Supporting Information

Highly selective conversion of CO_2 to C_2H_6 on graphene modified Chlorophyll Cu through multi-electron process artificial photosynthesis

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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 $FeCl_3$ or NH_4NO_3 (>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 O_2, HCl, and SO_3 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.

Supplementary Figures

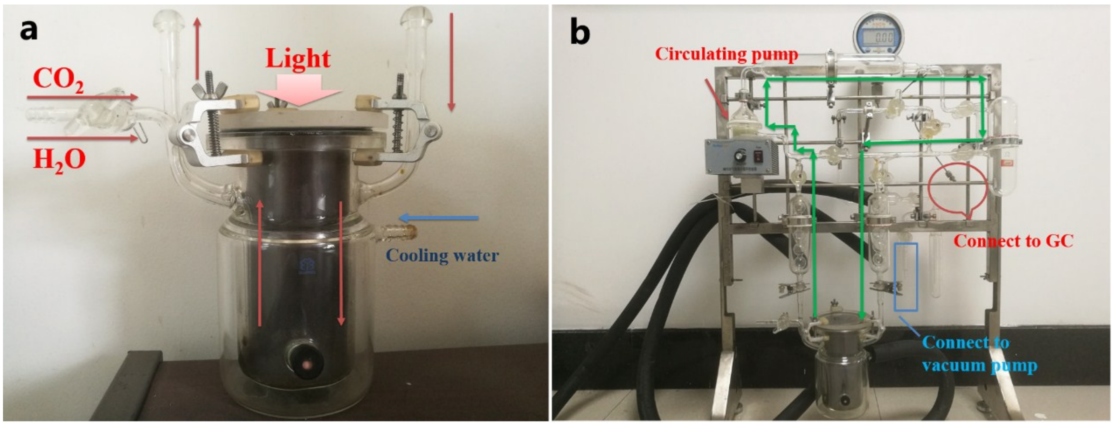

Figure S1 (a) Photograph of reaction chamber, the red arrows stand for the direction of air flow; (b) Photograph of on-line vacuum system, the green arrows stand for the direction of air flow

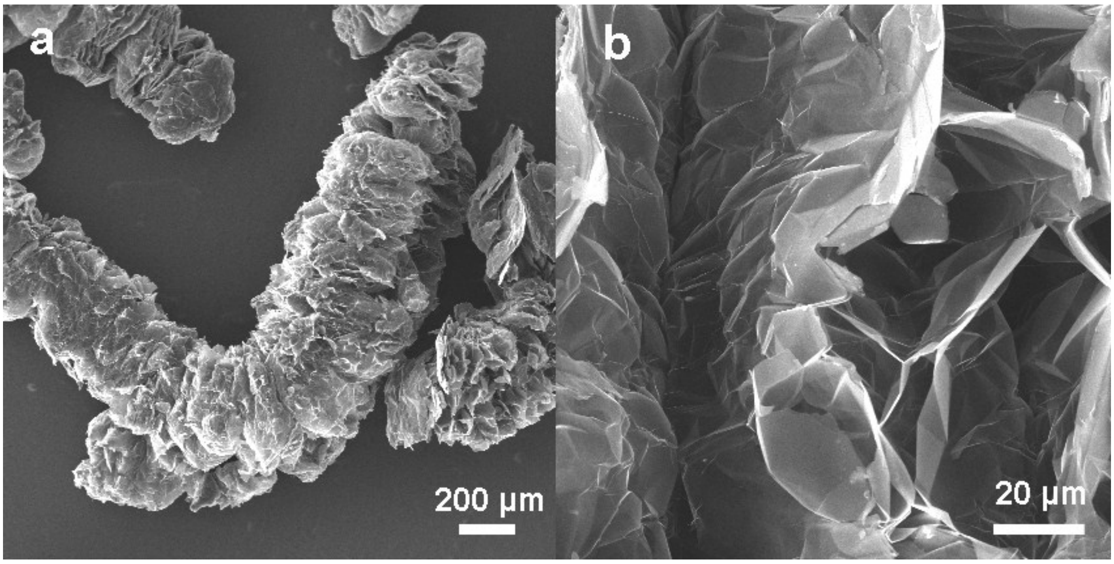

Figure S2 The SEM images of previously exfoliated graphite in low (a) and high (b) magnification.

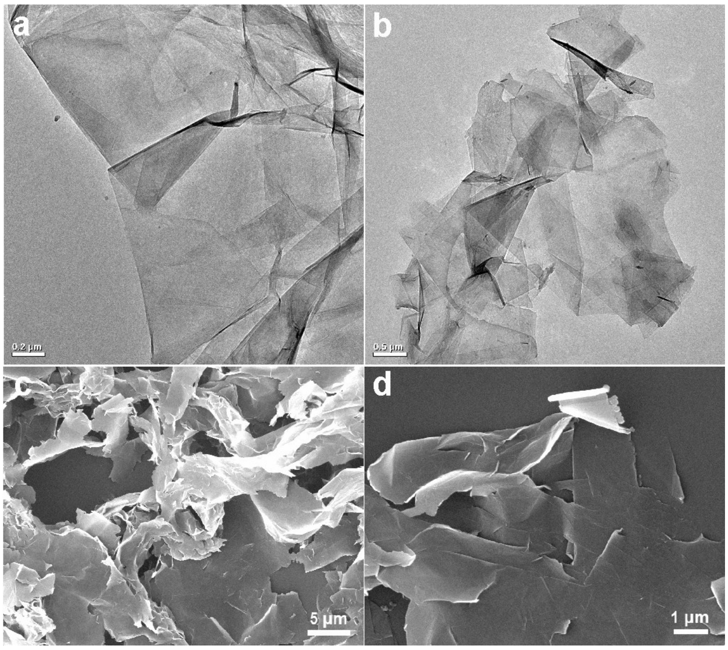

Figure S3 The TEM image (a,b) and SEM (c,d) image of as-prepared graphene sheets.

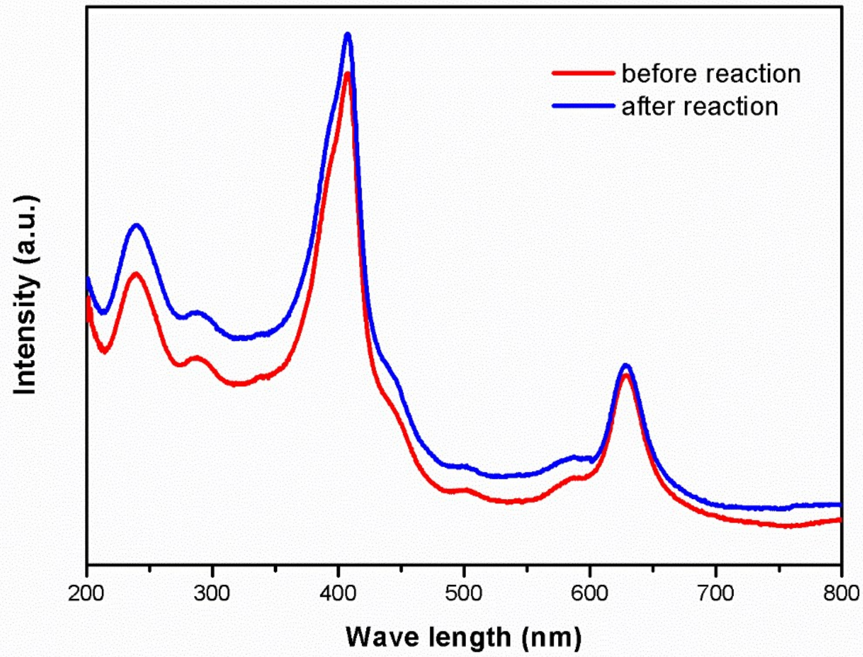

Figure S4 The UV-vis measurement of g-Chl-Cu before and after photoreduction reaction.

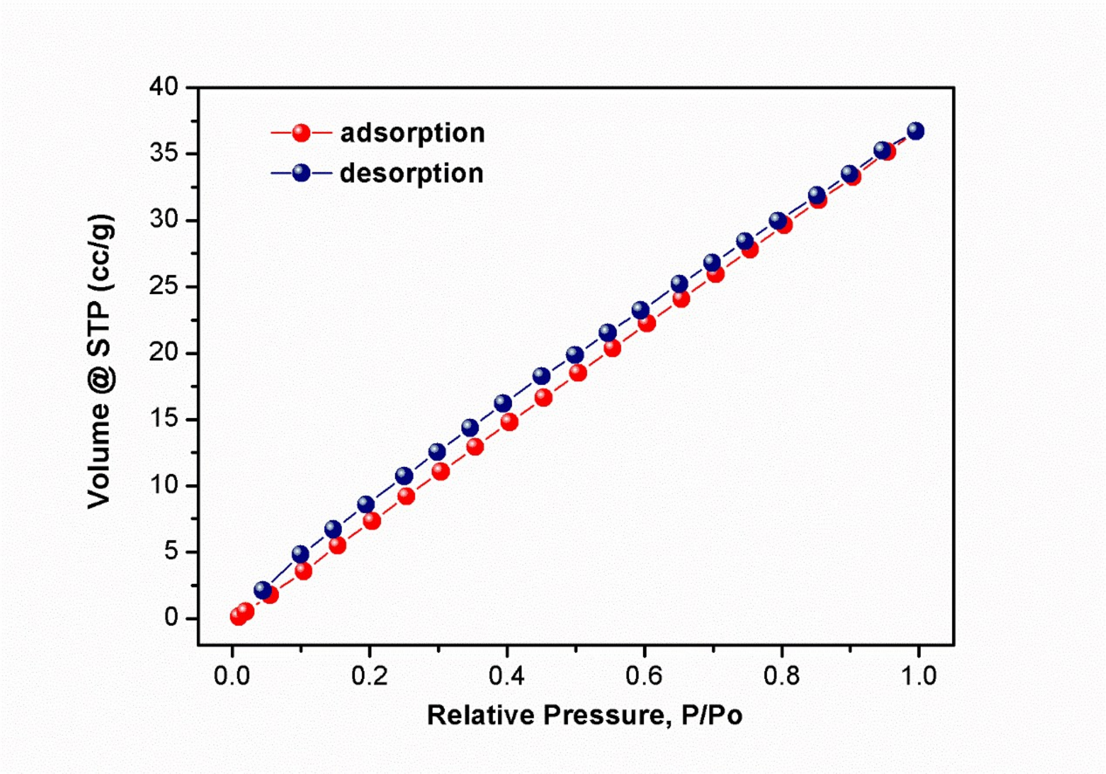

Figure S5. CO_2 sorption isotherms of g-Chl-Cu Photocatalyst powder at 25 °C.

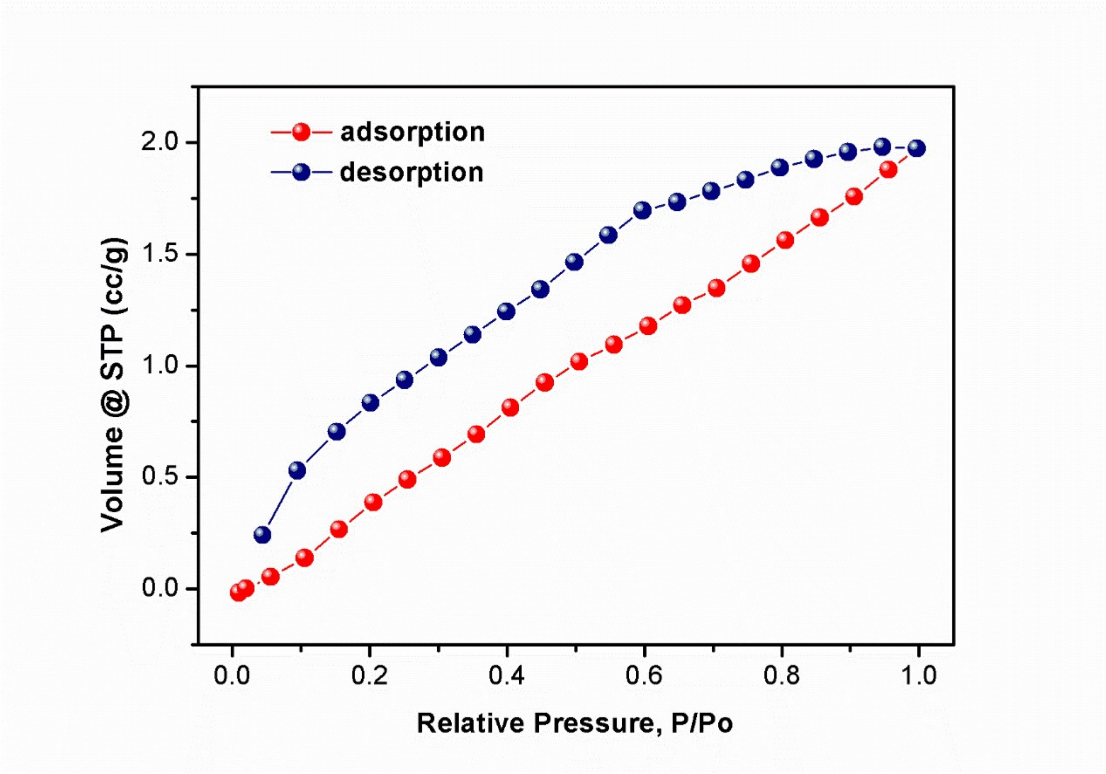

Figure S6. CO_2 sorption isotherms of Chl-Cu at 25 °C.

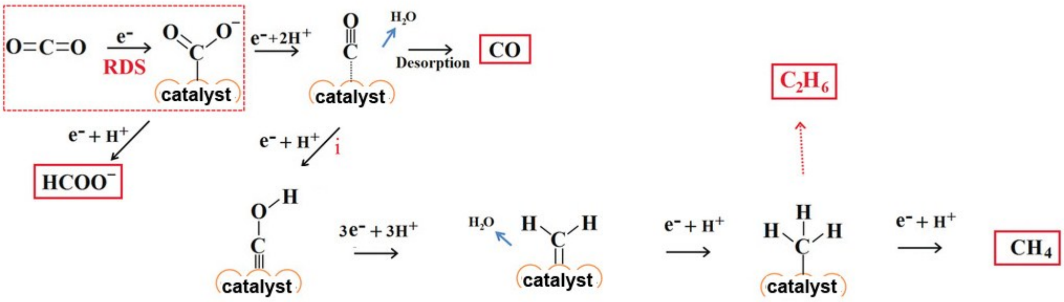

Figure S7. The first mechanism pathway of CO_2 reduced to C_2H_6 proposed by predecessors.