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Supplementary Information for

Photocatalytic Semi-Hydrogenation of Acetylene to Ethylene in Water Powered by a Copper-loaded Hydrogen-Bonded Organic Framework

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Materials and Methods

Safety Warning

Acetylene is an extremely flammable gas. Buildup of acetylene vapors can result in fire or explosions if triggered by sparks. Acetylene may displace oxygen and cause rapid suffocation. In our experimental setup, the acetylene cylinder was fitted with a CGA 510 regulator equipped with a flashback arrestor and connected, through stainless steel tubing and a flow regulator, to a purging station that was placed inside a fume hood.[1] A Snoop® solution was applied to fittings and joints to inspect for leaks, until no bubble formation was observed. There was no electrical equipment in the fume hood.

Materials

1,3,6,8-tetrakis(*p*-benzoic acid)pyrene (H_4TBAPy, BLDpharm, 97%), ethanol absolute (EtOH, VWR, >98%), copper nitrate trihydrate ($Cu(NO_3)_2{\cdot}3H_2O$, Sigma-Aldrich, 99%), dimethylformamide (DMF, Honeywell, ≥99.8%), acetonitrile (ACN, Sigma-Aldrich, anhydrous 99.8%), methanol (MeOH, VWR, gradient grade), acetone (Fisher Scientific, laboratory reagent grade ≥99%), (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO, Sigma-Aldrich, 99%), Vulcan XC-72–50 grams (bottle) (FUELCELL store, SKU: 16080001), tetrabutylammonium hexafluorophosphate ($TBAPF_6$, TCI, >98.9%), ascorbic acid (HAsc, VWR, >99%), sodium ascorbate (NaAsc, Sigma-Aldrich, ≥98.0%) and D_2O (Sigma-Aldrich, 99.9% atom D) were used as received.

Ultrapure water (MilliQ, >18.3 MΩ cm) was obtained using a PURELAB® flex 4system.

Synthesis of HOF-H_4TBAPy

Preparation of the H_4TBAPy framework was based on a published methodology.[2] 500.0 mg of H_4TBAPy were placed in a 100 mL heat-dried flask and then dissolved in 75.0 mL of dry DMF with the aid of an ultrasound bath (20 min). The obtained solution was filtrated with PTFE syringe filters (0.45 μm, 25 mm⌀) and placed in a 1L heat-dried flask. 600.0 mL of EtOH (99.8%) were added dropwise to the filtrated and now clear solution to obtain slow crystal growth. The suspension was let stirring at 700 rpm for 68 h. The crystalline powder was collected by vacuum filtration on a polypropylene (PP) filter (0.6 μm, 47 mm⌀), washed with Milli-Q water (3×20.0 mL) and acetone (synthetic grade, 3×20.0 mL). The obtained product was soaked in 600.0 mL of acetone for 72 h, vacuum filtrated on a polypropylene (PP) filter (0.6 μm, 47 mm⌀) and dried in oven at 60 °C for 24 h (251.0 mg, yield 50.2%).

Synthesis of Cu@HOF

Preparation of the Cu@HOF was based on a published methodology.[3] 230.2 mg of HOF-H_4TBAPy were dispersed in 90.0 mL of methanol with the aid of ultrasound bath (10 min). Then, the suspension was stirred at 600 rpm and 4.8 mL of a 0.1 M aqueous solution of $Cu(NO_3)_2{\cdot}3H_2O$ were added dropwise. The obtained green suspension was let stirring for 21 h. The final material was collected by vacuum filtration on a PP filter (0.6 μm, 47 mm⌀), washed with methanol (3×20.0 mL) and dried in oven at 60 °C for 24 h to obtain a yellow-green solid (223.4 mg).

Photocatalytic Reactions

The experiments were performed as follows: samples were prepared in a 9.0 mL screw cap vial equipped with a micro stir bar and closed with silicone/PTFE septum. Vials were sealed and purged for 10 minutes with Ar, followed by 5 minutes of C_2H_2 (≥ 99.5 vol.%) or C_2H_2/C_2H_4 mixture (1 vol.% C_2H_2, 30 vol.% C_2H_4, N_2 balance) by using steel needles as inlet (inserted through the cap inside the solution) and outlet (inside the headspace). The pressure of C_2H_2 (or C_2H_2/C_2H_4) in the headspace was then equilibrated to 1 atm. The vials were then illuminated using a homebuilt photoreactor made of royal blue (450 nm) LEDs (Cree XLamp XP−E2 Color High Power LED Star, LEDsupply.com) with a light intensity of 140 $mW·cm^{-2}$ (measured using an Optical Power Meter PM100D with Optical Sensor S120VC from Thorlabs). Each vial was suspended on top of a single LED, equipped with lens, using a homebuilt sample holder, and was continuously stirred at 500 rpm during the irradiation. After illumination the products were analyzed with a GC−TCD−FID equipped with an autosampler. For the experiments at different wavelengths, the homebuilt photoreactors were made of U60 (400−410 nm) LEDs (Ultraviolet (UV−A) High Power LED Star, LEDsupply.com) and blue (465−485 nm) LEDs (Cree Xlamp XP−E2 Color 49 High Power LED Star, LEDsupply.com) with a light intensity of 140 $mW·cm^{-2}$ (measured using an Optical Power Meter PM100D with Optical Sensor S120VC from Thorlabs).

Cu@HOF Recovery and Reuse

After the photocatalytic run, the Cu@HOF catalyst was recovered by centrifugation at 10,000 rpm for 10 minutes. The supernatant was carefully removed, and the resulting solid was washed with acetone (3 × 5.0 mL) to eliminate residual reactants and by-products. This washing step also serves to reactivate the porous structure of the HOF. The recovered solid was then dried overnight at 60 °C prior to its reuse in subsequent photocatalytic experiments.

Chromatographic Detection of Gases

GC−MS experiments were performed on an Agilent Technologies 7890A GC system coupled with a 5975C VL MSD with Triple−Axis Detector. The GC was equipped with a HPPLOT Q column, the inlet temperature was 200 °C, the He carrier gas flow was 1 $mL·min^{-1}$ at a pressure of 4.1 psi. For the detection of ethylene, acetylene, and ethane the oven temperature was kept at 110 °C for 6.50 min, and then heated to 250 °C using a 15 $°C·min^{-1}$ ramp (total run time 18.8 min). Headspace samples were manually injected using gas−tight Hamilton syringes (100 μL). GC experiments were performed on an Agilent Technologies 8860 GC system coupled with flame ionization detector (FID) and a thermal conductivity (TCD) detector. The system was equipped with a HP−PLOT U and a MS−5A column, Ar carrier gas flow was 6 $mL·min^{-1}$ at a constant pressure of 11.121 psi, the FID and TCD detectors were kept at 250 °C. For the detection of ethylene, acetylene, and ethane the oven temperature was kept at 40 °C for 5 min, then heated to 110 °C using a 20 $°C·min^{-1}$ ramp, and kept at 110 °C for 9 min (total run time 17.5 min). Headspace samples were injected using PAL3 series 2 Autosampler Systems equipped with a gas−tight syringe (SGE autosampler syringe) injecting 100 μL.

Calibration curves for C_2H_4, C_2H_2, C_2H_6 and H_2 were collected by injecting known quantities of gas mixture standards containing C_2H_4 (99.95 vol.% or 2.5 vol.% or 30 vol.%), C_2H_2 (2.5 vol.% or 1 vol.%), C_2H_6 (2.5 vol.%), or H_2 (99.95 vol.% or 2.5 vol.%). All calibration curves are reported in Figure S6. Injections were performed either using gas−tight Hamilton syringes (10−100 μL) or using PAL3 series 2 Autosampler Systems equipped with a gas−tight syringe (SGE autosampler syringe) injecting 100 μL. Calibration injections were performed at least in triplicate.

The selectivity for C_2H_4 ($S_{C_2H_4}$) was calculated as follows:

$$S_{C_2H_4}(\%) = \frac{mol\ C_2H_4}{mol\ C_2H_4 + mol\ C_2H_6} \times 100$$

$$S_{C_2H_4}(\%) = \frac{mol\ C_2H_4}{mol\ C_2H_4 + mol\ C_2H_6 + mol\ H_2} \times 100$$

C_2H_2 conversion ($C_{C_2H_2}$) and selectivity for ethylene ($S_{C_2H_4}$) for the photoreduction of the C_2H_4/C_2H_2 mixture were calculated as follows:

$$C_{C_2H_2}(\%) = \frac{[C_2H_2]_{feed} - [C_2H_2]_x}{[C_2H_2]_{feed}} \times 100$$

$$S_{C_2H_4}(\%) = \frac{[C_2H_2]_{feed} - [C_2H_2]_x}{[C_2H_2]_{feed} - [C_2H_2]_x + [C_2H_6]} \times 100$$

Where $[C_2H_2]_{feed}$ represents the quantity of acetylene in the feed (corresponding to 1.2×10^4 ppm) and $[C_2H_2]_x$ and $[C_2H_6]$ represent the quantity of acetylene and ethane in the product.

Absorption Spectroscopy

UV−Vis absorption spectra were recorded on a Shimadzu UV−2600i equipped with an ISR−2600Plus integrating sphere. Ultrafine $BaSO_4$ powder was used as a reference. The powders of the samples were placed in the holder up to ca. 3 cm diameter and 5 mm depth. The Kubelka−Munk function was applied to all spectra.

Powder X−Ray Diffraction (PXRD)

PXRD measurements were collected on a Bruker D8 Advance instrument operating with a Cu K_α ($\lambda = 1.54$ Å) radiation source generated at 40 kV and 40 mA. Samples were prepared by packing the materials powder into metallic flat disc transmission holders.

X−Ray Photoelectron Spectroscopy (XPS)

XPS analyses were performed using a Thermo Scientific ESCALAB QXi spectrometer with a monochromatized Mg K_α source (hν = 1253.6 eV). High resolution XPS spectra were obtained using a 50 eV pass energy and 0.1 eV steps. The XPS spectra were analyzed using the XPSPeak4.1 software and Origin 2025b.

Transmission Electron Microscopy (TEM)

TEM images were acquired using TEM JEOL F_{200} equipped with a cold−FE source. Samples powder was dispersed in acetone and drop-casted on Au grids, 400 mesh size.

Inductively Coupled Plasma Mass Spectrometry (ICP−MS)

The ICP−MS measurements were performed on an Agilent 7700x ICP−MS (Agilent Technologies International Japan, Ltd., Tokyo, Japan). The instrument features an octupole collision cell operating in kinetic energy discrimination mode, effectively removing polyatomic and argon−based interferences. For each sample, 1.5 mg of HOF was digested with 0.75 g of HNO_3 (63%) in a 15 mL

Falcon tube. After heating at 100 °C for 2 h, MilliQ water was added to reach a final weight of 14 g, and the resulting solution was filtered.
For the supernatant, 2.0 g of the supernatant was added to 0.75 g of HNO_3 (63%), followed by MilliQ water to reach a final weight of 14 g. The solution was then filtered.

Electron Paramagnetic Resonance (EPR)

Electron paramagnetic spectroscopy was performed using a Bruker Magnettech ESR5000, under dark or in situ irradiation with 450 nm LED: 9.49 Hz, 332-339 mT, 300 s sweep time, 0.2 mT amplitude modulation. The powders were transferred to an EPR tube (4 mm) and the spectra were collected at 77 K with liquid N_2.

Infrared Spectroscopy

FT-IR absorption spectra were carried out using a FT−IR NICOLET, model Nexus 670 spectrophotometer, at nominal resolution of 2 cm^{-1}, averaging 20 scans. Measurements were collected using an ATR accessory.

Electrochemical Characterization

Cyclic voltammetry (CV) was performed on a Pine Research Wavenow-xv potentiostat at room temperature, employing a three-electrodes cell: glassy carbon electrode (GCE, CH instruments, d = 3 mm) as working electrode, an Pt wire as counter electrode and an Ag wire as pseudoreference electrode. Working electrode was polished on a felt pad with 0.1, 0.3 and 0.05 µm Al_2O_3 suspensions. The counter and reference electrodes were polished on a sandpaper sheet. A blank scan was recorded before each sample (scan rate = 100 $mV \cdot s^{-1}$). The working electrode was prepared by suspending 1.5 mg of Cu@HOF and 1.5 mg of VulcanXC72 in a MeOH:MilliQ water (3:1) 600 µL solution together with 60 µL of Nafion® solution (5% w/w) and depositing the so prepared ink on the GCE. $TBAPF_6$ (0.1 M) was used as supporting electrolyte and the cell environment was purged for 15 minutes with N_2 before recording the CV.

Supplementary Figures

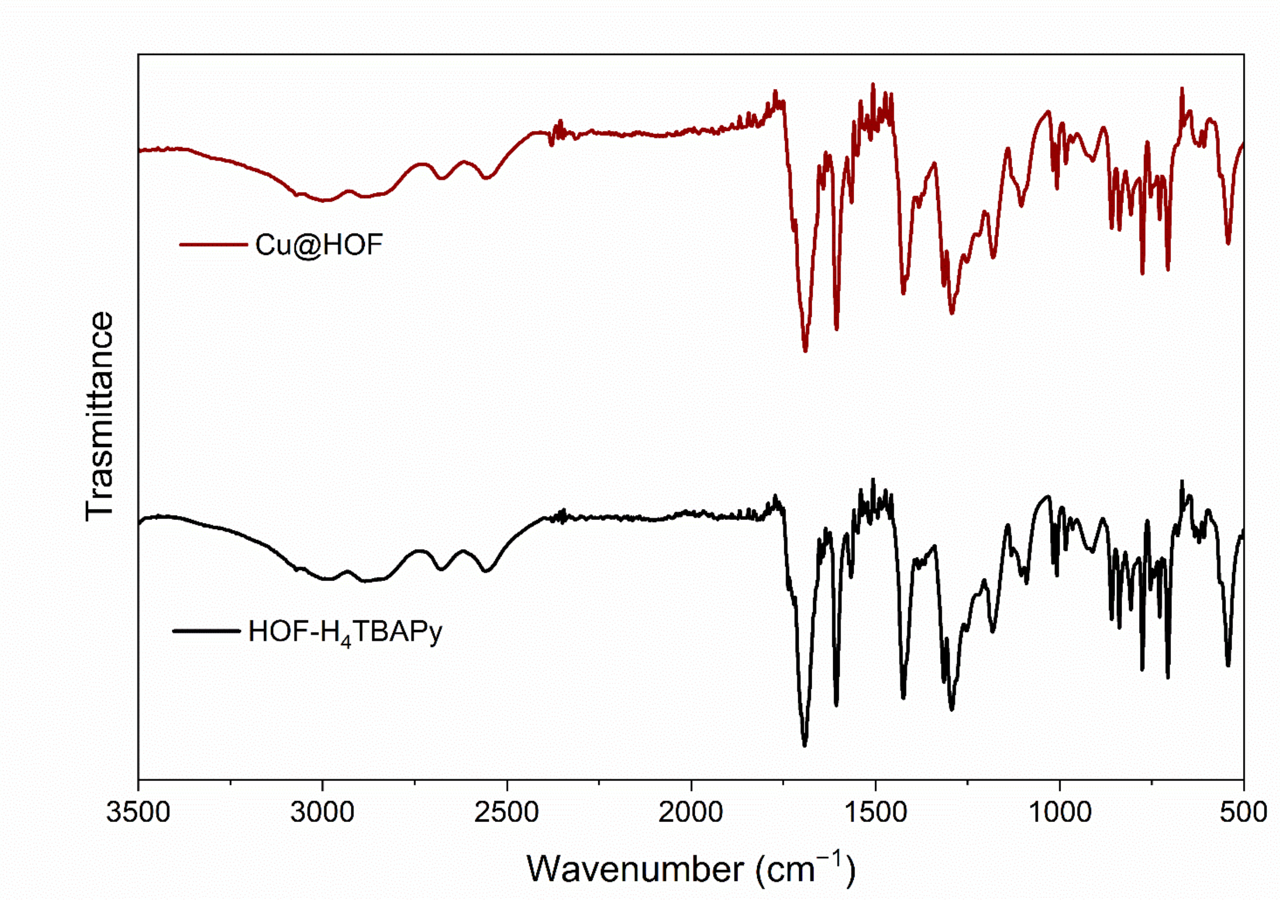

Figure S1. ATR-FTIR spectra of Cu@HOF (red) and HOF-H_4TBAPy (black).

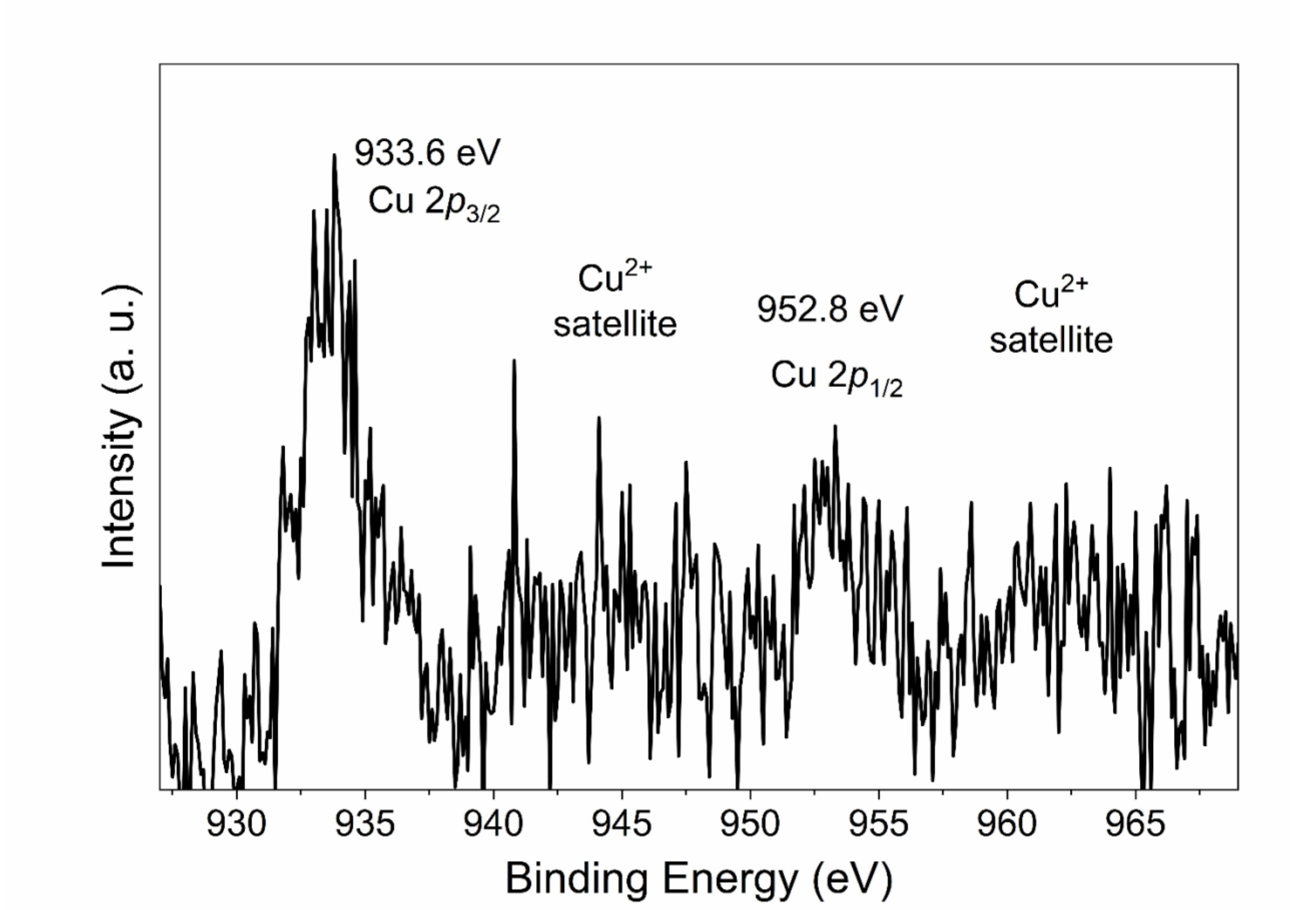

Figure S2. XPS spectrum of Cu@HOF (Cu 2*p*).

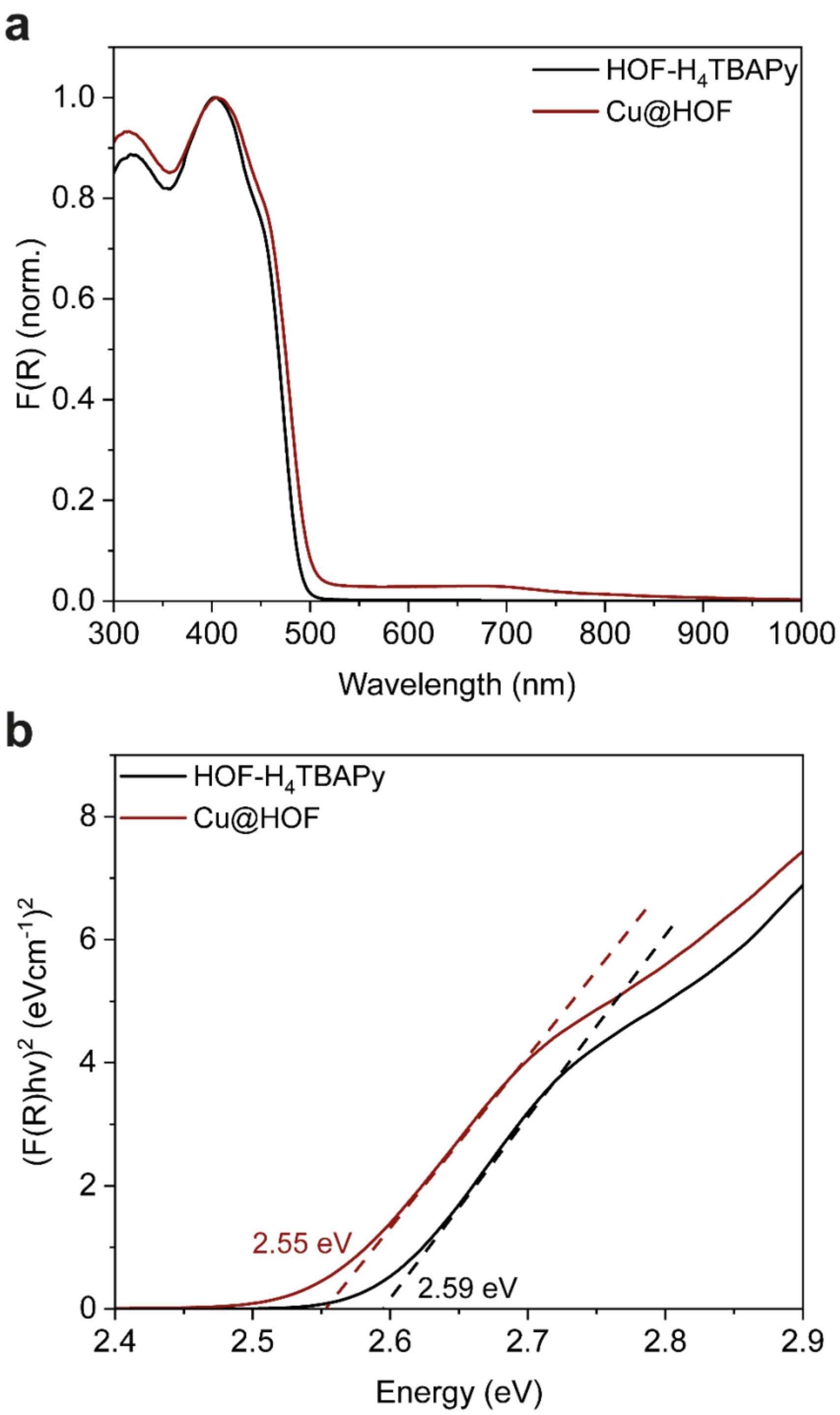

Figure S3. (a) (DR)UV–vis spectra and (b) Tauc plots of Cu@HOF (red) and HOF-H_4TBAPY (black).

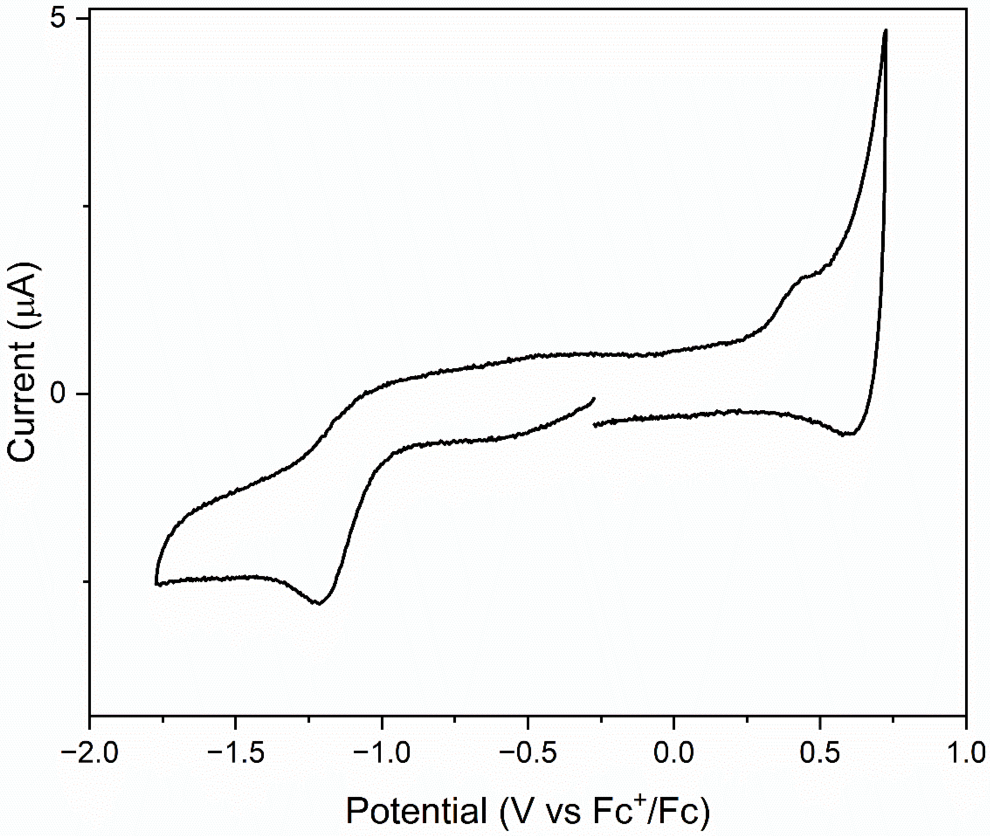

Figure S4. Cyclic voltammetry of Cu@HOF. The first reduction potential was determined to be –1.15 V vs Fc^+/Fc.

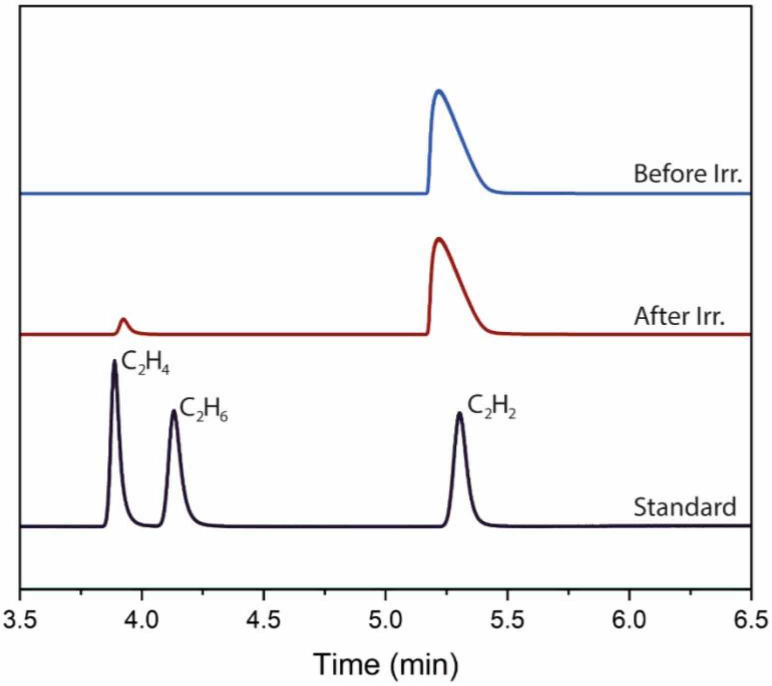

Figure S5. Typical gas chromatograms observed for the photoreduction of acetylene (retention time of C_2H_4, C_2H_6, and C_2H_2) detected with flame ion detection of a gas standard mixture (black) containing C_2H_4 (2.5 vol.%), C_2H_6 (2.5 vol.%) and C_2H_2 (2.5 vol.%) and the optimized system under C_2H_2 before (blue) and after (red) irradiation (450 nm, 140 $mW \cdot cm^{-2}$) for 4 h. The optimized system contained 1.00 ± 0.05 mg of Cu@HOF and 0.25 M ascorbic acid in pure water at pH = 4.0 ± 0.1.

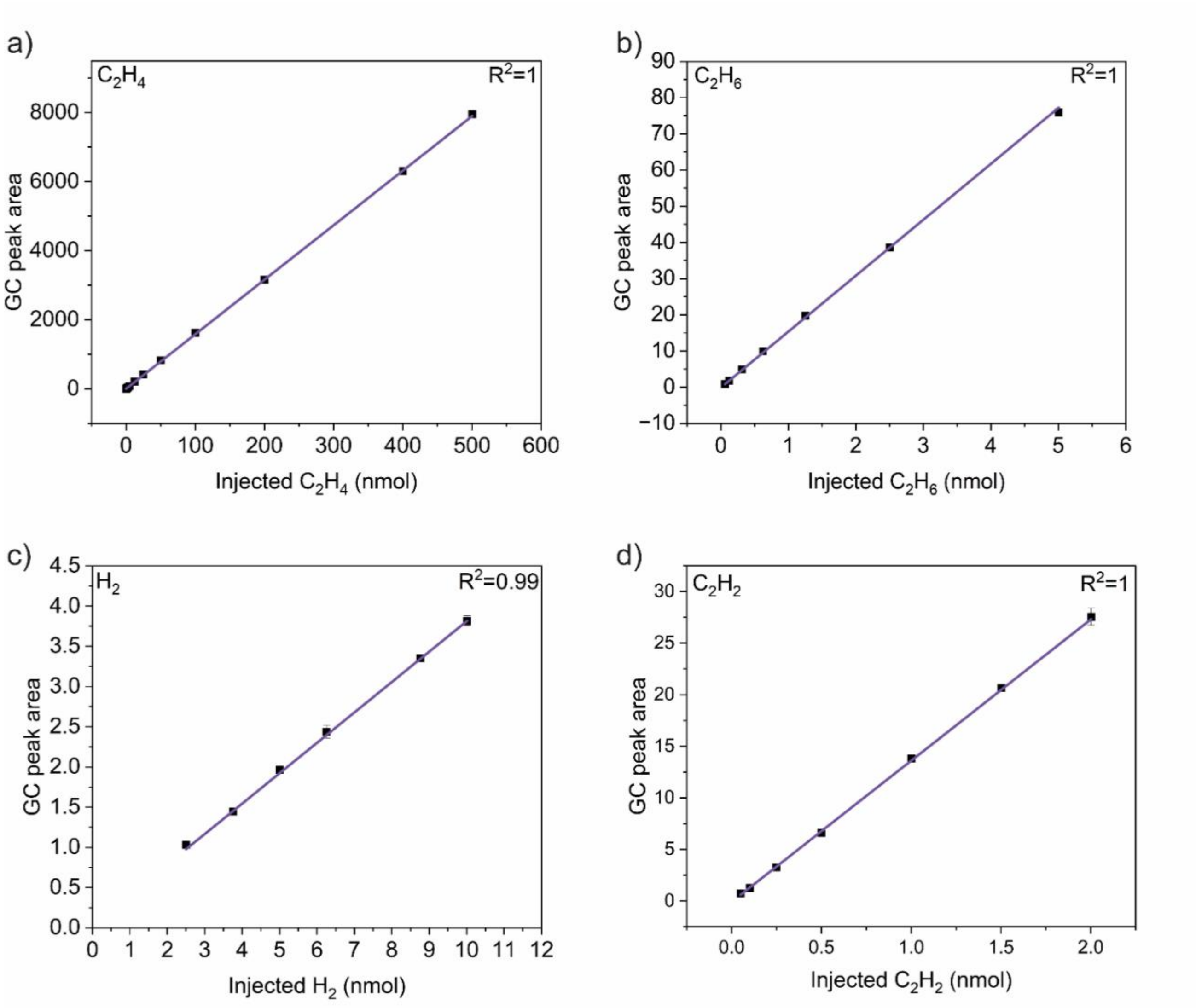

Figure S6. Calibration curves for quantification of gaseous products of the photoreduction of acetylene using GC-FID. (a) Calibration curve for C_2H_4 with the corresponding coefficient of linear correlation (R^2). (b) Calibration curve for C_2H_6 with the corresponding coefficient of linear correlation (R^2). (c) Calibration curve for H_2 with the corresponding coefficient of linear correlation (R^2). (d) Calibration curve for C_2H_2 with the corresponding coefficient of linear correlation (R^2). Error bars are calculated from three to four runs; uncertainty is $\leq$10%.

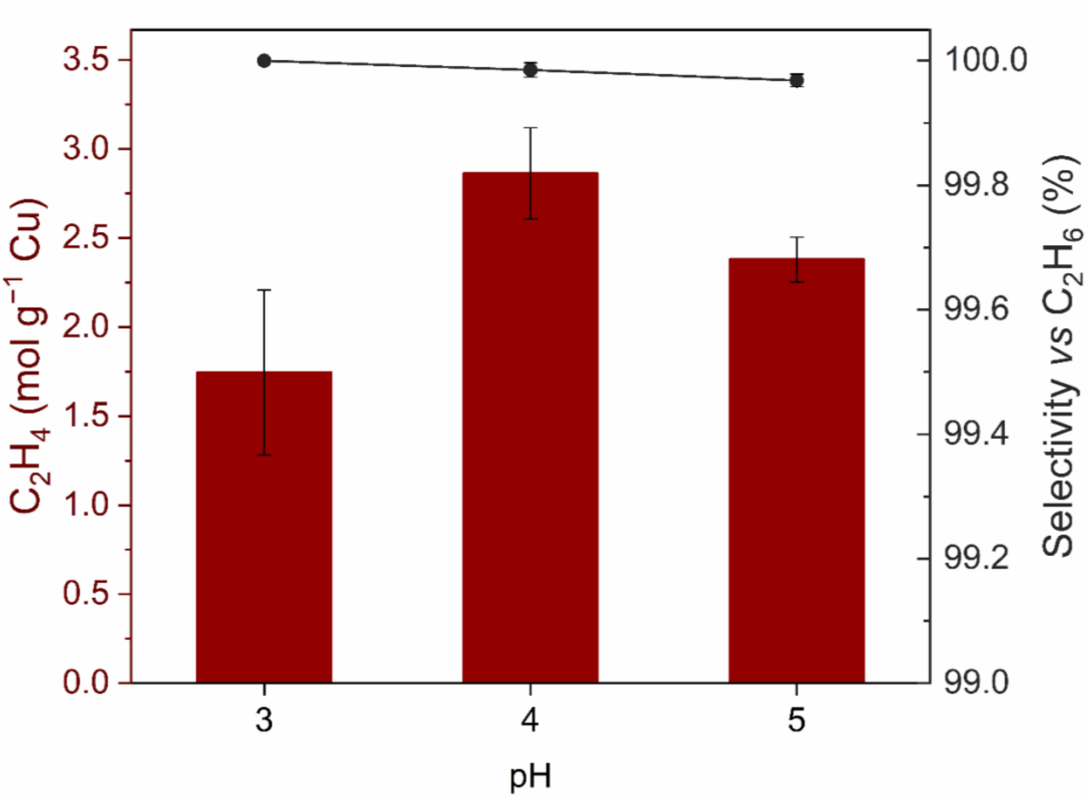

Figure S7. Photocatalytic ethylene production (left axis, red bar) and ethylene selectivity over ethane (right axis, black dots) through variation of pH. Amount of C_2H_4 produced through variation of pH in the presence of Cu@HOF (1.00 ± 0.05 mg) and ascorbic acid (HAsc, 0.1 M) in pure water under C_2H_2 (≥99.5 vol.%) after irradiation with 450 nm light (140 mW·cm^{-2}) for 4 h. Error bars are calculated from two to three runs, uncertainty is ≤10%.

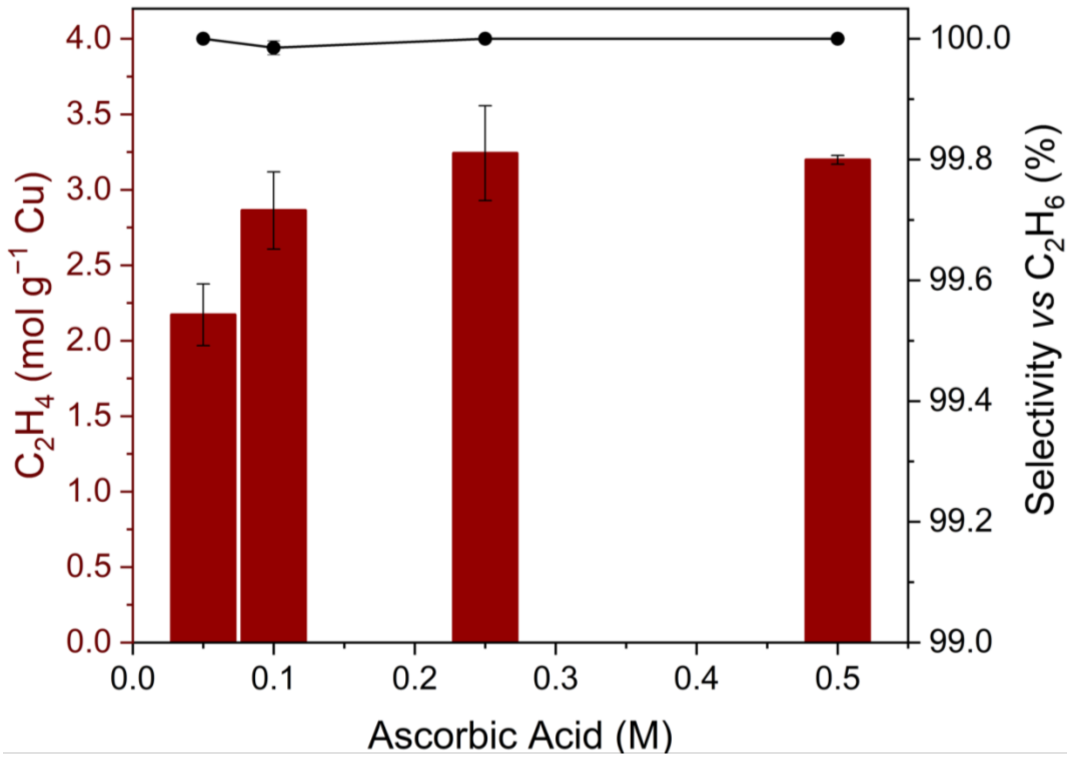

Figure S8. Photocatalytic ethylene production (left axis, red bar) and ethylene selectivity over ethane (right axis, black dots) through variation of ascorbic acid (HAsc) concentration. Amount of C_2H_4 produced through variation of [HAsc] in the presence of Cu@HOF (1.00 ± 0.05 mg) in pure water (pH = 4.0 ± 0.1) under C_2H_2 (≥99.5 vol.%) after irradiation with 450 nm light (140 mW·cm^{-2}) for 4 h. Error bars are calculated from two to three runs, uncertainty is ≤10%.

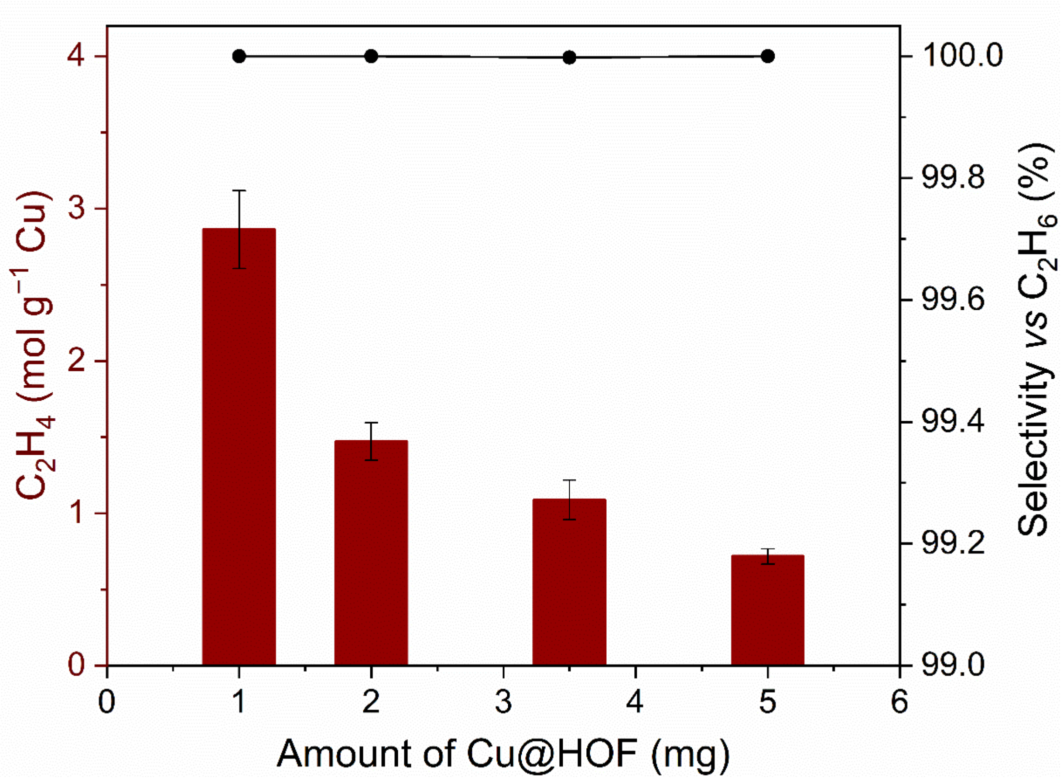

Figure S9. Photocatalytic ethylene production (left axis, red bar) and ethylene selectivity over ethane (right axis, black dots) through variation of Cu@HOF amount. Amount of C_2H_4 produced through variation of Cu@HOF in the presence of ascorbic acid (HAsc, 0.25 M) in water (pH = 4.0 ± 0.1) under C_2H_2 (≥99.5 vol.%) after irradiation with 450 nm light (140 mW·cm^{-2}) for 4 h. Error bars are calculated from two to three runs, uncertainty is ≤10%.

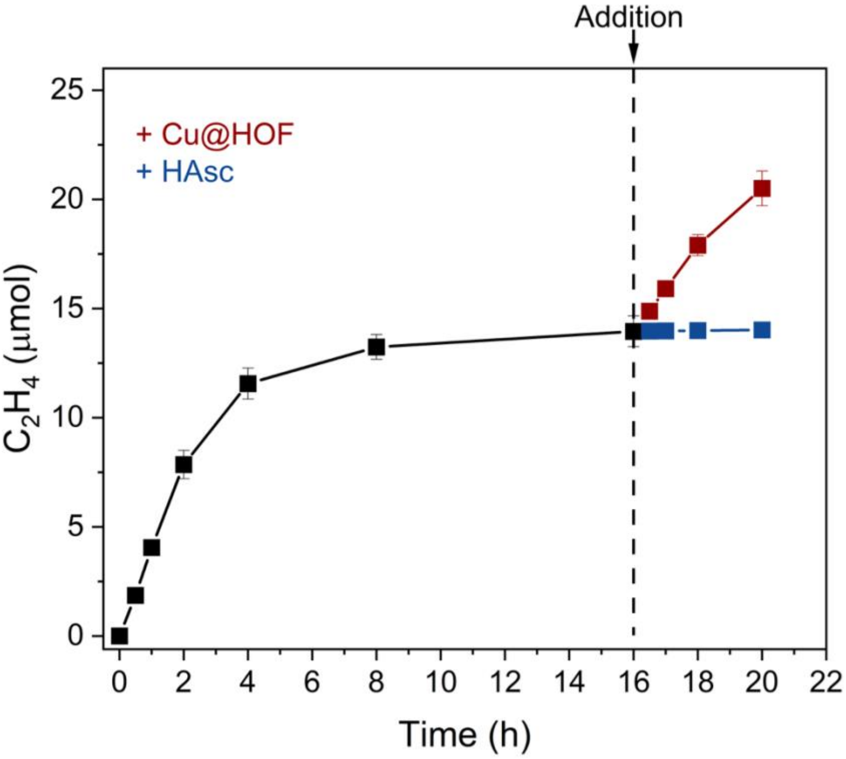

Figure S10. Re-addition experiments showing recovery of C_2H_4 production. Amount of C_2H_4 produced in the presence of ascorbic acid (HAsc, 0.25 M) in water (pH = 4.0 ± 0.1) under C_2H_2 (≥99.5 vol.%) after irradiation with 450 nm light (140 mW·cm^{-2}) as a function of irradiation time upon re-addition of 1.00 ± 0.05 mg Cu@HOF (red) and 0.25M HAsc (blue). Error bars indicate standard error of the mean, calculated from two to three runs.

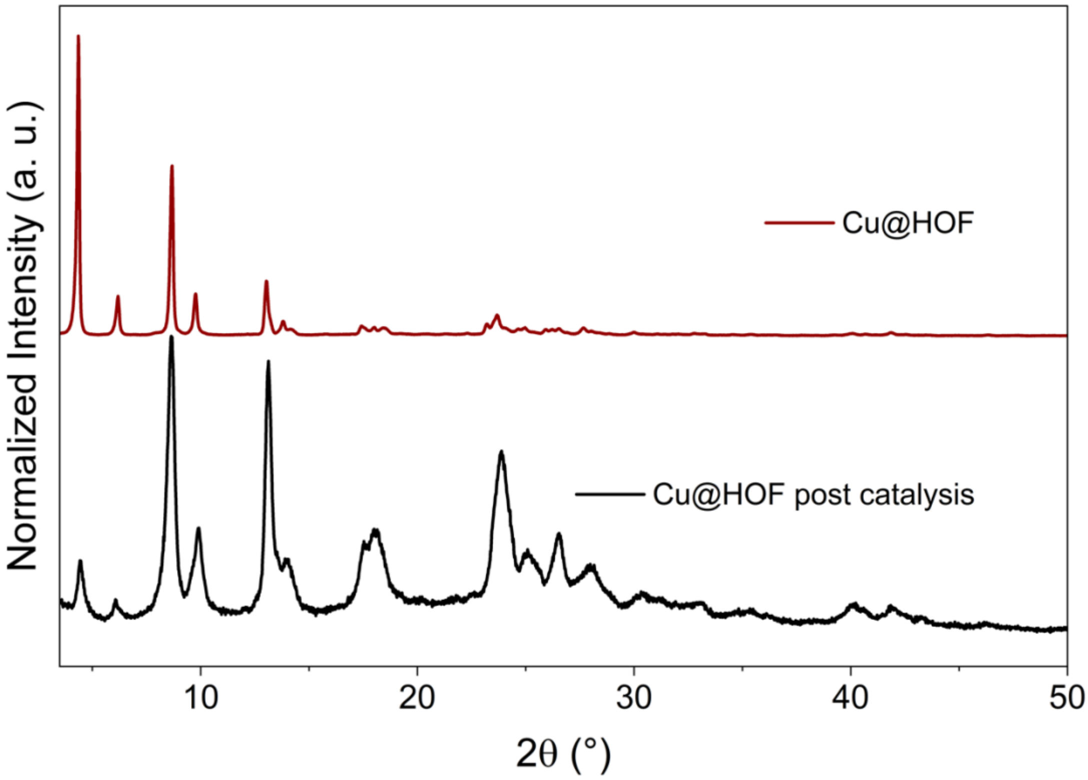

Figure S11. PXRD patterns of Cu@HOF (red) and Cu@HOF powder collected from catalytic mixture after 4 h of photocatalysis (black).

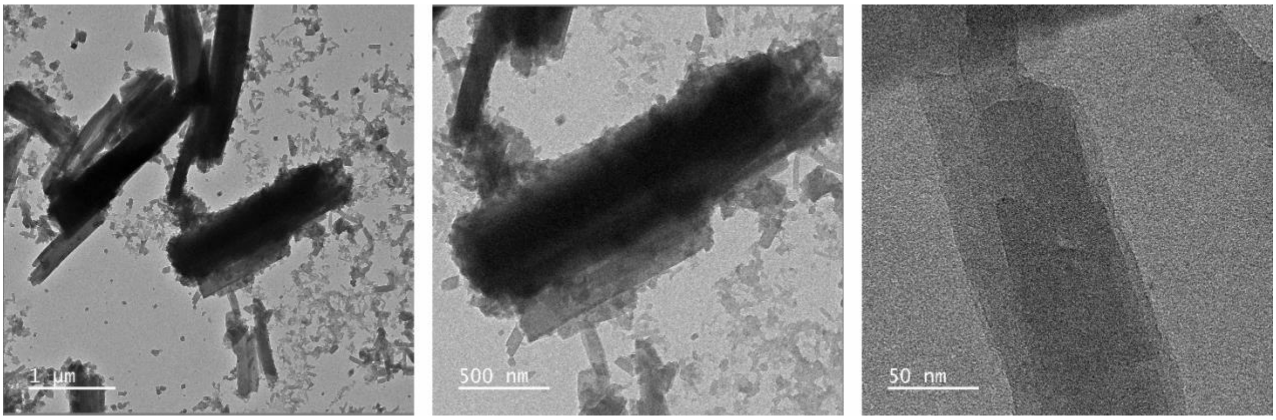

Figure S12. TEM images of Cu@HOF post-catalysis at three different magnifications.

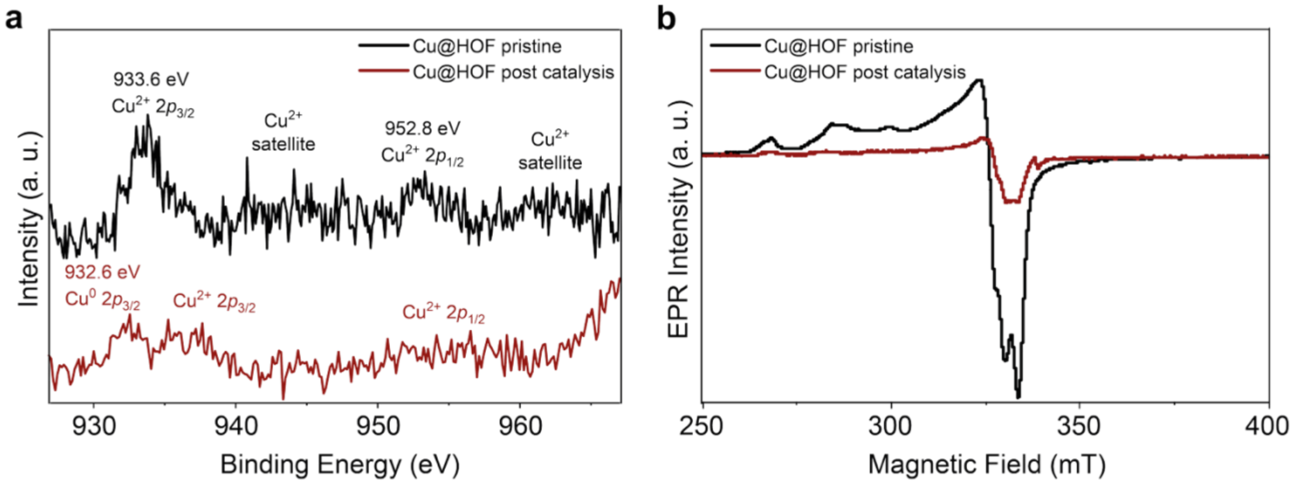

Figure S13. (a) XPS and (b) EPR spectra of Cu@HOF after 4 h of photocatalysis showing (a) partial reduction of Cu^{2+} to Cu^0 species, evidenced by (b) attenuation of the Cu^{2+} signal.

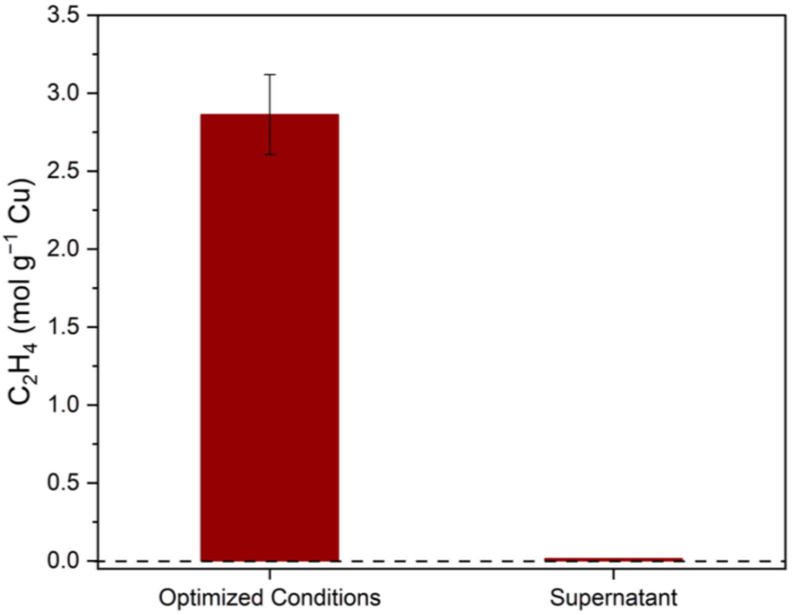

Figure S14. Photocatalytic ethylene production by the Cu@HOF system and the supernatant recovered after the reaction. The samples for the initial reaction contain Cu@HOF (1.00 ± 0.05 mg) and ascorbic acid (HAsc, 0.1 M) in water (pH = 4.0 ± 0.1) under C_2H_2 (≥99.5 vol.%) and were irradiated with 450 nm light (140 mW·cm^{-2}) for 4 h. Error bars are calculated from two to three runs, uncertainty is ≤10%.

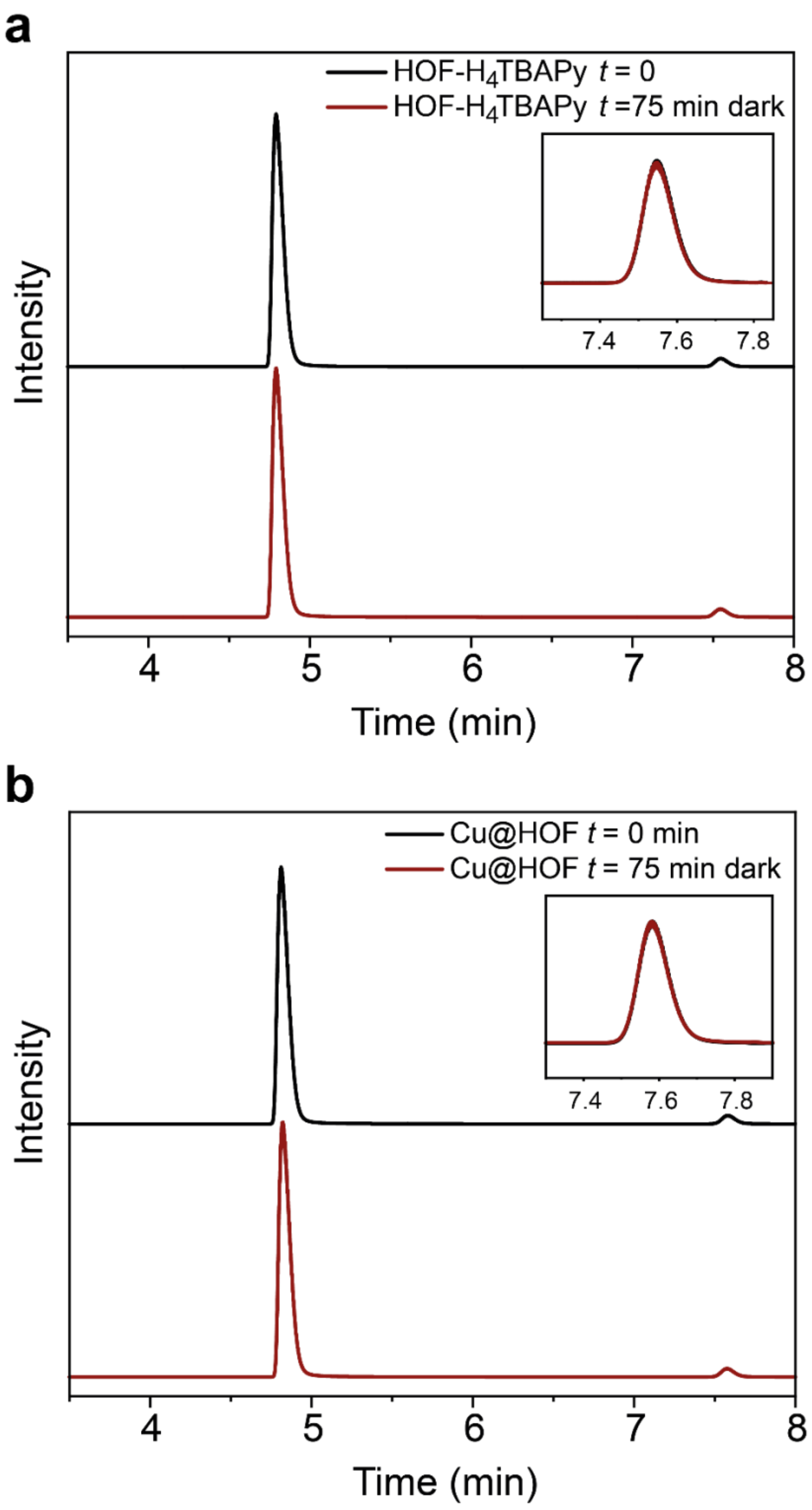

Figure S15. Typical GC-FID chromatograms of the control reactions for the photoreduction of the acetylene/ethylene mixture. Gas chromatograms of the HOF-H_4TBAPy (a) and Cu@HOF (b) system in pure water containing 1.00 ± 0.05 mg of Cu@HOF, 0.1 M HAsc (pH = 4.0 ± 0.1) under C_2H_2/C_2H_4 (1 vol.% C_2H_2, 30 vol.% C_2H_4, He balance) mixture before irradiation (time = 0, black) and after being kept in the dark for 75 min (red).

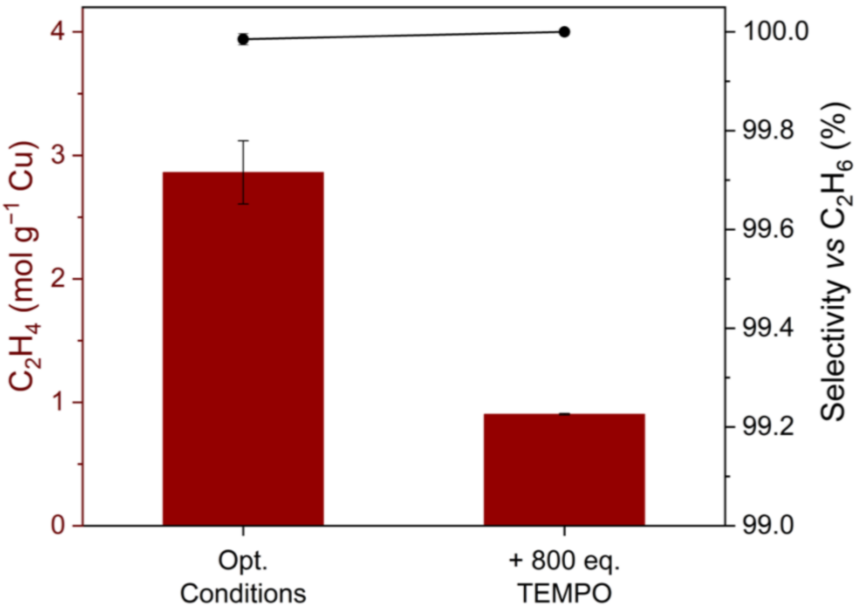

Figure S16. Comparison of the photocatalytic ethylene production in 4 h irradiation (450 nm, 140 mW·cm^{-2}) by the Cu@HOF under the optimized conditions or in the presence of 800 equiv. of TEMPO vs Cu. The optimized system contains Cu@HOF (1.00 ± 0.05 mg) and ascorbic acid (HAsc, 0.1 M) in water (pH = 4.0 ± 0.1). Error bars are calculated from two to three runs, uncertainty is ≤10%.

Supplementary Tables

Table S1. ICP quantification.

Sample	Cu (% w/w)
Cu@HOF	0.45 ± 0.02
Cu@HOF after 16 h of photocatalysis	0.37 ± 0.03

Table S2. Comparison of catalytic performance with heterogeneous photocatalytic systems for reduction of C_2H_2 to C_2H_4 in batch.

Photocat. Mixture†	C_2H_4 production under pure C_2H_2	Sel$_{C2H4}$	Longevity‡	Time for C_2H_2 reduction in C_2H_4 co-feed	Sel$_{C2H4}$ under C_2H_4 co-feed	Recyclability	Reference
Co-PCN-222 MOF (Cat.) $[Ru(bpy)_3]^{2+}$ (PS) TEOA (SD and PD) CH_3CN	1.60 mol g^{-1} Co	99.7%	168 h	87 h	99.9%	5 cycles	*ACS Energy Lett.* **2023**, *8*, *11*, 4684-4693
Cu-Co-MNSs MOF (Cat.) $[Ru(bpy)_3]^{2+}$ (PS) NaAsc (SD) Bicarbonate buffer H_2O (PD)	3.61 mmol g^{-1} Co	99.5%	12 h	68 h	90.3%	n.r.	*Chem. Eur. J.* **2024**, *30*, e202302816
ZrCo-MOF (Cat.) $[Ru(bpy)_3]^{2+}$ (PS) BIH (SD) TFE (PD) CH_3CN	698 mmol g^{-1} Co	99.9%	n.r.	4 h	99.9%	6 cycles*	*Adv. Mater.* **2025**, *37*, 2408658
Cz-Co-COF-H (Cat.) $[Ru(bpy)_3]^{2+}$ (PS) NaAsc (SD) H_2O (PD)	1.755 mmol g^{-1} Co h^{-1}	99.9%	12 h	96 h	Traces of C_2H_6	5 cycles	*Angew. Chem. Int. Ed.* **2025**, *64*, e202423091
Co-CN (Cat. and PS) TEOA (SD) H_2O (PD)	390 mmol g^{-1}Co	99.9%	960 h	n.r.	n.r.	5 cycles	*Small Methods*, **2025**, *10*, 2500527
CoO_4-MOF (Cat.) $[Ru(bpy)_3]^{2+}$ (PS) TEA (SD) H_2O/CH_3CN	852.68 µmol g^{-1} h^{-1}	n.r.	14 h	n.r.	n.r.	6 cycles	*Angew. Chem. Int. Ed.* **2025**, *65*, e22056
Pd/TiO_2 (Cat. And PS) MeOH 10% H_2O	4.47 mmol g^{-1} h^{-1}	77.35%	n.r.	n.r.	n.r.	n.r.	*Small* **2025**, *21*, 2503604
C_3N_4-OH/$Ni(OH)_2$ (Cat. and PS) TEOA (SD) H_2O	15.7 mmol g^{-1} h^{-1}	98.2%	n.r.	2 h	n.r.	5 cycles	*Angew. Chem. Int. Ed.* **2026**, *65*, e24752

Cu@HOF (Cat. and PS) **HAsc (SD)** **H_2O (PD)**	**3.01 mol g^{-1} Cu**	**99.9%**	**16 h**	**75 min**	**99.8%**	**4 cycles**	**This work**

[†]Cat. = (heterogeneous) catalyst; PS = photosensitizer; SD = sacrificial donor; PD = proton donor. [‡]Saturation of ethylene production under pure acetylene conditions. [*]Recyclability tested under industrial mixture conditions. n.r. = not reported.

Supplementary References

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