Cuprous Oxide/ reduced Graphene Oxide (Cu_2O/rGO) Composite PhotoCatalyst for Hydrogen Generation: Employing rGO as Electron Acceptor to Enhance Photocatalytic Activities and Stability of Cu_2O

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Supporting Information

1. Cu_2O/rGO composite preparation

To prepare Cu_2O/rGO composite with a weight ratio of 15/1 (denoted as Cu_2O/rGO(15)), 10 mg graphene oxide (GO) (Sinocarbon) was dispersed into 60mL deionized water by ultrasonication for 2h. 380 mg copper (II) acetate ($Cu(Ac)_2$, 2.10mmol) was then added and the resulting suspension was stirred overnight for ensuring adsorption of the copper precursor onto graphene oxide surface. Solution of 420 mg NaOH (10.5mmol) in 50 mL deionized water was added to this suspension dropwised resulted in precipitation of $Cu(OH)_2$/GO which was collected by centrifugation. $Cu(OH)_2$/GO powder was then loaded into 50mL Teflon line autoclave with 567mg glucose (3.15mmol), 15mL deionized water and 4.0 mg K_2PtCl_6 ($8.2\ 10^{-3}$ mmol). The autoclave was heated up to 100°C and kept at this temperature for 10h. Cu_2O/rGO(15) composite obtained was collected by centrifugation, washed several times with deionized water and ethanol. Cu_2O/rGO powder was dried at RT in vacuum oven overnight before using.

2. Characterizations

Morphologies of Cu_2O/rGO composites were characterized by transmission electron microscopy (TEM, JEOL JEM-2100F). X-ray diffraction pattern (XRD, Cu-Kα radiation) was obtained by using Bruker D8 Advance. UV-vis absorption analysis was performed employing lambda 750S UV-vis spectrometer (Perkin Elmer) using $BaSO_4$ reference. Photoelectrochemical measurement was carried out using CHI 852C potentiostat. A self designed two compartment cells with a planar quartz window as the working electrode compartment was employed. Conventional three electrode configuration was used with Ag/AgCl reference electrode (CHI), Pt mesh counter electrode, and Cu_2O/FTO working electrode. Light irradiated area on working electrode was kept at $1cm^2$ by masking the rest with epoxy resin. Electrolyte was 0.1M potassium phosphate buffer at pH7 which was carefully degased before measurements. 150W Xe lamp with a 400 nm cut-off filter was employed to provide visible light irradiation. Power density on working electrode was kept at $100mW.cm^{-2}$ by adjusting distance between this electrode and light source.

3. Hydrogen Photogeneration Experiments

In photoelectrolysis experiment coupled with H_2 quantification, a bias of -0.4V vs. Ag/AgCl was applied along with visible light irradiation on Cu_2O/FTO electrode for 1h. When electrolysis was completed, gas from head cap of the closed cell was sampled and

analyzed by gas chromatography (GC). Produced H_2 was quantified following the calibration curves performed on the GC using the 5% H_2/Ar and 1% H_2/Ar mixtures.

To investigate the photocatalytic activities of Cu_2O/rGO photocatalysts for H_2 generation using methanol as a sacrificial electron donor, 10 mg of these photocatalysts were added to 20mL methanol/H_2O (2/8 v/v) solution in a 50mL glass schlenk tube. This suspension was then sonicated for 30min followed by saturation with nitrogen gas to eliminate oxygen. Visible light irradiation was performed by using 150W Xe lamp with 400 nm cut-off filter. Power density at the reaction vessel was 100 mW.cm^{-2}. Gas from head cap of the vessel was manually sampled and analyzed by GC. For comparison, H_2 photogeneration efficiencies were normalized per gram of photocatalysts.

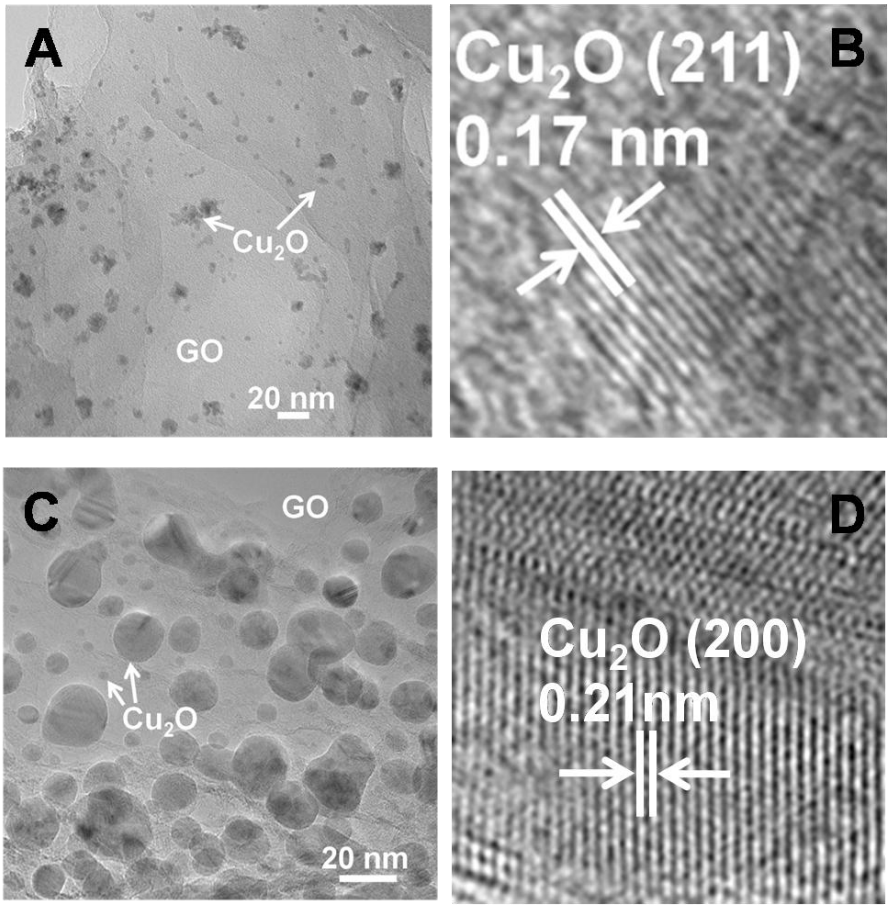

Figure S1: TEM images of Cu_2O/rGO(15) (A, B) and Cu_2O/rGO(25) (C,D)

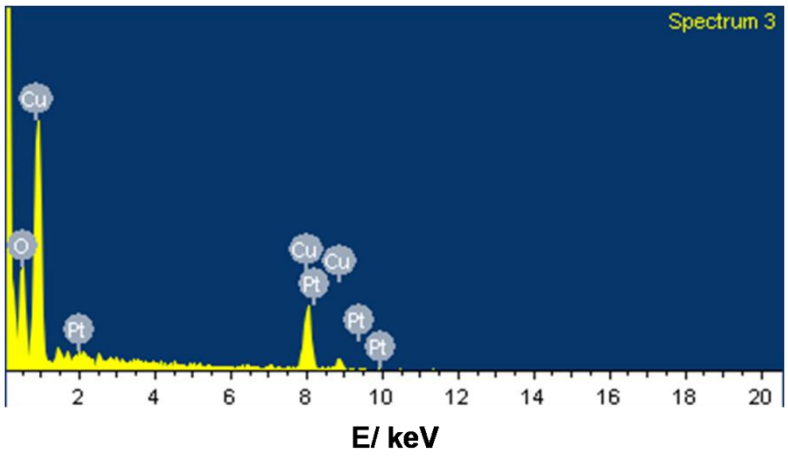

Figure S2: Energy Dispersive Energy analysis on Cu_2O/rGO(15) with 1% (wt%) Pt loaded

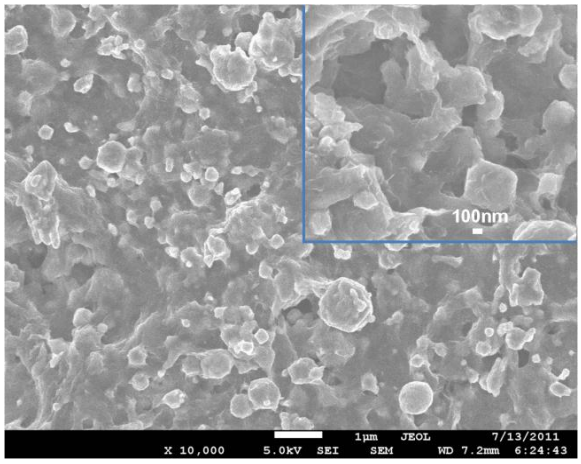

Figure S3: SEM image on a Cu_2O/rGO(15)/FTO electrode prepared by spin coating a dispersion of Cu_2O/rGO composite in ethanol on FTO electrode

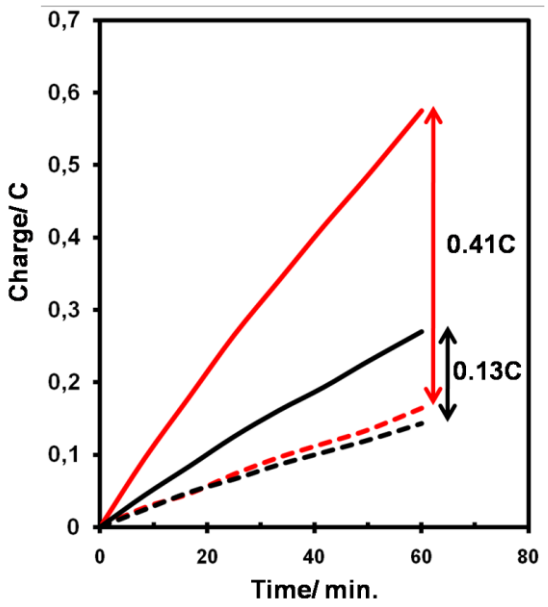

Figure S4: Electrolysis at applied potential of -0.4V *vs.* Ag/AgCl in pH7 0.1M potassium phosphate buffer solution using Cu_2O/FTO (black) and Cu_2O/rGO(15)/FTO (red) electrodes. Electrolysis was performed under dark (dash) and under visible light irradiation, 100mW.cm^{-2} (bulk).

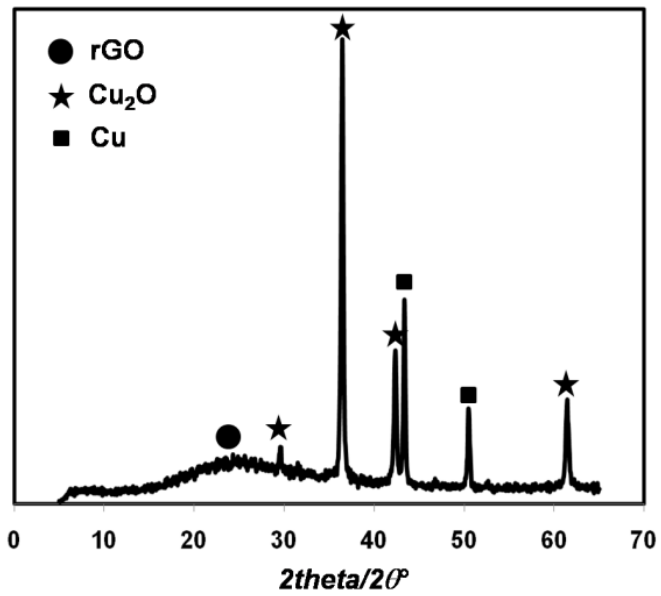

Figure S5: XRD analysis on Cu_2O/rGO(15)/FTO photoelectrode after 1h irradiated by visible light, 100mW.cm^{-2} at applied bias of -0.4V *vs.* Ag/AgCl. New Cu^0 peaks were observed confirming partial photo-reduction of Cu_2O into Cu metal.

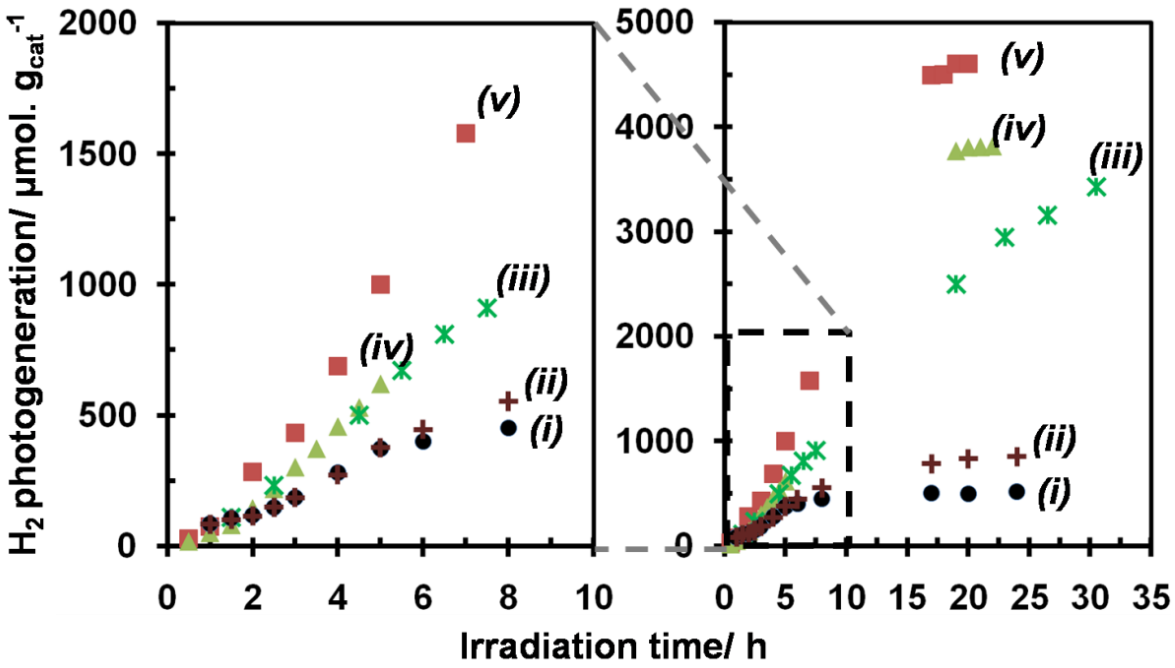

Figure S6: Hydrogen photogeneration from methanol/H_2O solution (v/v 2/8) using Cu_2O nanoparticles (i), mixture of Cu_2O nanoparticles and rGO (25/1 wt/wt) (ii), and Cu_2O/rGO(x) composites photocatalysts (x=50 (iii), 15 (iv), 25 (v)).

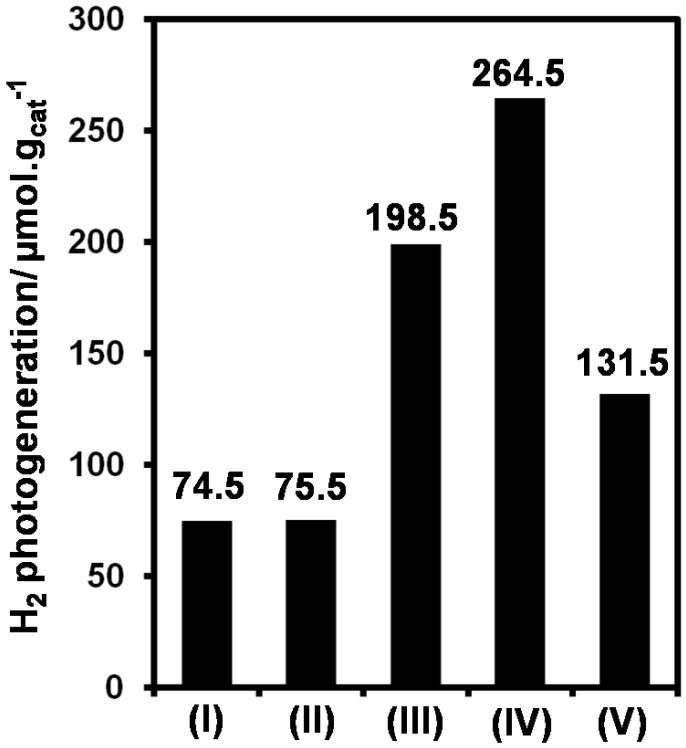

Figure S7: Hydrogen production rate for different Cu_2O based photocatalysts. (**I**): Pristine Cu_2O; (**II**): mixture of Cu_2O nanoparticles and rGO (25/1 wt/wt); (**III**): Cu_2O/rGO(15) composite; (**IV**): Cu_2O/rGO(25) composite; and (**V**) Cu_2O/rGO(50) composite.