Supplementary Material

Insight into Mechanism for remarkable photocatalytic hydrogen evolution of Cu/Pr dual atom co-modified TiO_2

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Experimental Section

Materials and Reagents: The tetrabutyl titanate ($Ti(OC_4H_9)_4$), nitric acid (HNO_3), Praseodymium nitrate hexahydrate ($Pr(NO_3)_3 \cdot 6H_2O$), Copper(II) chloride ($CuCl_2$), acetylacetone, acetone, and absolute ethanol were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All reagents were of analytical grade and used without further purification. Deionized (DI) water and hydrolytic inhibitor (a mixture of acetylacetone, acetone, and absolute ethanol) were prepared by our group.

Characterizations: Powder X-ray diffraction (XRD) was carried out on an X-ray diffractometer (RIGAKUTTRIII-18KW) with a Cu Kα source. The morphology was observed by transmission electron microscope (TEM) (JEM-2100). The aberration-corrected high-angle annular dark-field (ac-HAADF) STEM for the Cu/Pr-TiO_2 was obtained using JEM-ARM300F equipment. The photoluminescence (PL) spectra and time-resolved fluorescence decay spectroscopy were obtained by an FLS 1000 fluorescence spectrophotometer (UK), where the sample powder was placed on a copper support. When testing the steady-state PL, 351 nm was selected for excitation. For PL decay testing, 400 nm and 500 nm were respectively selected for excitation and detection.

Photocatalytic Experiments: The hydrogen production performance is tested by the high air tightness automatic online photocatalytic analysis system (PCX-50C, Beijing Perfectlight Technology Co., Ltd.). The catalyst (10 mg) and 20 ml of water with 30% methanol (10 mL) were mixed in a reaction cell, irradiated with the 365 nm LED wavelengths after removing the air. Meanwhile, the cooling water was used to maintain the temperature at 298.15 K. The generated H_2 was analyzed via a gas chromatograph (GC9790II).

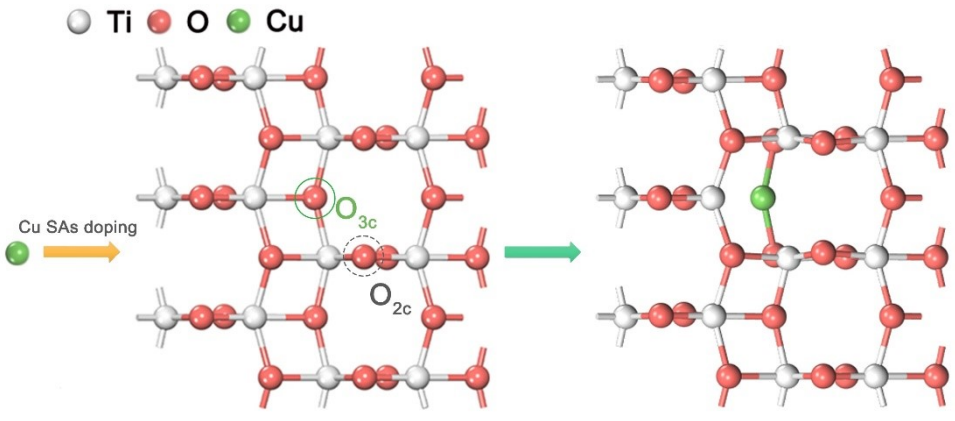

Fig. S1 The most stable slab model of Cu/TiO_2.

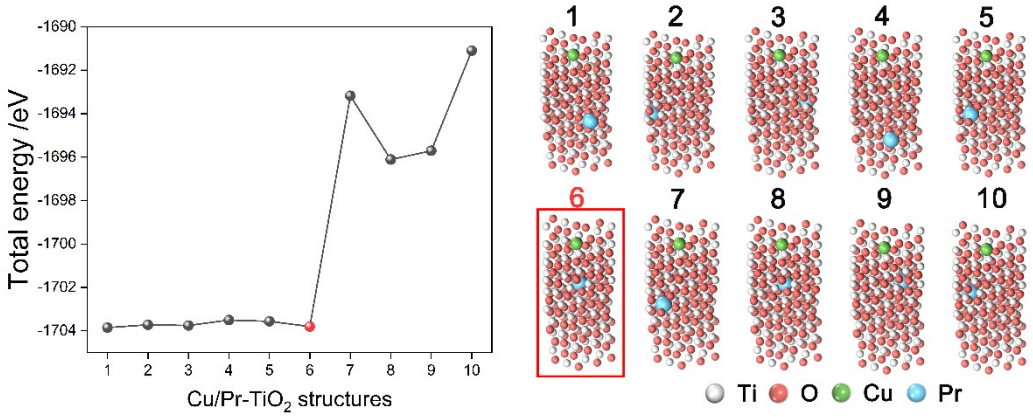

Fig. S2 The most stable slab structure model of Cu/Pr-TiO_2.

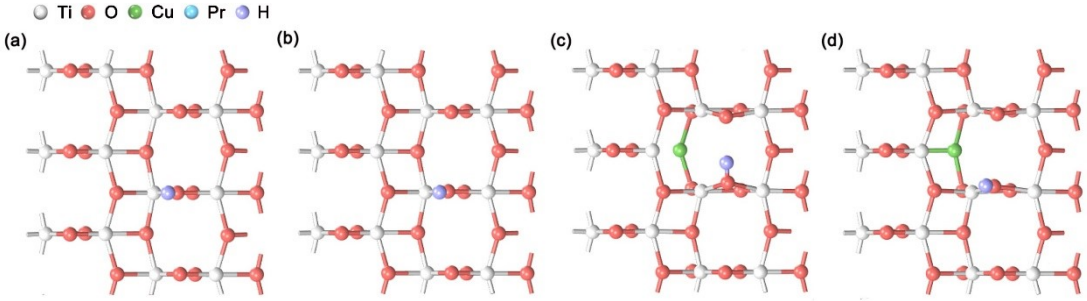

Fig. S3 Top view of the most stable H* adsorption structures of O site for (a) TiO_2, (b) Pr-TiO_2, (c) Cu/TiO_2 and (d) Cu/Pr-TiO_2.

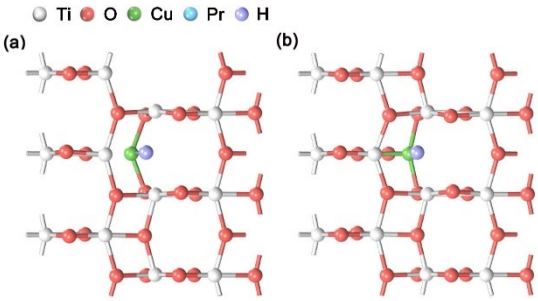

Fig. S4 Top of the most stable H* adsorption structures of Cu site for (a) Cu/TiO_2 and (b) Cu/Pr-TiO_2.

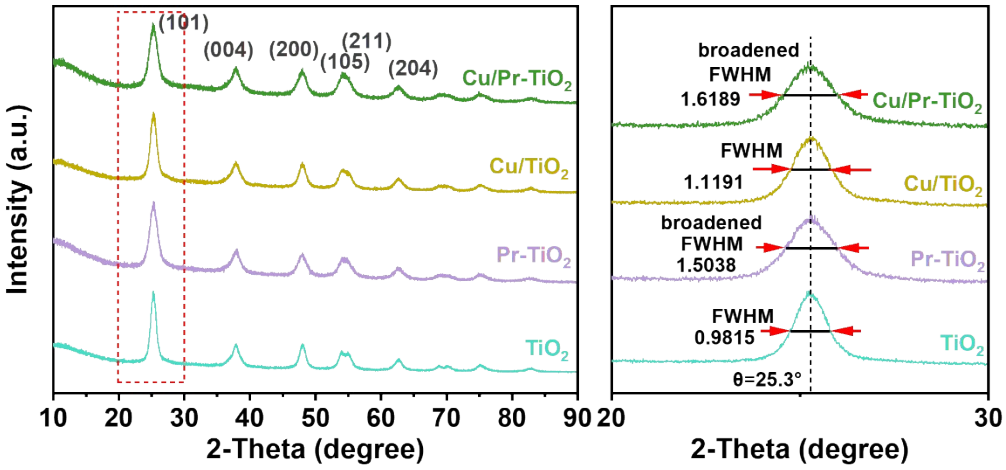

Fig. S5 XRD pattern of TiO_2, Pr-TiO_2, Cu/TiO_2 and Cu/Pr-TiO_2.

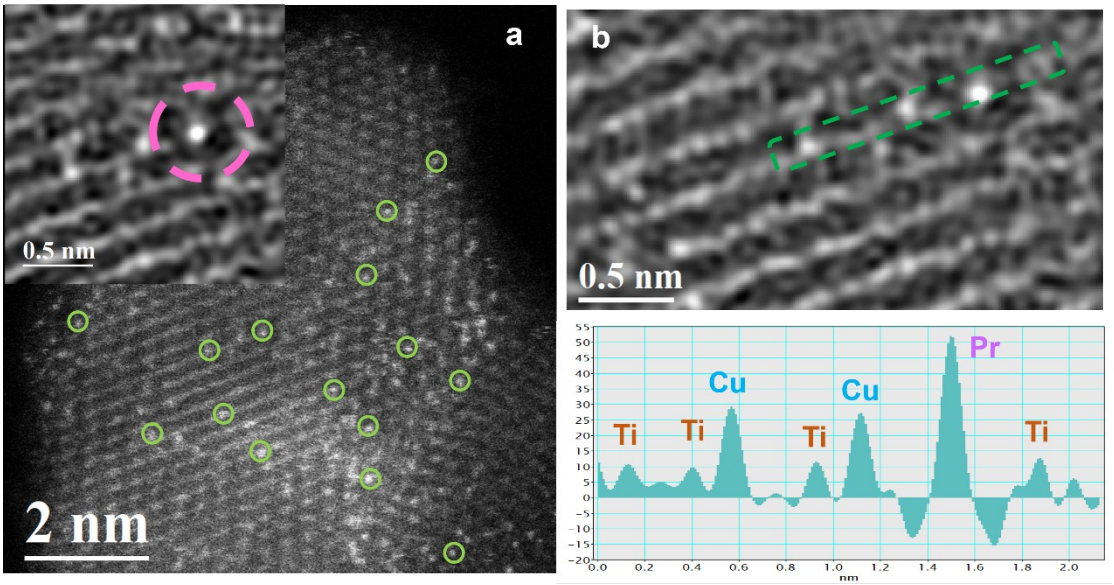

Fig. S6 a) HAADF-STEM image of Cu/Pr-TiO_2 (Cu single atoms marked by green circles). b) A zoomed-in HAADF-STEM image of Cu/Pr-TiO_2 with atomically dispersed Cu site and Pr site and corresponding intensity profiles.

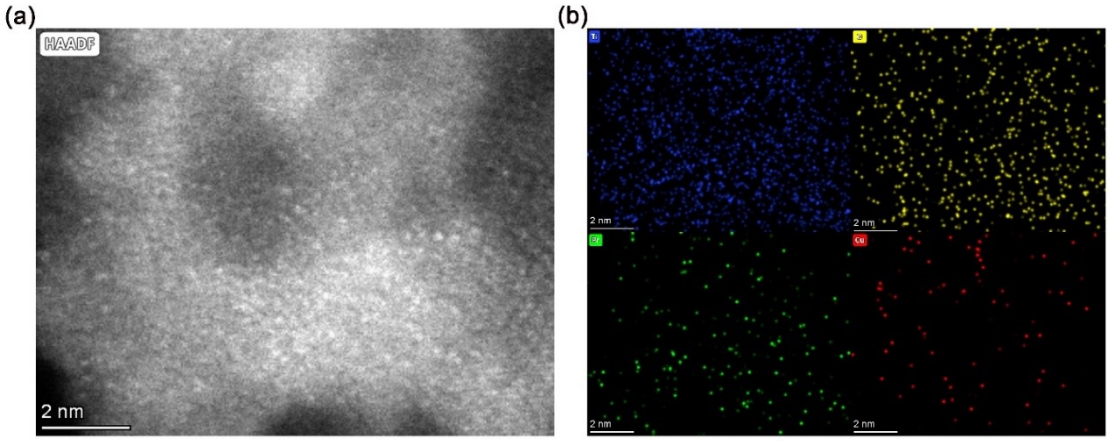

Fig. S7 EDS element mapping images of Cu/Pr-TiO_2.