Electronic Supplementary Material (ESI) for Dalton Transactions.

A sandwiched Co_4-added Polyoxometalate for Efficient Visible-light-driven Hydrogen Evolution

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Content

1. Eperimental section

FT-IR spectra were measured by using a Nicolet iS10 FT-IR spectrometer in the range of 400–4000 cm^{-1} with KBr pallets. Powder X-ray diffraction (PXRD) patterns were recorded on a Bruker D8 Advance XRD diffractometer with Cu Kα radiation (λ = 1.54056 Å). Thermogravimetric analyses were conducted in under N_2 flowing on a Mettler-Toledo TGA/DSC 1000 with the heating rate of 10 °C min^{-1} from 25 to 1000 °C. UV-Vis absorption spectra were obtain using a SP-1901 UV-Vis spectrophotometer. H_2 was analysed using a gas chromatograph (GC9790 Ⅱ) with a TCD and a 5 Å molecular sieve column (3 m × 3 mm) with Ar as the carrier gas. Electrochemical measurements (transient photocurrent response, Mott–Schottky spots) were using an electrochemical workstation CHI 670E. A three-electrode system was employed in a cell with an Ag/AgCl as the reference electrode, a carbon rod as the counter electrode, and the indium tin oxide (ITO) coated glass as the working electrode. The electrolyte solution is Na_2SO_4 (0.5 M). The area of working electrodes was set constant at 1.0 × 1.0 cm^2. Photocatalytic reactions were carried out by Beijing Perfectlight Multi-channel photochemical reaction system PCX-50C equipped with white light source (electric power: 10 W). ICP-OES test was test on Agilent 725-ES. Field emission scanning electron microscopies (FE-SEM) were performed on a Ultra Plus model Zeiss microscope operating at an accelerating voltage of 10.0 kV.

2. Supporting Figures

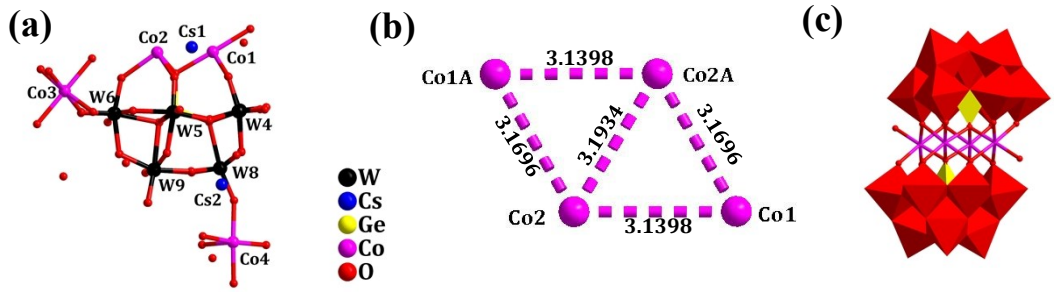

Figure S1 (a) Asymmetric unit of **1**; (b) Schematic diagram of {Co_4} existing in **1** and the distance between Co-Co; (c) Polyhedral view of anion clusters {Co_4GeW_9}.

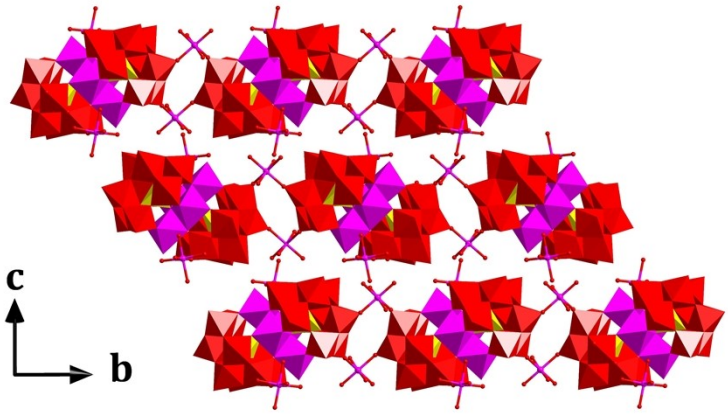

Figure S2 The stacking diagram of **1** along the a-axis direction.

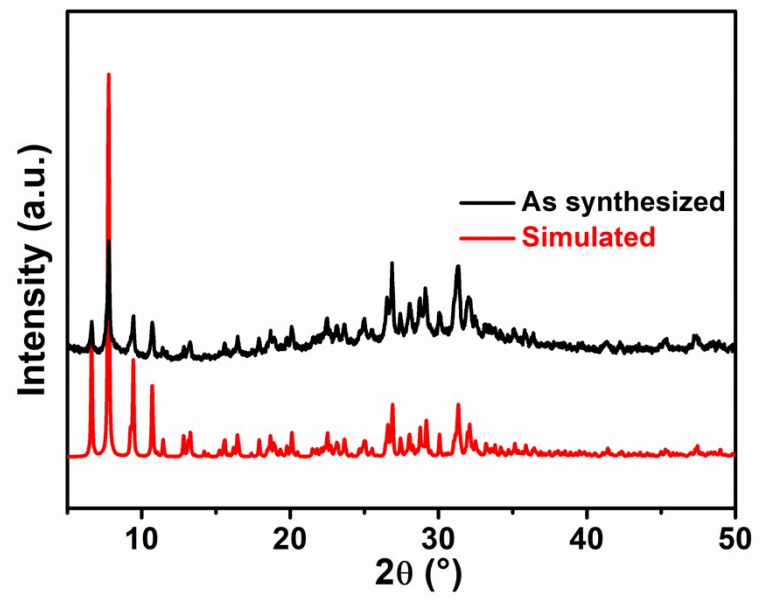

Figure S3 Synthesized and simulated PXRD pattern of **1**.

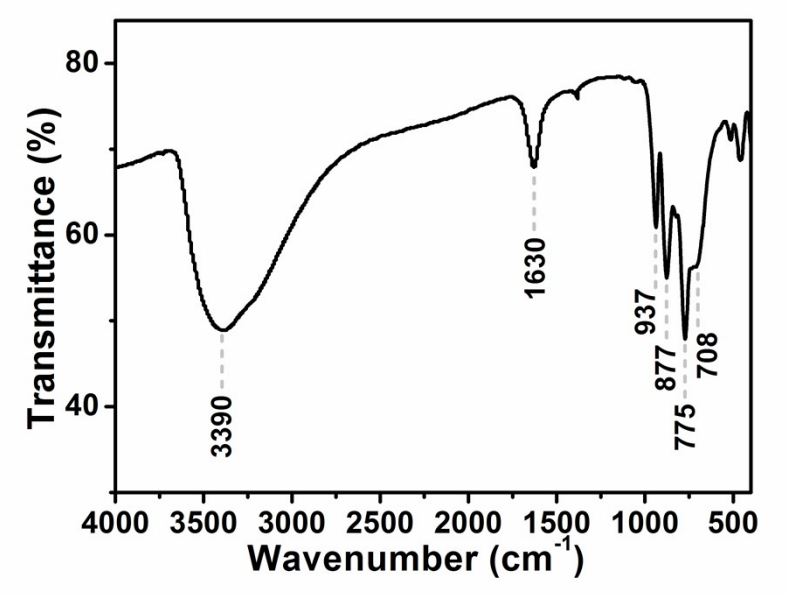

Figure S4 The FT-IR of **1**.

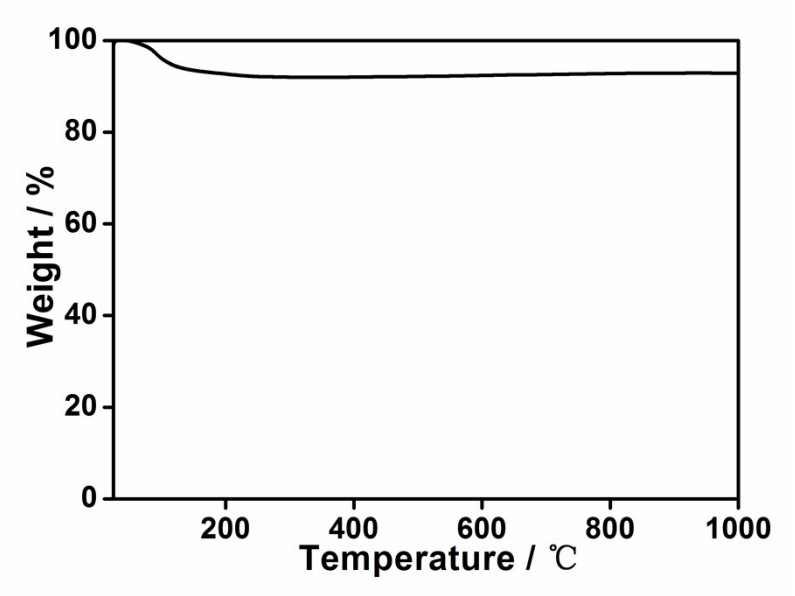

Figure S5 Thermogravimetric analysis curve of **1**.

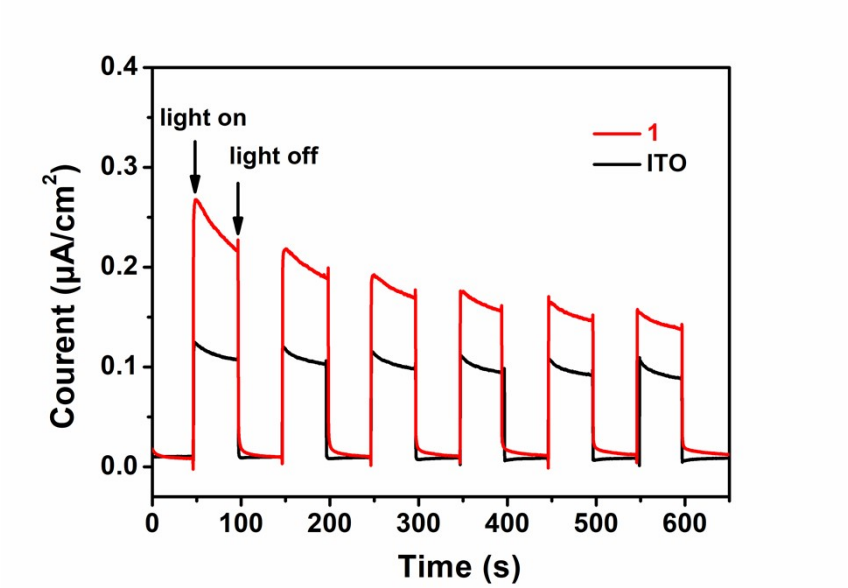

Figure S6 Transient photocurrent responses (I-t curves) of ITO conductive glass and ITO conductive glass loaded with compound **1**.

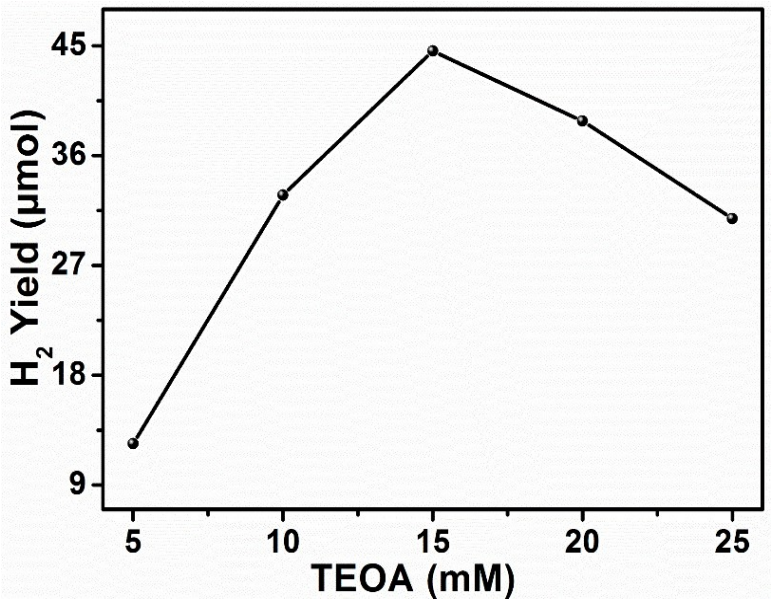

Figure S7 Photocatalytic H_2 evolution with different concentrations of TEOA (5–25 mM) after 10 hours of reaction. Conditions: white light (400−800 nm, 10W), $[Ir(ppy)_2(dtbbpy)][PF_6]$ (0.2 mM), catalyst of **1** (3 mg), 3 mL of CH_3CN/DMF (1/3), and H_2O (2 M) deaerated with Ar/CH_4 (4/1).

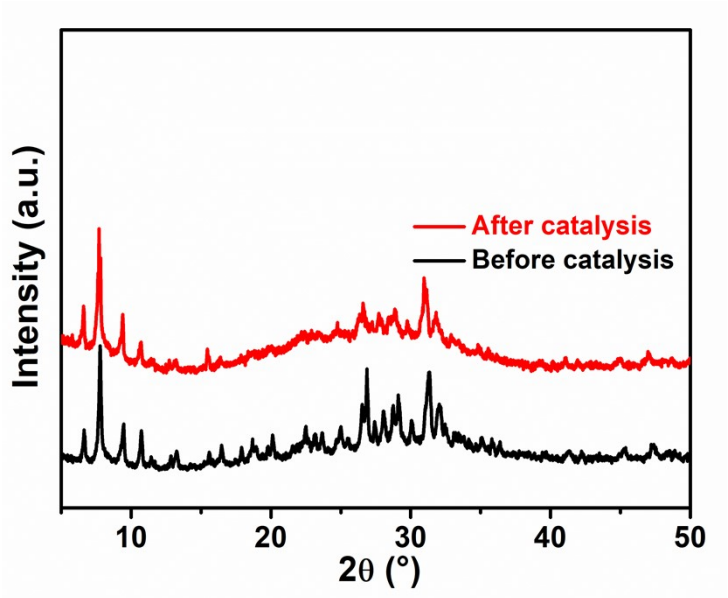

Figure S8 The powder X-ray diffraction patterns for **1** before and after reaction.

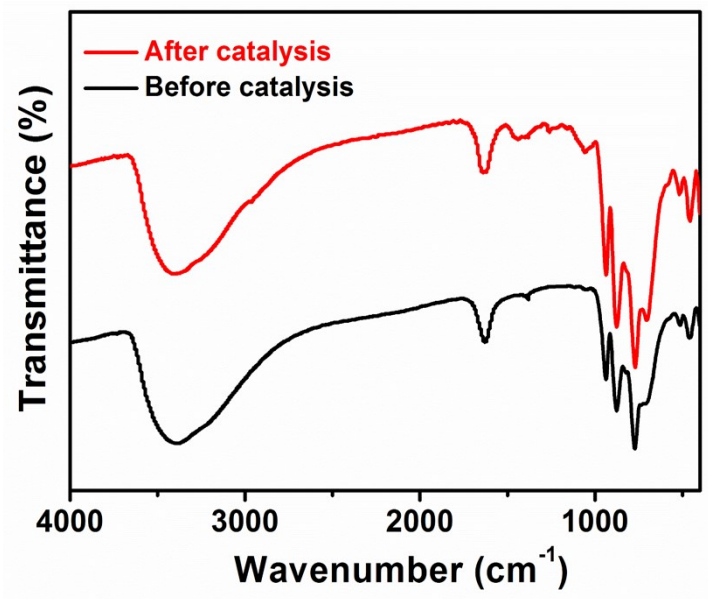

Figure S9 The FTIR spectra for **1** before and after reaction.

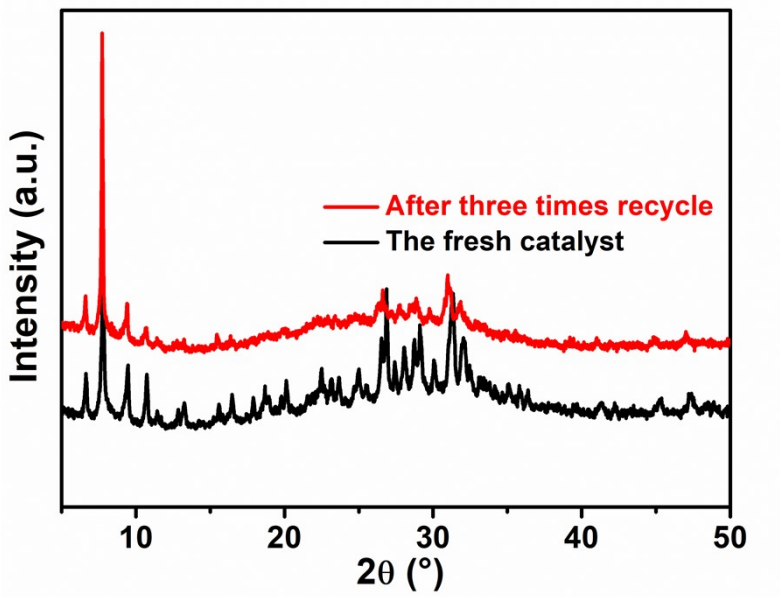

Figure S10 The PXRD patterns after three times recycle of catalyst **1**.

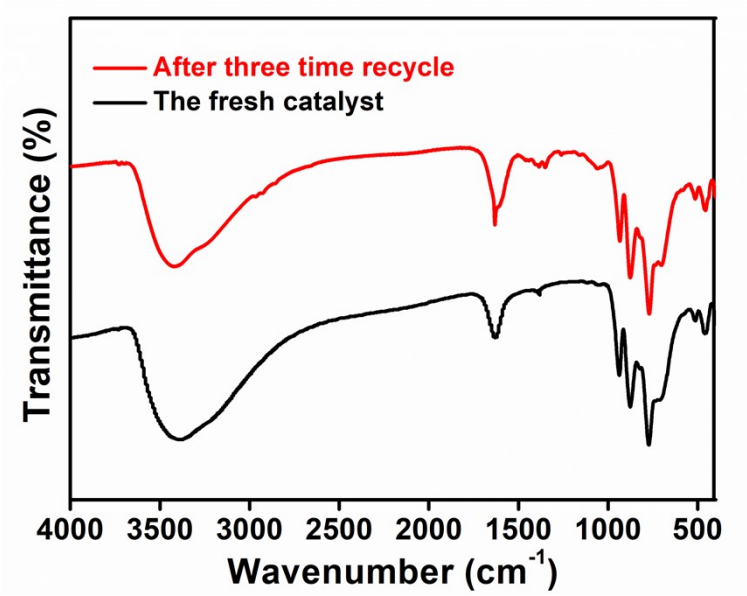

Figure S11 The FT-IR spectra after three times recycle of catalyst **1**.

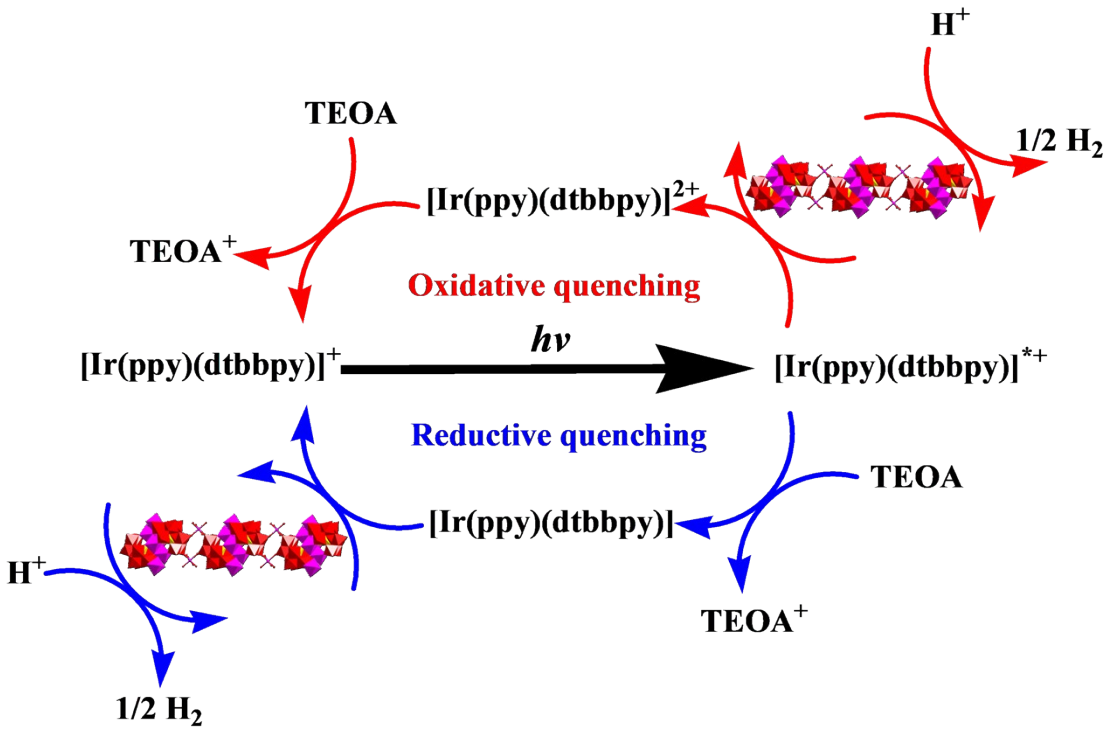

Figure S13 Proposed mechanism for visible-light-driven H_2 evolution catalyzed by **1** with oxidative and reductive quenching mechanism.