Supporting Information
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Photocatalytic Overall Water Splitting over MIL-125(Ti) upon CoPi and Pt Co-catalyst Deposition

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Experimental Section

Materials. All reagents were of analytical grade, and were used without further purification.

Synthesis of MIL-125(Ti). MIL-125(Ti) was prepared by a solvothermal method, which was reported previously. Terephthalic acid (0.250 g, 1.5 mmol), titanium isoproproxide Ti(OiPr)4 (0.3 mL, 1 mmol) were mixed in a solution of 9 mL of dimethylformamide (extra-dry) and 1 mL of dry methanol. After stirring for 5 min at room temperature, the precursor solution was introduced into a 40 mL Teflon lined autoclave, heated to 150 °C and kept at this temperature for 2 days and then cooled to room temperature. The obtained white solid was filtrated, washed three times with DMF and acetone and ultimately dried at room temperature under air.

And we used the method of precipitation in situ to deposite CoPi to MIL-125(Ti) firstly (sample MIL-125(Ti)-CoPi). Then the method of photo-reduction was used to load Pt to MIL-125(Ti)-CoPi, getting the sample of MIL-125(Ti)-CoPi-Pt.

Preparation of work electrodes. The electrodes were prepared using the spin-coating method. The COOH-functionalized FTO sections
were prepared in advance and stored in isopropanol for further use. MOF layers were spin-coated on the COOH-terminated FTO by the Spinner after the as prepared sample powders were grinded in ethyl alcohol. The FTO electrodes were dried in air for 5 hours at 100 °C.

**Characterizations.** The X-ray power diffraction (XRD) measurement of the as-prepared sample was performed on an X-ray powder diffraction (Bruker AXS D8). A Micromeritics ASAP 2020 analyzer was applied to measure the Brunauer-Emmett-Teller (BET) surface areas of the sample at liquid nitrogen temperature. The morphologies of as-prepared samples were determined by high-resolution transmission electron microscopy (TEM, JEM 2100). The microstructures of as-prepared samples were determined by scanning electron microscopy (Hitachi S-4800). The UV/Vis diffuse reflectance spectra were performed on a Shimadzu UV 2550 recording spectrophotometer, which was equipped with an integrating sphere and BaSO₄ was used as a reference. PL spectra were obtained on an F-4500 FL Spectrophotometer. The thermogravimetry analysis (TG) was performed in a thermogravimetric analyzer (Diamond TG).

**Photocatalytic Reaction.** Photocatalytic gas evolution reaction was carried out in a top-irradiation vessel connected to a glass-enclosed gas circulation system. In a typical procedure, 30 mg of catalyst was suspended in 30 mL water with constant stirring. The reaction temperature was maintained at 7 °C. The amount of O₂ and H₂ evolved was determined by using a gas chromatograph (Shiweipx GC-7806), Ar as carrier gas.

**Electrochemical measurements.** The electrochemical measurements were carried out using a 263A Princeton Applied Research (PAR) potentialstat/galvanostat. The photocurrents were measured by an electrochemical analyzer in a standard three-electrode system, with the MOF-coated FTO as working electrode, a Pt foil as counter electrode, and a saturated calomel electrode (SCE) as reference electrode. The light source was a 300 W Xe arc lamp. The electrolyte was 0.2 M LiCl acetonitrile solutions.
Figure S1. Thermal analysis of MIL-125(Ti) under air atmosphere (heating rate of 5 °C per minute).

The molecular formula of MIL-125 is Ti₈O₈(OH)₄[O₂C-C₆H₄-CO₂]₆ (as-synthesised; solv: methanol, DMF). The TG curve shows two steps of primary weight loss. The first weight loss of 34.5 % between room temperature and 350 °C is attributed to the release of the guest molecules, methanol and DMF. And the second weight loss between 350 and 800 °C, corresponds to the degradation of the framework to produce TiO₂ (obs. loss : 40.0 %; calc. 40.5 %). These results confirm that no amorphous TiO₂ exist in the as-prepared MIL-125(Ti), and the photocatalytic overall water splitting does come from MIL-125(Ti).
Figure S2. Photocatalytic overall water splitting over MIL-125(Ti)-Pt-CoPi in comparison to MIL-125(Ti)-CoPi-Pt. Reaction conditions:

30 mg of catalyst, 30 mL water. Light source, Xe lamp (300 W).
Figure S3. Photocatalytic overall water splitting over MIL-125(Ti)-CoPi-Pt for long time. Reaction conditions: 30 mg of catalyst, 30mL water. Light source, Xe lamp (300 W).
Figure S4. TEM images of MIL-125(Ti) (a), MIL-125(Ti)-Pt (b), MIL-125(Ti)-CoPi (c) and MIL-125(Ti)-CoPi-Pt (d).
SEM images of the samples are shown in Figure S5. It shows that MIL-125(Ti), MIL-125(Ti)-Pt, MIL-125(Ti)-CoPi and MIL-125(Ti)-CoPi-Pt have the same morphology composed of square blocks of a thick of about 1.5 µm. No significant difference is observed for the particle size.
Figure S6. Transient photocurrent responses upon chopped UV-visible light illumination of the as-prepared MIL-125(Ti) series of samples with bias = -0.3 V.
References

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Author Contributions

Y. An prepared the samples and carried out the experiments; B. Huang, B. Xu, Z. Wang, P. Wang, X. Qin, X. Zhang and Y. Dai co-supervised the project; Y. An and Y. Liu co-wrote the paper. Y. An, Y. Liu and B. Huang discussed the results and commented on the manuscript.