

Electronic Supplementary Information

Enhanced Photocatalytic CO₂ Conversion over LaPO₄ by Introduction of CoCl₂ as Hole Mediator

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Experimental Section

Preparation of samples. LaPO_4 samples were synthesized by hydrothermal method. All reagents were of analytical purity and used without further purification. 3 mmol $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and 3 mmol $(\text{NH}_4)_2\text{HPO}_4$ were dissolved in 35 mL of deionized water with stirring, respectively. Then $(\text{NH}_4)_2\text{HPO}_4$ solution was added into the $\text{La}(\text{NO}_3)_3$ solution dropwise under vigorous stirring. After stirring for 1 h, the mixture was transferred into a 100 mL Teflon liner. The autoclaves were heated at 180 °C for 24 h, and then cooled to ambient temperature naturally. The precipitates were washed with distilled water several times before it was dried at 60 °C to obtain the final product. LaPO_4 -Pt samples were prepared via impregnating LaPO_4 powder in H_2PtCl_6 aqueous solution followed by NaBH_4 reduction.

Sample characterization. The Powder X-ray diffraction (XRD) was analyzed on a Bruker D8 Advance X-ray diffractometer. Fourier transformed infrared (FTIR) spectra were recorded using a Nicolet Magna 670 FTIR spectrometer in KBr at a concentration of ca. 1 %wt. Photoluminescence (PL) spectra were performed on an Edinburgh

FL/FS900 spectrophotometer at room temperature. Absorption spectra of solution were analyzed using a Varian Cary 50 Scan ultraviolet–visible spectrophotometer. A HP 5973-Agilent 6890 gas chromatography mass spectrometry (GC-MS) was employed to analyze the products of the $^{13}\text{CO}_2$ isotopic experiment. Photocurrent and cyclic voltammetry (CV) measurements were performed on a CHI Electrochemical System, using Pt plate and Ag/AgCl electrode as the counter electrode and reference electrode, respectively. The working electrode was made by dip-coating catalyst slurry ($5\text{ mg}\cdot\text{mL}^{-1}$ in EtOH) on fluorine-doped tin oxide (FTO) glasses, the area of which was controlled as 0.25 cm^2 , and followed by air-drying. 0.2 M of Na_2SO_4 solution was used as electrolyte.

Photoreduction of CO_2 . The photocatalytic reduction of CO_2 was evaluated at 1 atm CO_2 partial pressure in a 200 ml reactor with an inner irradiation quartz reaction cell. The reactor was kept at $20\text{ }^\circ\text{C}$ as controlled by cooling water. A 125 W high-pressure Hg lamp (GGZ125, Shanghai Yaming Lighting Co, Ltd with a maximum emission at about 365 nm) was used as light source. Typically 50 mg photocatalyst was suspended in $70\text{ mL H}_2\text{O}$. Before irradiation, the whole reaction system was first evacuated by a mechanical pump to ensure the air was eliminated. Secondly, CO_2 (99.999% purity) was filled into the reactor for 1 h with stirring to get a CO_2 -saturated aqueous solution. The gas products were analyzed by GC (Agilent 6890N). The apparent quantum

yield (AQY) was also measured under the same photocatalytic reaction conditions. The incident light intensity of high pressure mercury lamp was measured by SpectriLight ILT950. The total number of incident photons was measured using a calibrated silicon photodiode. The AQY was calculated according to the following Eqs:

$$\text{AQY (\%)} = \frac{\text{number of reacted electrons}}{\text{number of incident photons}} \times 100$$

$$= \frac{\text{number of CH}_4 \text{ molecules} \times 8 + \text{number of H}_2 \text{ molecules} \times 2}{\text{number of incident photons}} \times 100$$

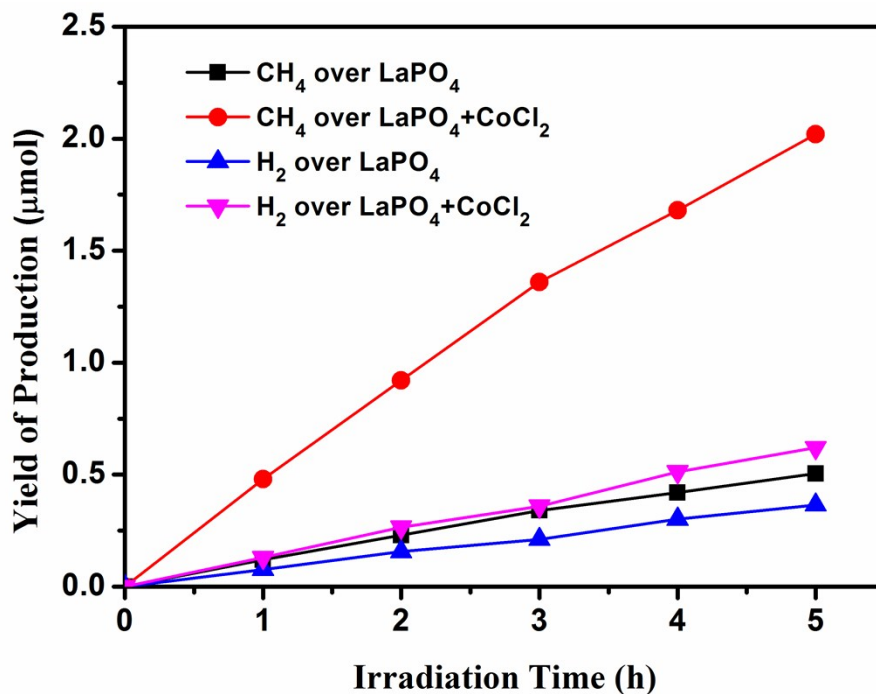


Fig.S1 Production of CH₄ and H₂ formed as a function of irradiation time.

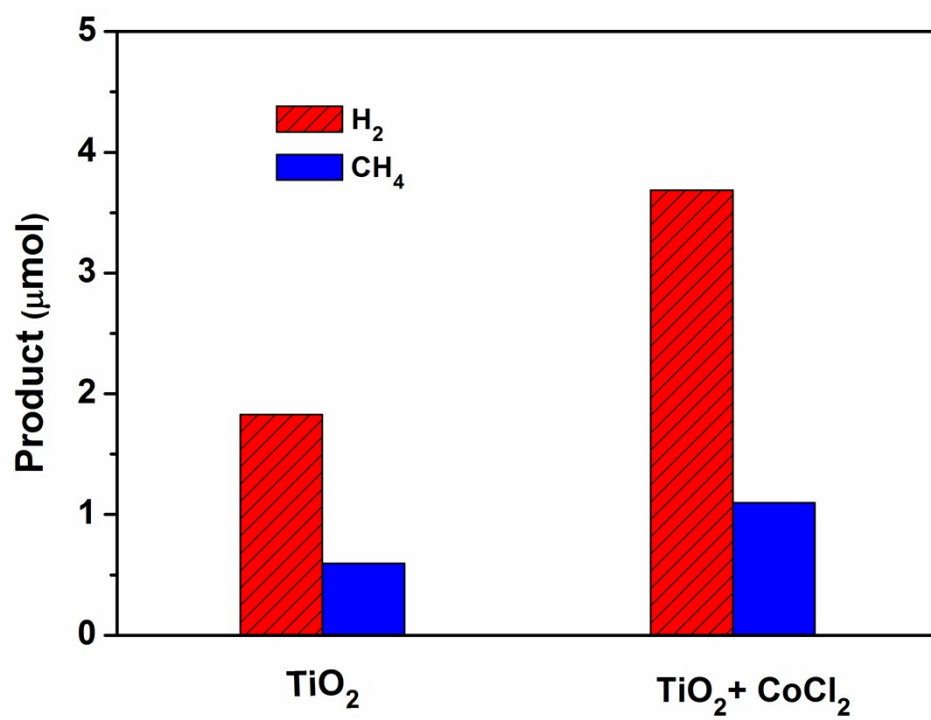


Fig. S2 The production of CH₄ and H₂ generated over TiO₂ (P25) sample with and without introduction of CoCl₂ for 5h.

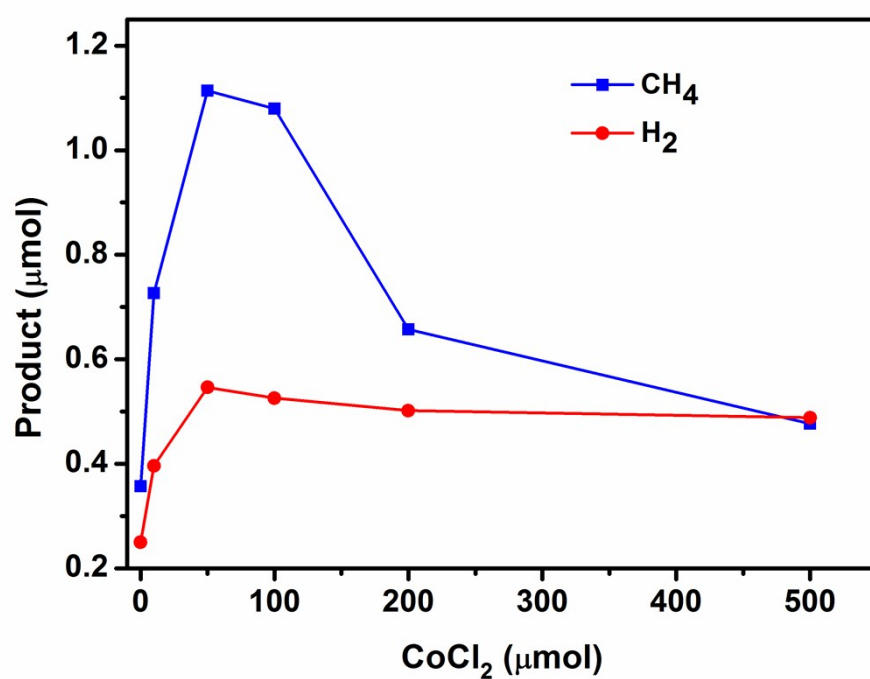


Fig. S3 The effect of the CoCl_2 amount on the CH_4 and H_2 evolution from the CO_2 photoreduction system.

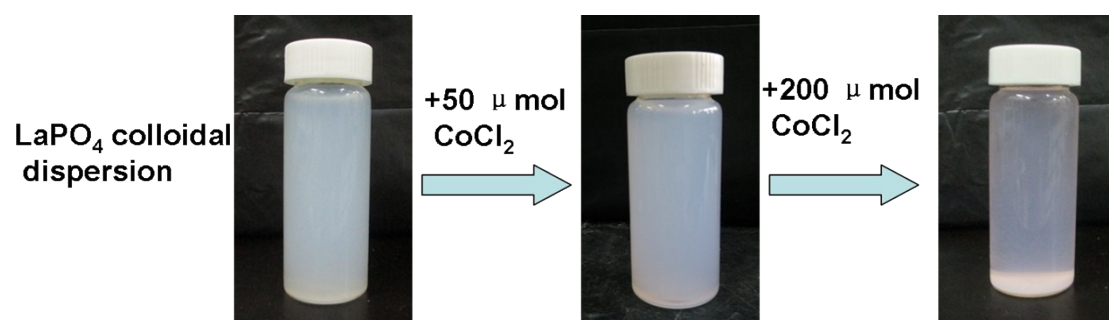


Fig.S4 Photographs of the LaPO₄ colloidal dispersion with different amounts of CoCl₂ adding.

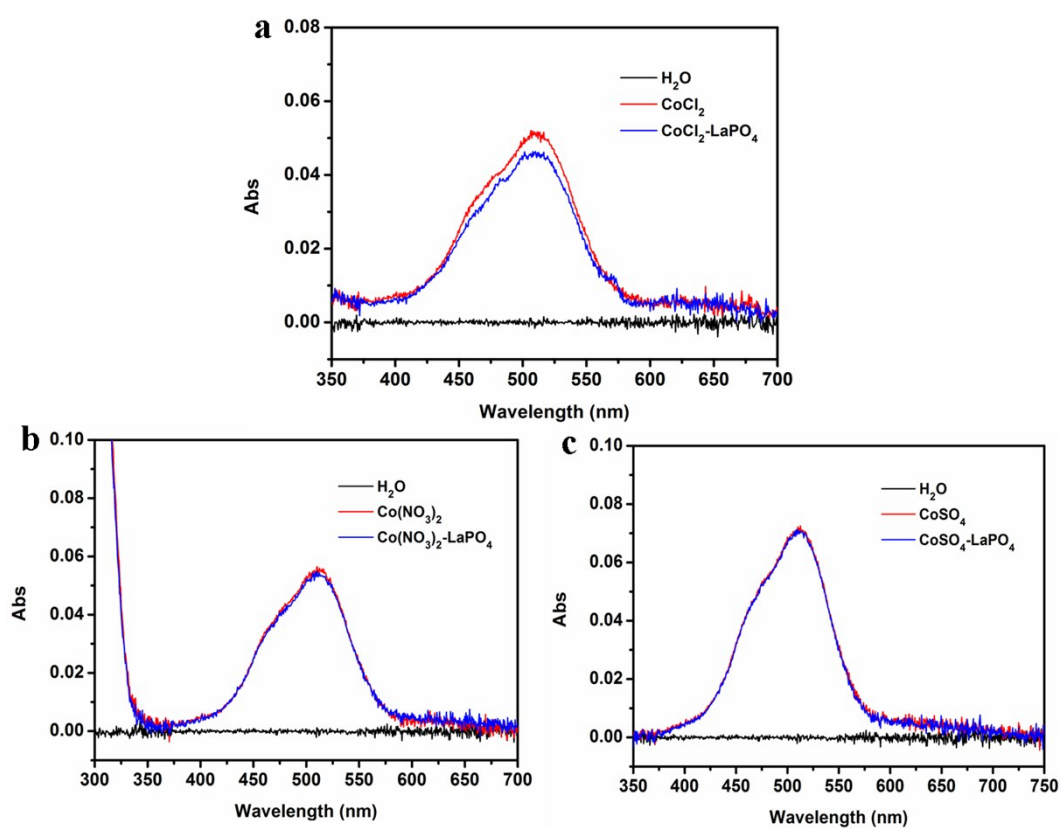


Fig. S5 The UV-vis absorption spectra of CoCl_2 (a), $\text{Co(NO}_3)_2$ (b) and CoSO_4 (c) solution before and after the mixing with LaPO_4 colloid in the dark.

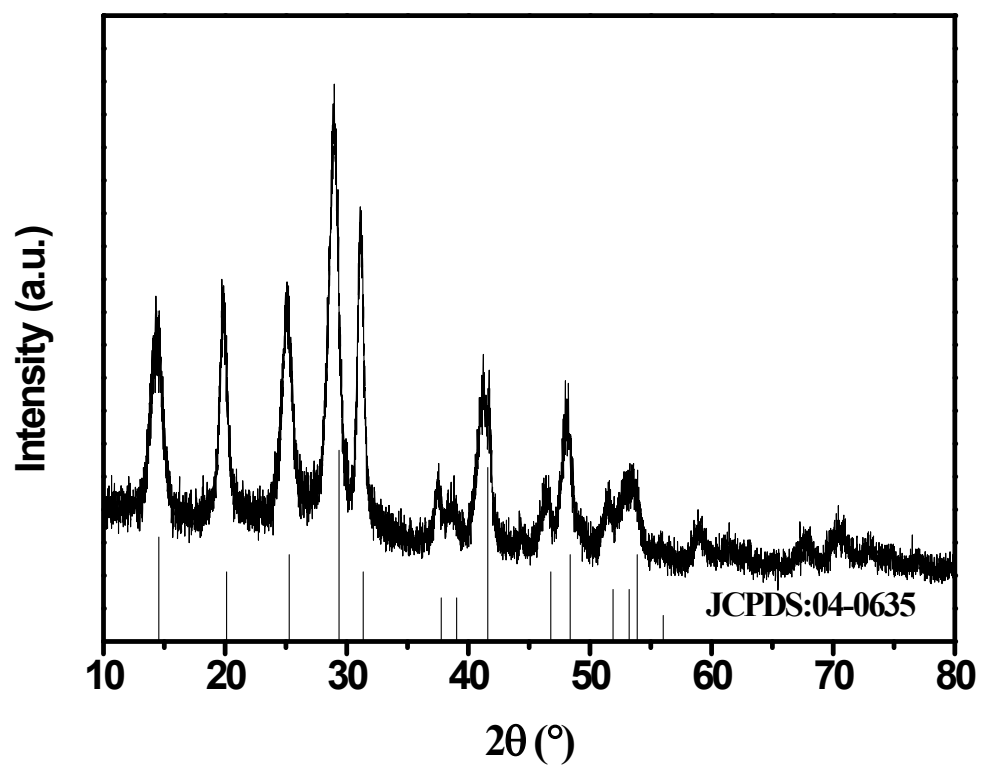


Fig. S6 XRD of the prepared LaPO_4 sample.

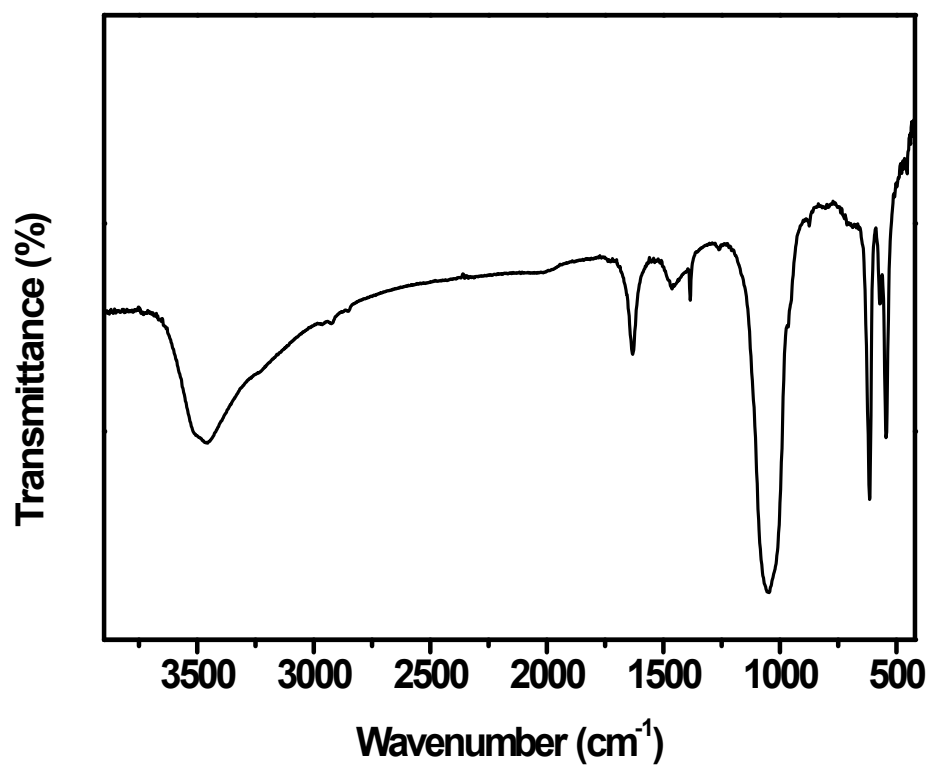


Fig. S7 FT-IR of the prepared LaPO₄ sample.