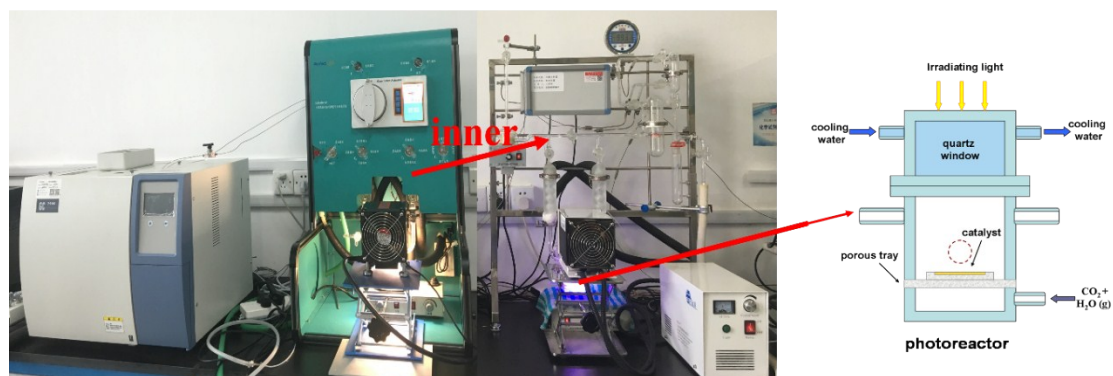


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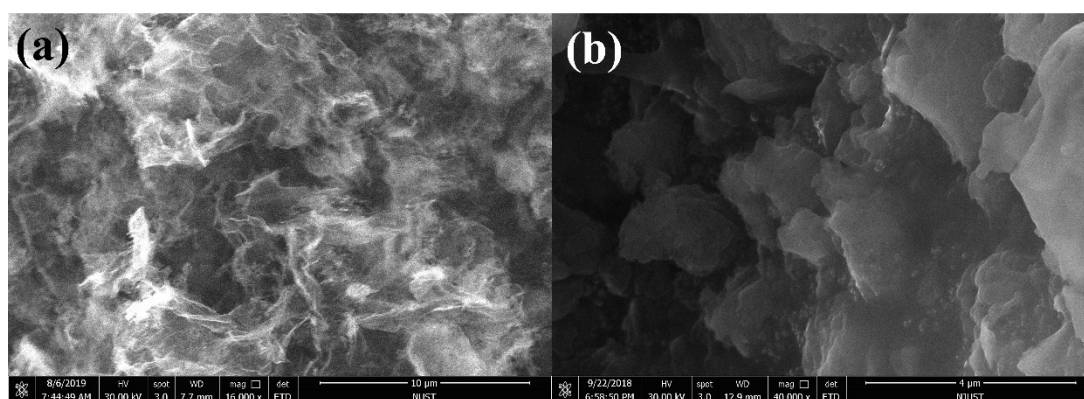


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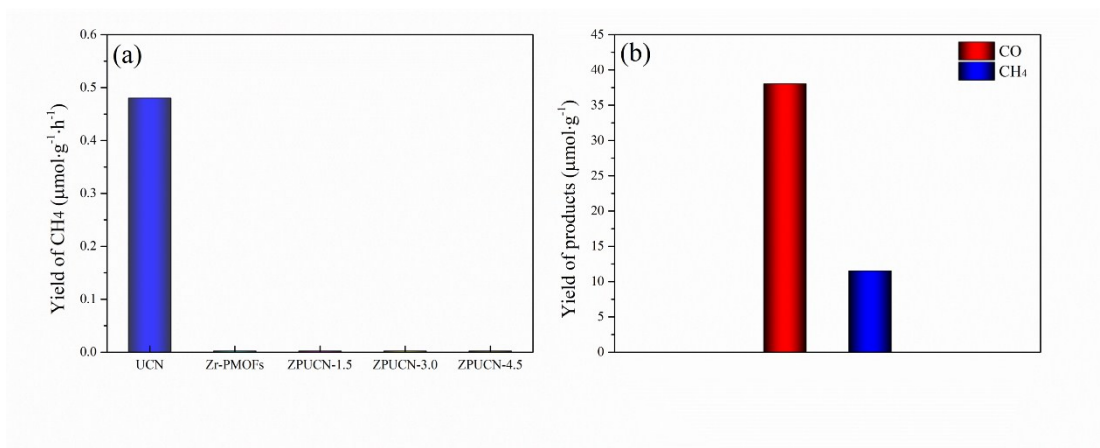


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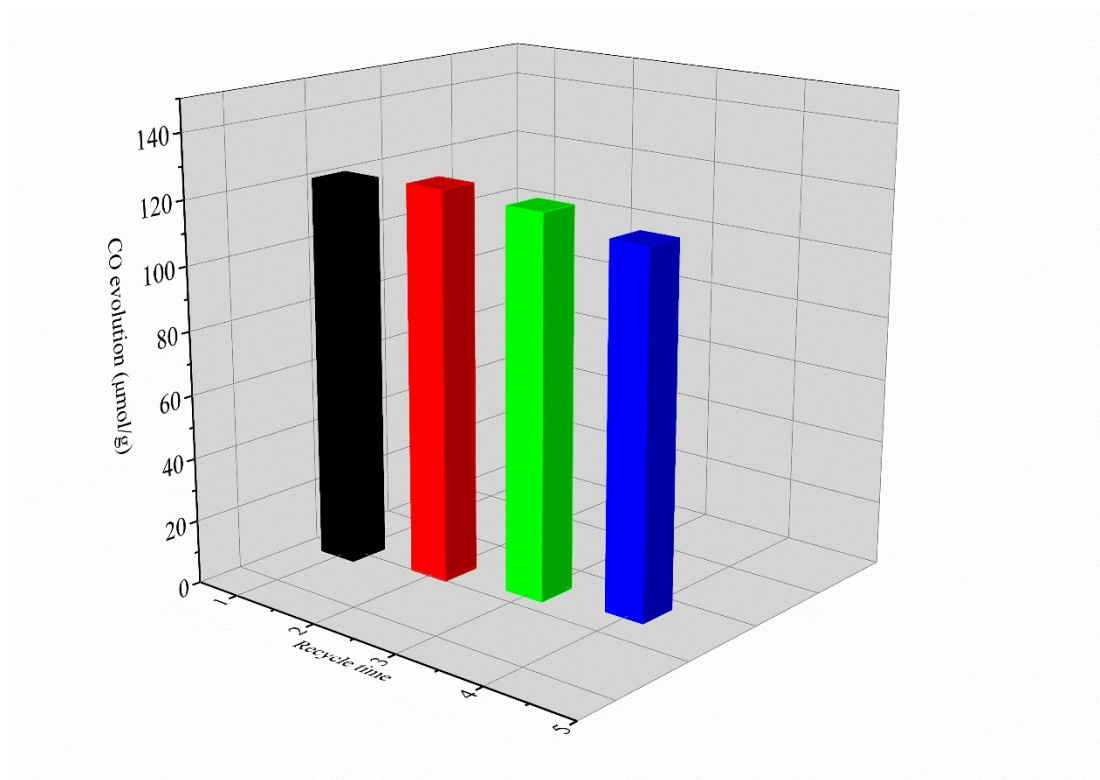


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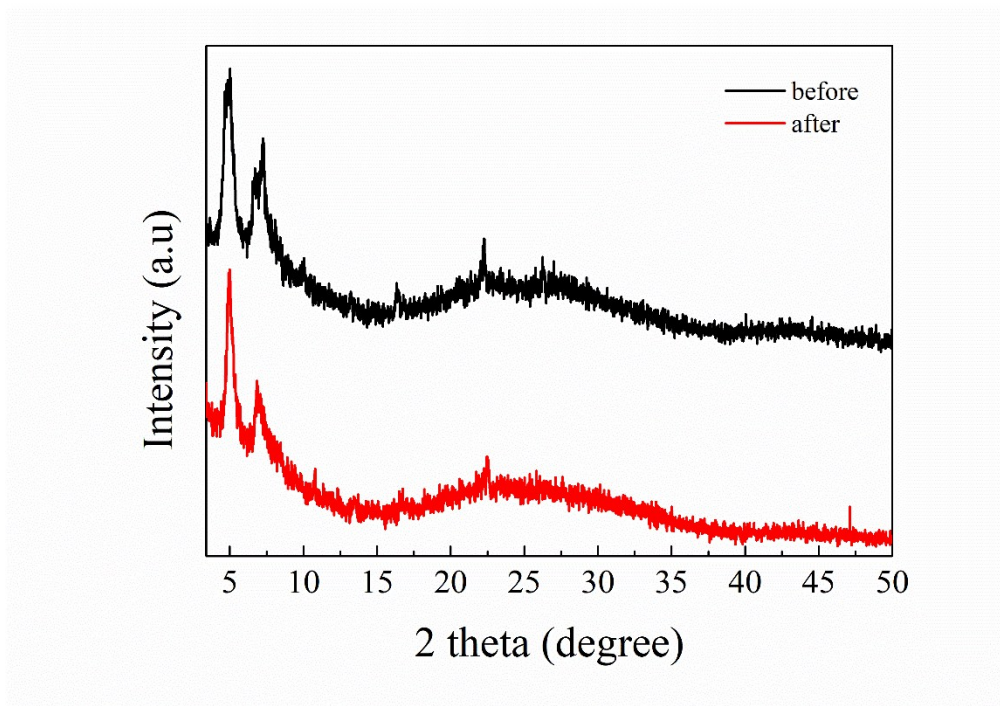


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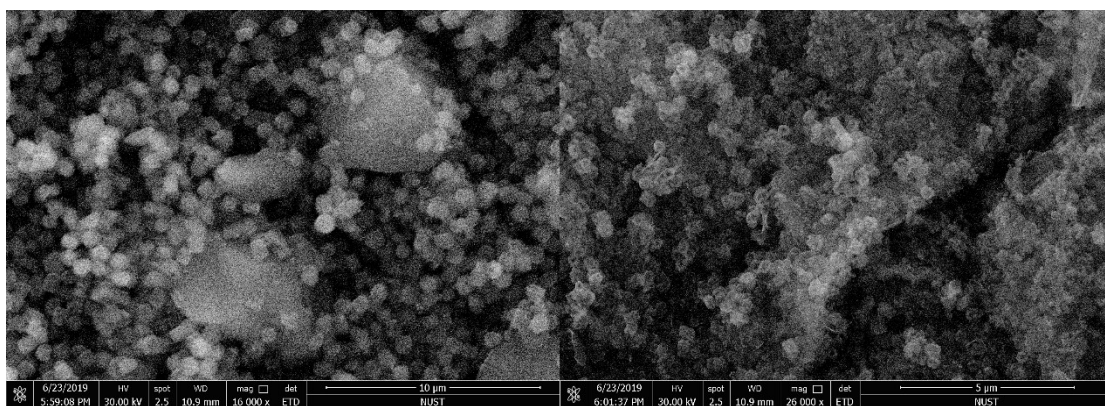


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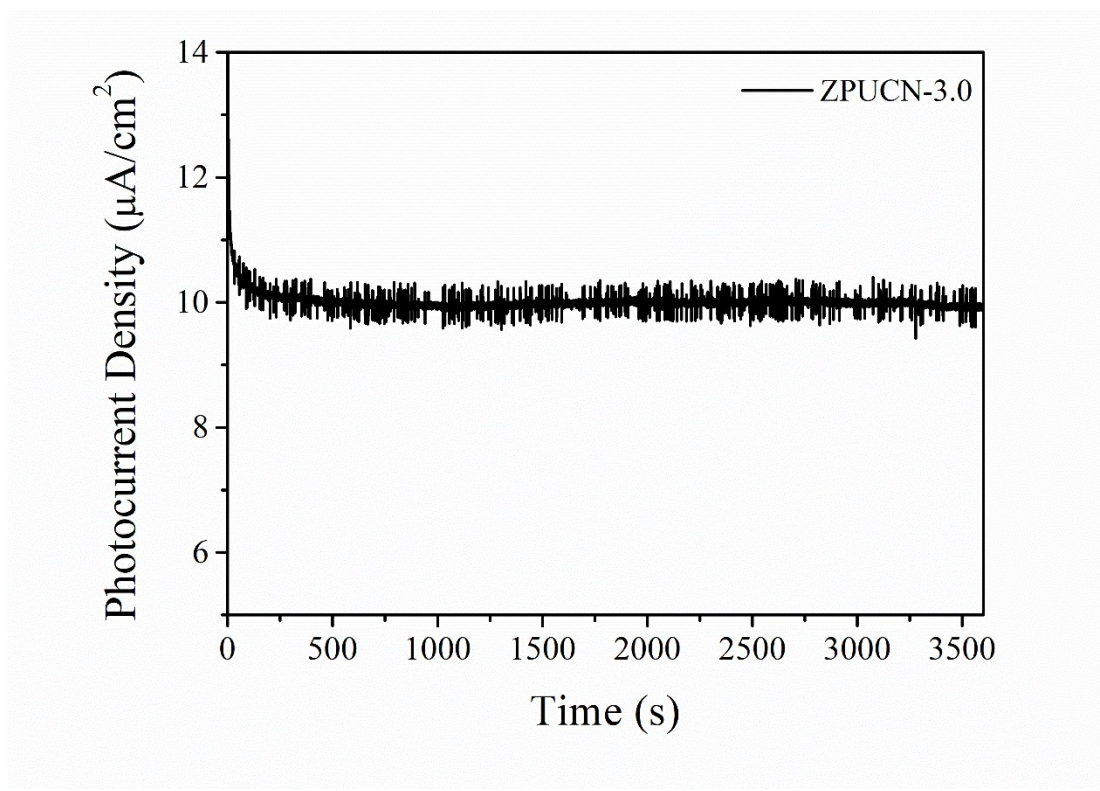


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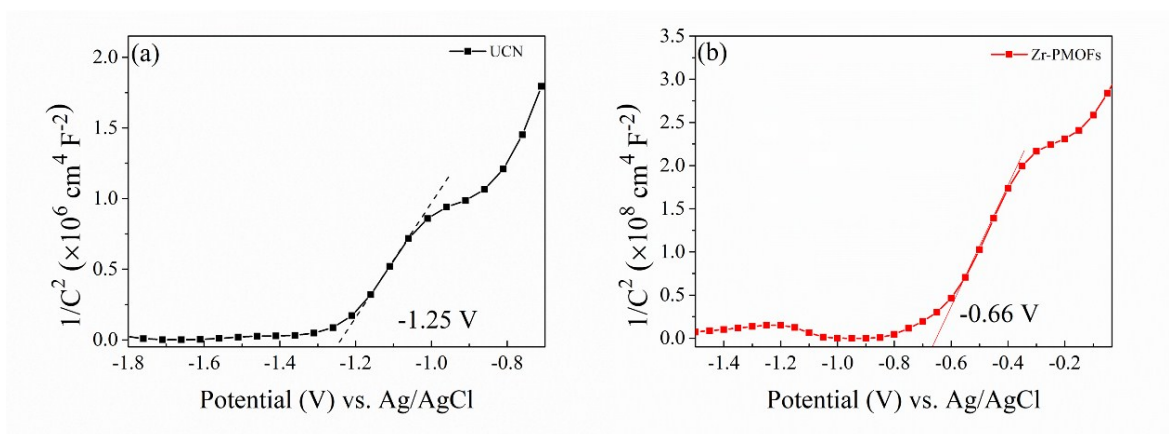


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