Photocatalytic Activity of 2D Copper Porphyrin Metal-Organic Framework for Visible Light Overall Water

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Experimental section

2D Cu_2(CuTCPP) synthesis: 185 mg of $Cu(NO_3)_2 \cdot 3H_2O$ (Merck) and 200 mg of the metal-free porphyrin (H_2TCPP; Frontier Specialty Chemical) were dissolved together in 450 ml of DMF in a 500 mL round flask. Then, the obtained solution was sonicated for 10 minutes and, subsequently, the temperature of the solution was increased up to 85°C, and held for 24 h under vigorous stirring and reflux. The resulting purple solids were recovered by filtration and profusely washed with DMF and ethanol. Finally, the 2D MOF was further purified with methanol in a Soxhlet extractor and dried in vacuum at 150°C overnight.

Characterization

PXRD patterns were acquired with a Shimadzu XRD-7000 diffractometer employing a Cu k_a irradiation source (λ=1.5418 Å) operating at 40 kw and 40 mA. All data acquisition was done at a scanning speed of 10 °/min in the 2θ range 2-90 °. The chemical composition of all samples was determined via combustion chemical analysis employing a CHNS FISONS elemental analyzer. DR UV-VIS spectra were acquired using a Varian Cary 5000 spectrophotometer in the range 200-800 nm. ATR-FTIR spectra were acquired with a Bruker Tensor 27 instrument equipped with a diamond ATR accessory. XPS analyses were recorded through a SPECS spectrometer equipped with a Phoibos 150 MCD-9 detector. The nonmonochromatic X-ray source composed of Al and Mg was operated at 200 W. Before data acquisition, the samples were evacuated at 10^{-9} mbar in the spectrometer prechamber. The measured intensity ratios of the components were obtained from the area of the corresponding peaks after nonlinear Shirley-type background subtraction and corrected by the transition function of the spectrometer. FESEM images were acquired using a ZEISS GeminiSEM 500 electron microscope. The samples were applied directly on the support and subsequently investigated. TEM images were recorded via a JEOL JEM 2100F microscope operating under an accelerating voltage of 200 kV. The samples were uniformly dispersed in an

ethanol solution and subsequently dropped casted on carbon coated Ni TEM grids which were allowed to dry at room temperature. AFM measurements were carried out in a Bruker Multimode 8 Nanoscope instrument with a vertical resolution of 3 Å and a horizontal resolution of 5 nm

Photocatalytic tests: Photocatalytic H_2 evolution, O_2 evolution and overal water splitting were investigated upon irradiation of 1 mg/mL solutions containing the photocatalysts, water and the corresponding sacrificial agent (MeOH for H_2 evolution and $Ce(NH_4)_2(NO_3)_6$ in the case of O_2 evolution), with a 150 W Xe Lamp (0.1 W/cm^2 intensity) filtered with a 450 nm cut-off filter. The reaction vessel is made of quartz and equipped with manometer. Prior photocatalytic reactions the suspensions were purged with Ar for 10 minutes and, eventually, the internal pressure assessed at 1 bar. Analysis of the evolved gases has been carried out through a micro-GC with two columns (Molsieve 5A and PorePlot Q) and TC detector that allowed us to monitor and quantify H_2, O_2, CO_2, among other gases.

Electrochemical characterization: All photoelectrodes employed were prepared by drop-casting a dispersion of the CuTCPP MOF, ethanol and nafion binder onto FTO glass, which was subsequently left to dry at room temperature. All electrochemical experiments employed a one-compartment cell with a Ag/AgCl reference electrode and a platinum counter electrode. The electrolyte employed was a 0.1M aqueous solution of KCl. All photoelectrochemical data was acquired via a VersaStat3 potentiostation. The light source employed for the photoelectrochemical experiments was a 150 W Xe lamp equipped with an optical fibre, and the spectral contribution was adjusted via a 450 nm cut-off filter. Nyquist plot measurements were carried out both under light irradiation and dark conditions. Points were acquired in the frequency range of 0.1 – 10^6 Hz. Mott-Schottky experiments were preformatted under 5 different frequencies (1500, 1750, 2000, 2250 and 2500 Hz), and datapoints were acquired between -1 and 1V (vs Ag/AgCl). Photo-action data was recorded by irradiating the cell with a 150 W Xe lamp source light passing through a triple grating monochromator from Optics Focus. The light intensities were recorded via a photodiode system from Hamamatsu.

External quantum efficiency values (EQE) were calculated employing the following formulas:

$$SR(\lambda) = \frac{I(\lambda)}{P(\lambda)} \text{ in } \textit{(A/W)}; \qquad EQE(\lambda)\% = \frac{1240 \cdot SR(\lambda)}{\lambda};$$

where SR(λ) is the spectral response, I(λ) is the photocurrent recorded by the system upon light irradiation, P(λ) is the power of incident irradiation at each wavelength and λ is the wavelength of the incident photons.

Table S1. Analytical data of the samples under study obtained from combustion elemental analysis and ICP-OES.

	C (wt.%)	H (wt.%)	N (wt.%)	O (wt.%)	Cu (wt.%)	Fe (wt.%)
Cu_2(CuTCPP)	57.9	2.8	6.4	16.9	16.0	-
Cu_2(FeTCPP)	-	-	-	-	9.2	3.9

Table S2. Summary of some reported examples of MOF-based photocatalysts for overall water splitting including the light source conditions, productivity and stability.

Photocatalysts	**Reaction conditions**	**Photocatalytic activity**	**Stability**	**Ref.**
Al-ATA-Ni	300W Xe lamp	66.7 μL/h H_2 and 33.3 μL/h O_2		[1]
Pt@NH_2-UiO-66@MnO_x	300+UV arc lamp with a UV-cut off filter (λ≥400 nm)	20 μmol/g·h H_2 10 μmol/g·h O_2	-	[2]
IEF-13	UV-vis 150 W Xe lamp	160 μmol/g H_2 46 μmol/g O_2	22h	[3]
Pt and RuO_x, MIL-125(Ti)-NH_2	300 W Xenon lamp	218 and 85 μmol/$g_{photocatalyst}$ at 24 h for H_2 and O_2, respectively	24h	[4]
IEF-11	simulated sunlight	672 μmol/$g_{catalyst}$ in 22 h of H_2	10 d	[5]
UiO-66(Zr/Ce/Ti)	xenon lamp (150 mW cm^{-2})	230 and 110 μmol/g of H_2 and O_2, respectively, upon UV light irradiation, and 210 and 70 μmol/g of H_2 and O_2, respectively, under visible light irradiation	24h	[6]
Liposome-MOF@Pt-porphyrin and Ir-bipyridine	400 nm + 450 nm LEDs	836 μmol g^{-1} of H_2 and stoichiometric amounts of O_2	72 h	[7]
MIL-125(Ti)-CoPi-Pt	Xe lamp (300 W) 1 mg/mL	42 μL/h H_2 and 21 μL/h O_2	-	[8]
Cu_2(CuTCPP)	LED (visible light) (λ> 450 nm)	120 μmol_{H2} $g_{catalyst}^{-1}$ h^{-1}	5 consecutive uses	This report

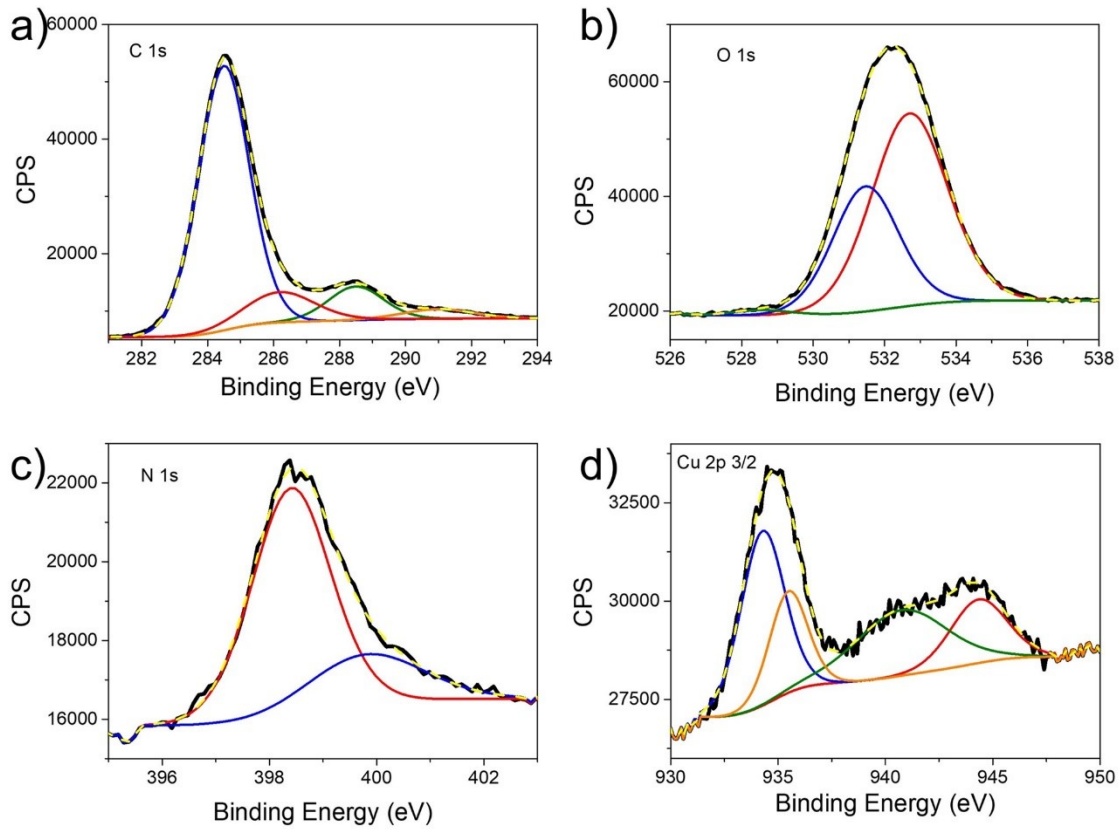

Figure S1. High-resolution XPS spectra and their best deconvolution of C1s (a), O 1s (b), N 1s(c) and Cu 2p 3/2 (d) of Cu_2(CuTCPP).

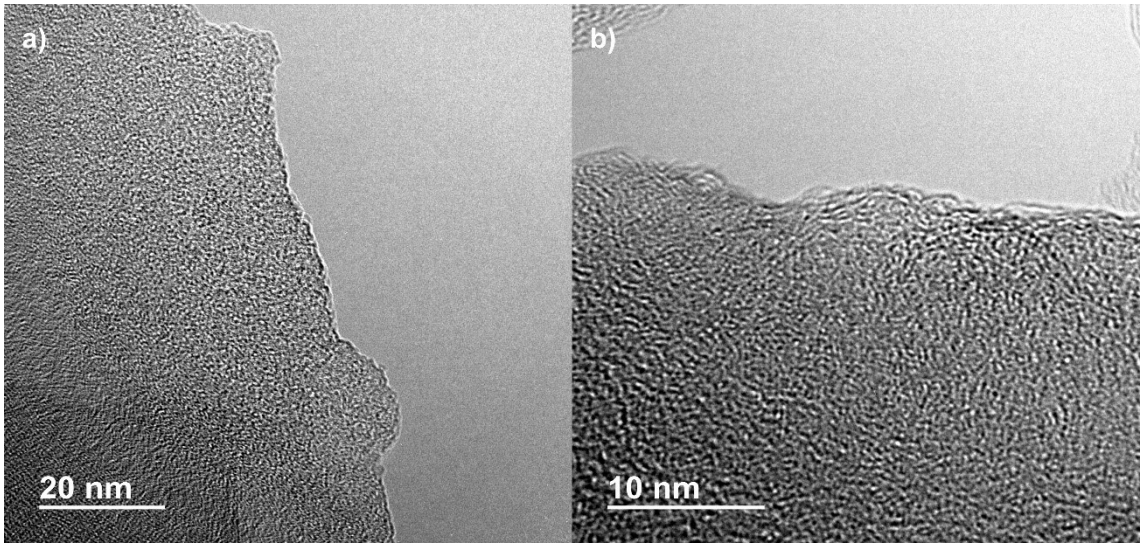

Figure S2. HRTEM images of the Cu_2(CuTCPP) MOF.

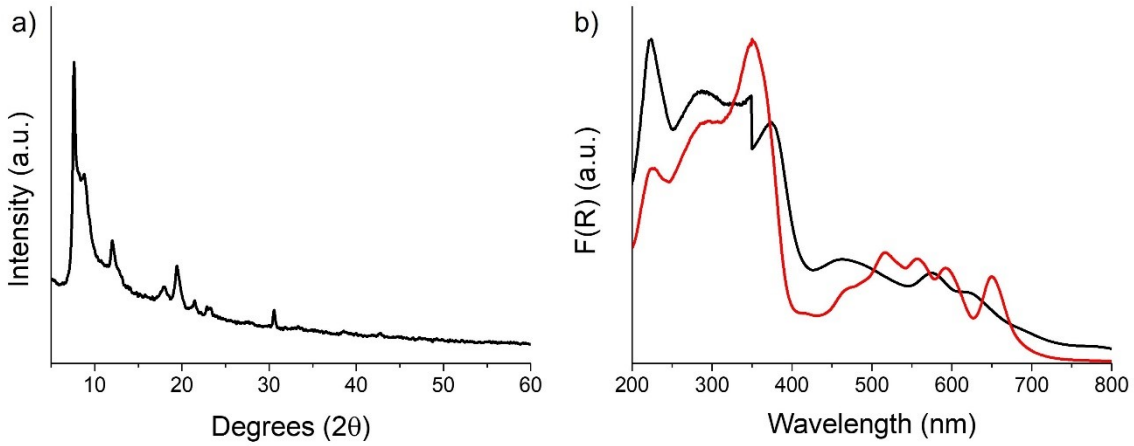

Figure S3. (a) XRD pattern of Cu_2(FeTCPP) and (b) diffuse reflectance UV-vis spectra of Cu_2(FeTCPP) (black) and H_2TCPP (red).

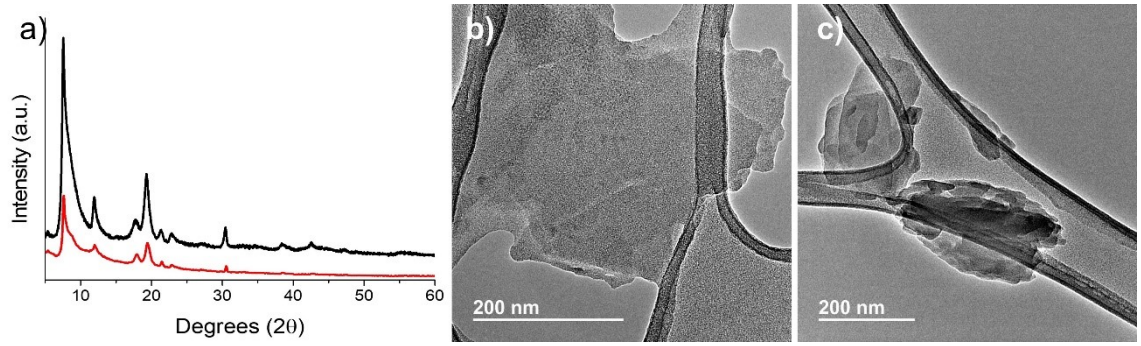

Figure S4. (a) XRD pattern of fresh (black) and after 5 uses (red) Cu_2(CuTCPP). (b) TEM image of as-prepared Cu_2(CuTCPP). (c) TEM image of Cu_2(CuTCPP) after 5 uses.

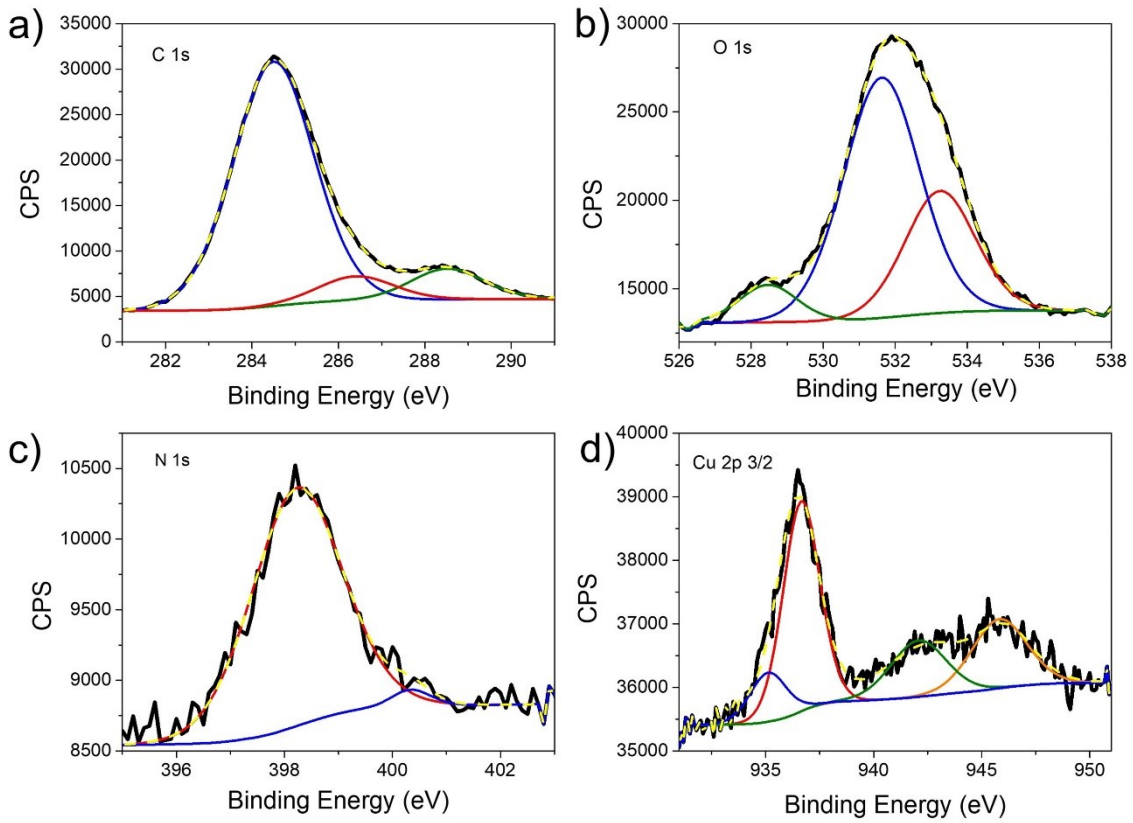

Figure S5. High-resolution XPS spectra and their best deconvolution of C1s (a), O 1s (b), N 1s(c) and Cu 2p 3/2 (d) of Cu_2(CuTCPP) after 5 consecutive uses.

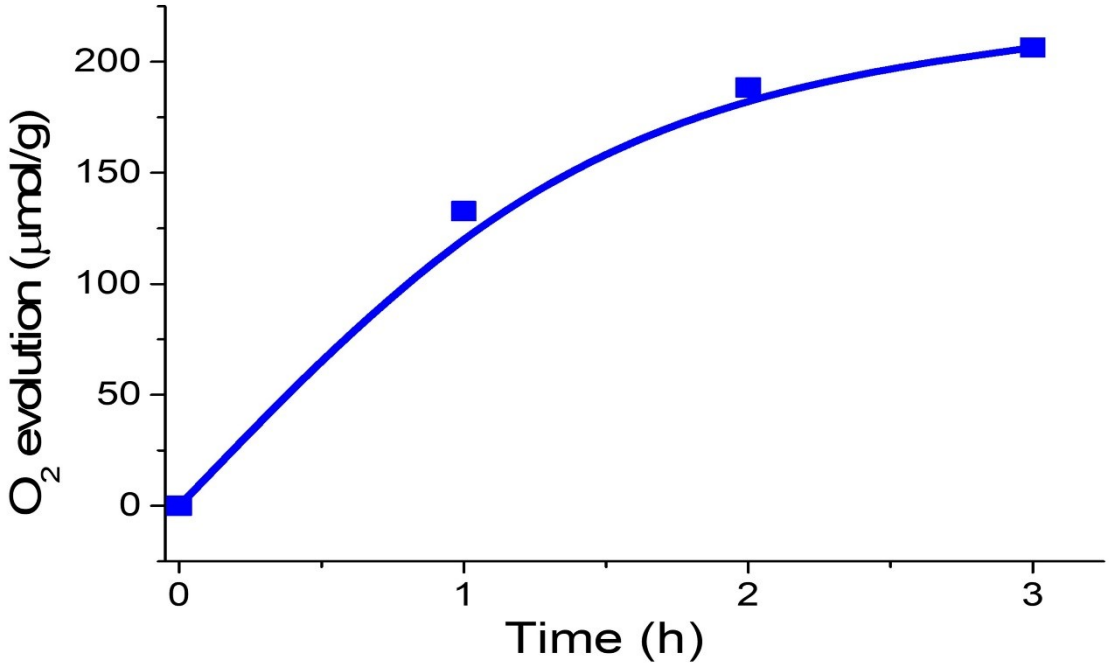

Figure S6. O_2 evolution under visible light irradiation (λ > 450 nm) in the presence of $Ce(NH_4)_2(NO_3)_6$ as sacrificial electron acceptor agent.

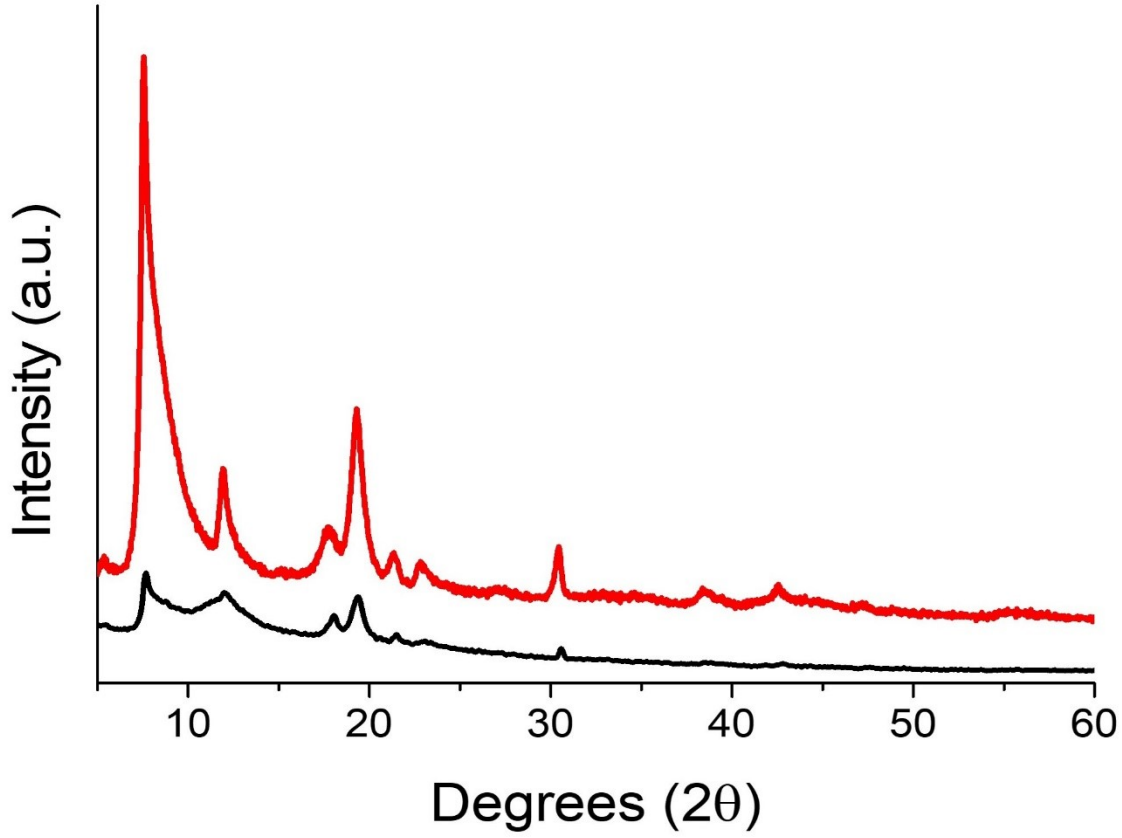

Figure S7. XRD pattern of Cu_2(CuTCPP) prior (red) and after (black) photocatalytic overall water splitting reaction.

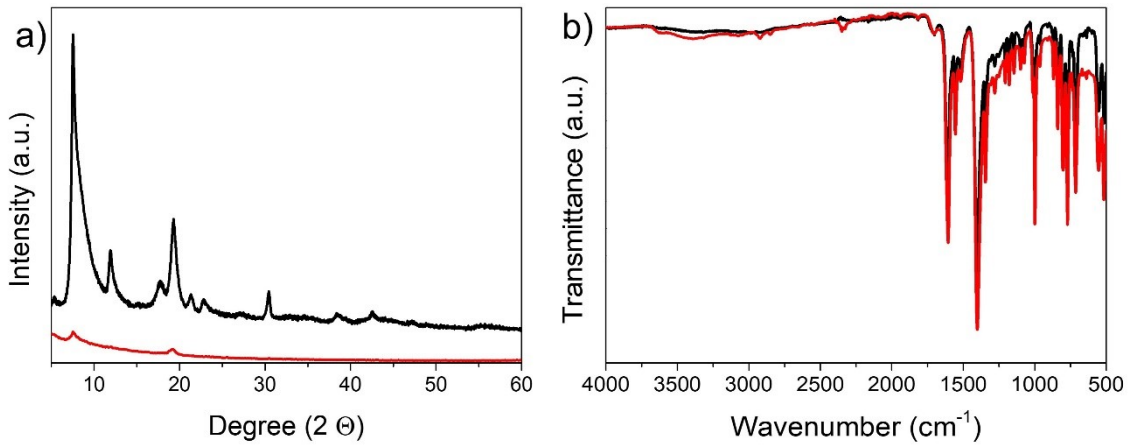

Figure S8. XRD patterns (a) and FTIR spectra (b) of Cu_2(CuTCPP) prior (black) and UV irradiated (red).

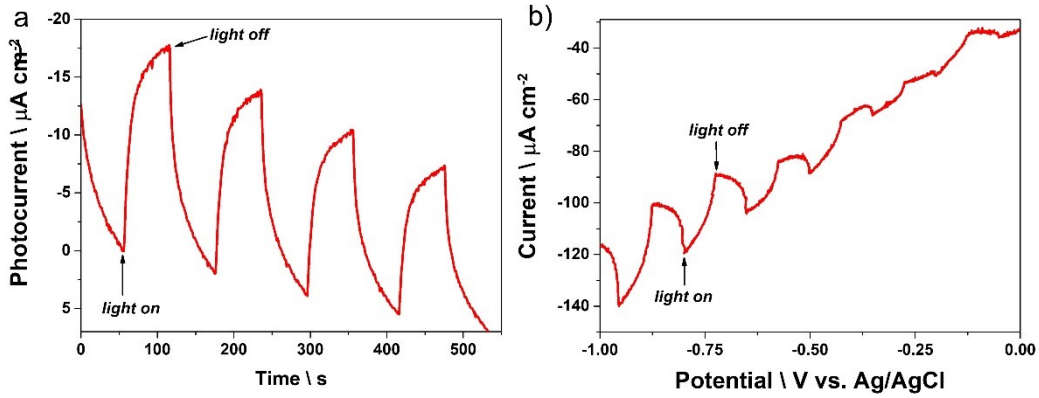

Figure S9. Photocurrent experiments in Cu_2(CuTCPP)-based photoelectrodes at -0.28 V vs. NHE (a) and under voltage increase from 0 to -1 V vs. Ag/AgCl. Aqueous electrolyte at 0.1 M KCl. Pt wire and Ag/AgCl as counter and reference electrodes, respectively. Electrolyte: 0.1M aqueous solution of KCl.

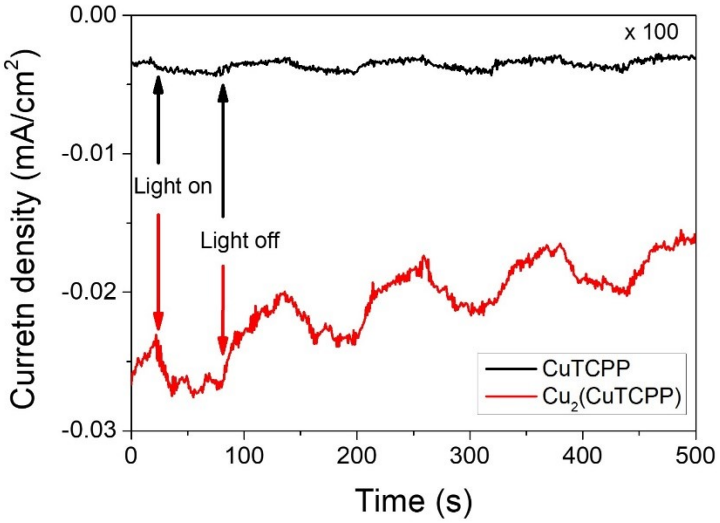

Figure S10. Photocurrent experiments in Cu_2(CuTCPP) and CuTCPP-based photoelectrodes at -0.1 V vs. Ag/AgCl. Aqueous electrolyte at 0.1 M KCl. Pt wire and Ag/AgCl as counter and reference electrodes, respectively. Electrolyte: 0.1M aqueous solution of KCl.

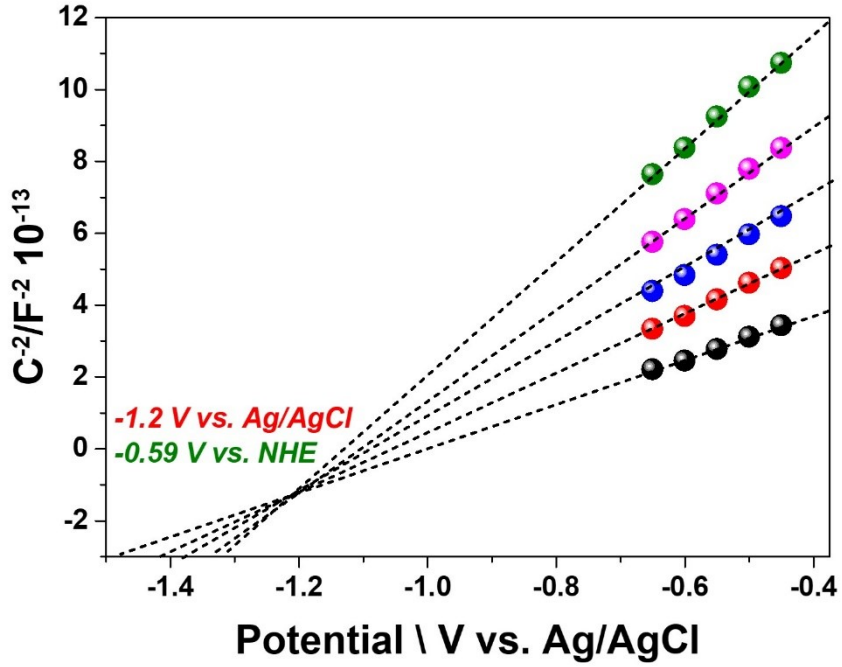

Figure S11. Mott-Schottky plot from a Cu_2(CuTCPP)-based electrode, using a Pt wire and Ag/AgCl electrodes as counter and reference electrodes, respectively, and measured at 1500, 1750, 2000, 2250 and 2500 Hz frequencies. Electrolyte: 0.1M aqueous solution of KCl.

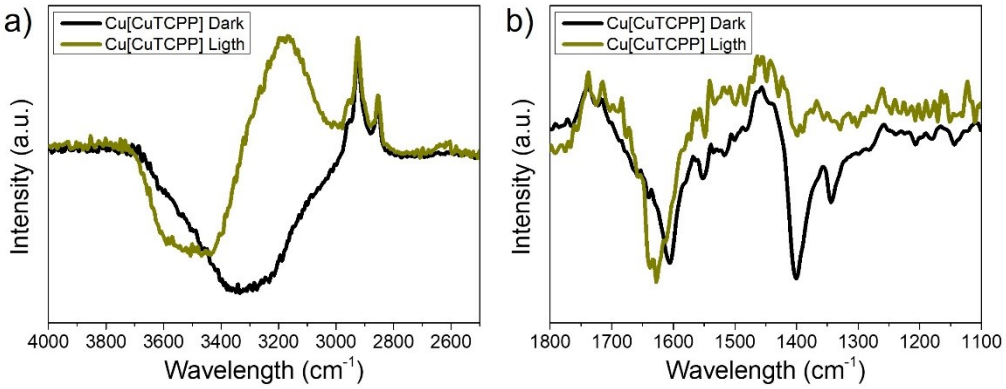

Figure S12. ATR-FTIR spectra of Cu_2(CuTCPP) dispersion in ultrapure water in the dark (black) and under visible light irradiation (dark yellow) in the spectral regions from 2500 to 4000 cm^{-1} (a) and from 1100 to 1800 cm^{-1}(b). The aqueous Cu_2(CuTCPP) dispersion spectra have been acquired after baseline subtraction. The baseline consisted in a ATR-FTIR measurement of a water drop.

References

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