

Supporting information

A Carbon-Based Photocatalyst Efficiently Converted CO₂ to CH₄ and C₂H₂ In Visible Light

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1. Preparation of photocatalyst

1.1 Preparation of previously exfoliated graphite (PEG) In order to fully exfoliate graphite into graphene, a solid-exfoliation process was employed to prepare PEG. Natural flaked graphite was mixed and saturated with acids consisting of concentrated sulfuric acid and concentrated nitric acid in a volume ratio of 4:1. The reaction system was stirred with excess FeCl₃ or NH₄NO₃ (>0.25 g/ml in the mixture) for 24 h to form the intercalated graphite compound. The concentration of nitric acid should be maintained at 10 mol/L (as higher concentrations will reduce the

conductance of the resulting graphene). The mixture was then carefully vacuum filtered and washed with deionized water for 5 times until the pH of the solution was 6. After being dried at 60 °C in a vacuum oven for 2 h, the graphite was loaded in a ceramic vessel, placed in a microwave oven, and irradiated at 500 W for 90 s. Under microwave irradiation, the precursors expanded rapidly, accompanied by “lightening.”

1.2 Preparation of graphene In a typical synthesis of graphene, the PEG was dispersed in chlorosulfonic acid (CSA) and ultrasonicated for 10 min, forming a stable dispersion which attributed to the protonation of the graphitic material. The dispersion was allowed to settle for 2 h, allowing better intercalation of CSA. Then, hydrogen peroxide was slowly added into the dispersion to react with the intercalated CSA. The generated O₂, HCl, and SO₃ gases exfoliated the graphite to form graphene sheets (GS). Excess hydrogen peroxide is needed to ensure that CSA is quenched completely. After washing out the acid, the GS floated to the top of water and could be easily collected by filtration.

1.3 Preparation of photocatalyst films. A convenient film preparation method involved mist spray has been applied here. The typical process was as following: An appropriate commercially available THPP (20 and 60 mg) or CoTHPP (22 and 65 mg) was dissolved in 100 milliliters 0.2 mg/mL of GS suspended in 1, 2 dichloroethane (DCE), and the dispersion was ejected out of a spray lance onto a solid substrate (quartz or polyethylene terephthalate (PET) film), driven by N₂ at a certain pressure, while the substrate was held at 100 °C. In order to dispel the adsorbed solvent

molecules on the photocatalyst, the prepared films were placed in a 100 °C vacuum drying chamber for 2 h.

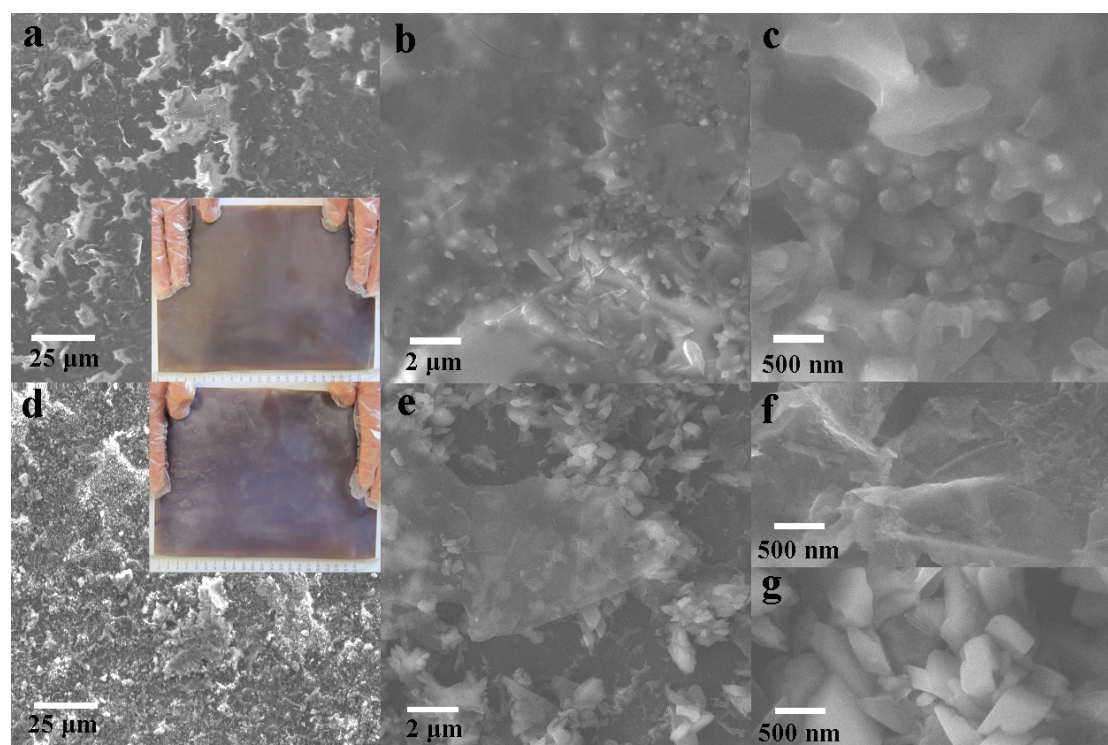


Figure S1. SEM images of G/CoTHPP (a) and G/THPP (d) film catalyst, and corresponding magnified SEM images (b, c) & (e, f, g), the inserts are the corresponding optical photograph of the films.

2. Electrochemical Measurement of porphyrin.

The acetone solution of CoTHPP or THPP was modified on Glassy Carbon Electrode, and dried at room temperature. A Pyrex electrolytic cell was employed, filled with 20 mL of Ar-purged 0.5 M Na₂SO₄. A Pt wire and Ag|AgCl electrode were employed as the counter and reference electrodes, respectively. Impedance measurements were recorded using a CHI660 electrochemical workstation. This measurement is to investigate the relations of impedance with potential change at fixed frequency.

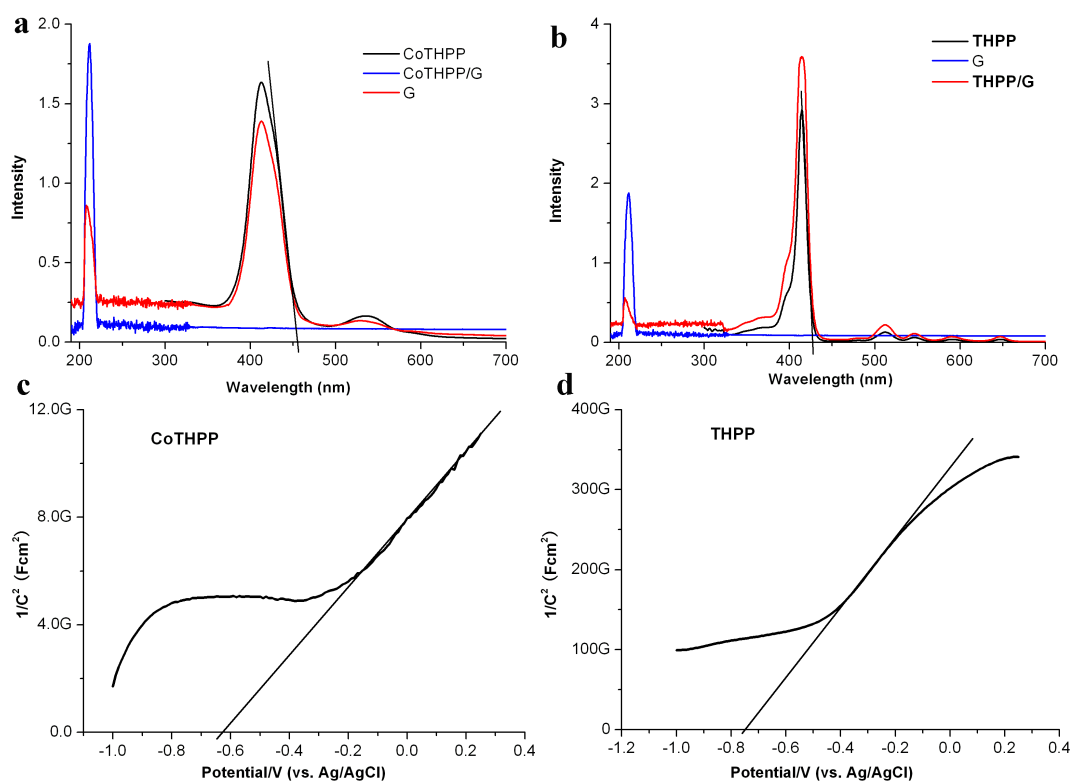


Figure S2. UV-vis spectra of CoTHPP (a) and THPP (b). Mott-schottky plots of CoTHPP (c) and THPP (d) under pH 7 condition.

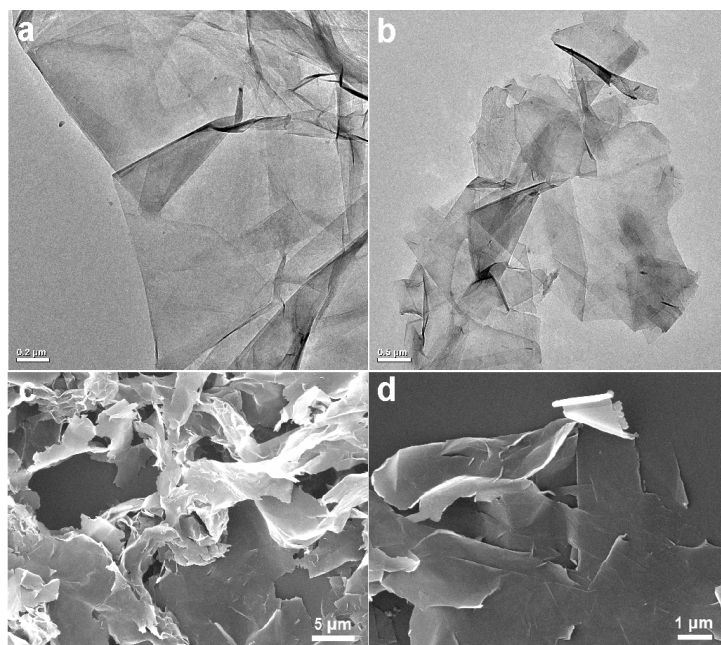


Figure S3. The TEM image (a,b) and SEM (c,d) image of as-prepared graphene sheets.

3. Experiment of photocatalysis

A photocatalytic film with appropriate area was placed in a one liter of quartz chamber with valves for evacuation and gas feeding. After loading of the sample, the chamber was evacuated to about 10 mTorr using a mechanical pump and then sealed. Carbon dioxide (99.99% pure) was forced to pass through a bubbler containing deionized water before entering the reaction chamber. After the processing of evacuation and CO₂ pumping was repeated for three times. The nominal excess pressure is of less than 1.0 psi. All photocatalytic carbon dioxide conversion experiments were performed under irradiation of solar simulator. The light power density was 100mW/cm². The equilibrium temperature of the samples was about 45 °C (± 5 °C). Although the experiments have also been conducted at lower temperatures (~35 °C), no definite influence of temperature on product formation rates has been found.

4. Computational Details

All geometry optimizations were carried out by the DFT approach with the Gaussian 09 suite of programs using B3LYP functional. All atoms except Co were described by the standard 6-31G (d) basis set. The Co atom was described by the LANL2DZ basis.

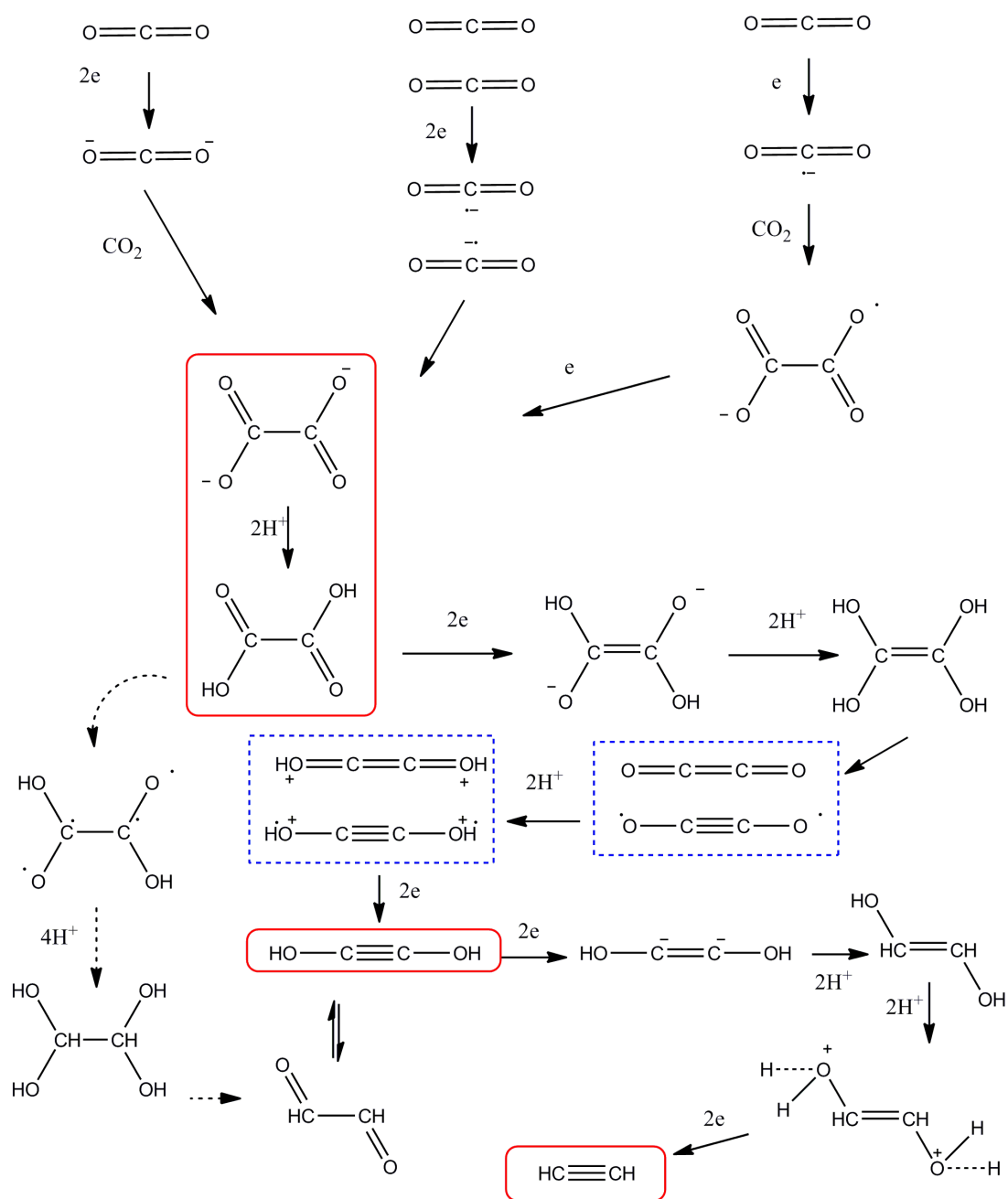


Figure S4. Proposed mechanistic steps in photo-reduction of CO_2 to C_2H_2 on graphene.

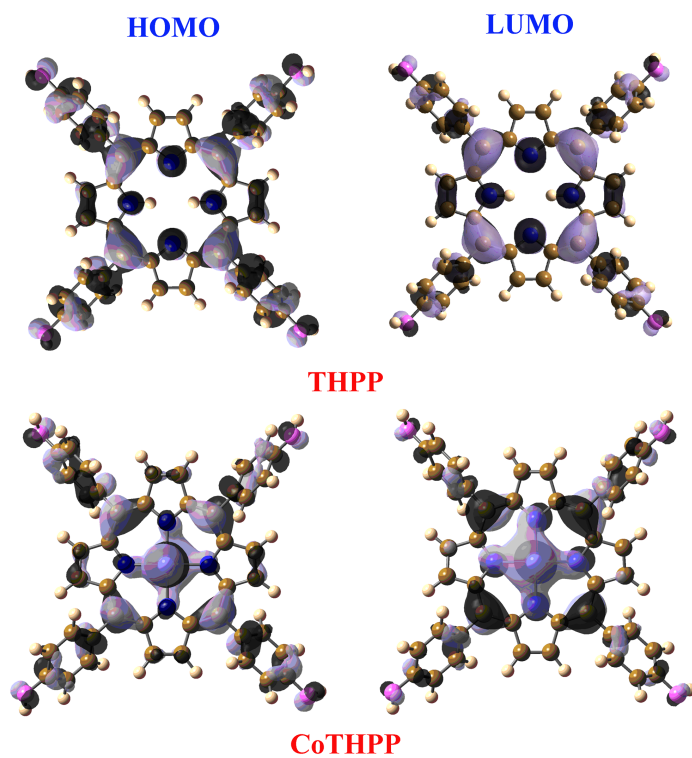


Figure S5. Electronic density contours of the HOMO and LUMO orbitals.