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Hypercrosslinked polymers as a photocatalytic platform for visible-light-driven CO₂ photoreduction using H₂O

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Abstract: The design of robust, high-performance photocatalysts is key for the success of solar fuel production *via* CO₂ conversion. Herein, we present hypercrosslinked polymer (HCP) photocatalysts for the selective reduction of CO₂ to CO, combining excellent CO₂ sorption capacities, good general stabilities, and low production costs. HCPs are active photocatalysts in the visible light range, significantly out-performing the benchmark material, TiO₂ P25, using only sacrificial H₂O. We hypothesise that superior H₂O adsorption capacities led to concentration at photoactive sites, improving photocatalytic conversion rates when compared to sacrificial H₂. These polymers are an intriguing set of organic photocatalysts, displaying no long-range order or extended pi-conjugation. The as-synthesised networks are the sole photocatalytic component, requiring no co-catalyst doping or photosensitiser, representing a highly versatile and exciting platform for solar-energy conversion.

Keywords: Carbon dioxide photoreduction • Hypercrosslinked polymers • Photocatalysis • Porous organic polymers • Solar fuels

Introduction

The ever-increasing global energy demand requires a significant overhaul of current production processes if humanity is to address climate change. Carbon management and renewable energy must play a key role in our energy outlook, challenging researchers to reshape our energy portfolio. Research efforts are focused on the development of efficient carbon capture, utilisation, and storage (CCUS) technologies, as well as the improvement of methods to harness renewable energy.^[1] The use of sunlight shows promise towards the building of a sustainable chemical industry. Solar fuels are synthetic fuels produced via the conversion of solar energy into chemical energy, namely H₂ from H₂O, and C₁ and C₁₊ chemicals from CO₂. This conversion can be done by a variety of processes, including photochemical (often named artificial photosynthesis), thermochemical, and electrochemical reactions. However, overcoming the high thermodynamic and kinetic barriers to conversion is challenging, and so a catalyst is required to improve energy efficiency and, ultimately, render these processes viable.^[2-3]

Here, we focus on a photochemical route to solar fuel production, namely photocatalysis, whose main advantage lies in the simplicity of its implementation. To date, 'traditional' semiconductors, *e.g.* metal oxide/sulfides and transition metal complexes, such as TiO₂, CdS, ZnO, WO₃, Ru-, Re- and Pd-based complexes have received much attention as photocatalysts, owing to their ability to generate charge carriers under light irradiation.^[4-7] However, a lack of structural versatility and notoriously difficult to tune frontier energy levels in inorganic materials often limit their performance, while the requirement of rare-earth metals presents significant sustainability issues. Moreover, traditional semiconductors are often predominantly active at ultraviolet wavelengths, constituting just ~4% of the solar spectrum, prompting great interest in the development of visible light-active photocatalysts for improved efficiency.

The development of new classes of photoactive materials, including inorganic-organic hybrids, such as metal-organic frameworks (MOFs), or organic-based materials, such as porous organic polymers, have emerged as promising alternatives to traditional photocatalysts.^[8-12] The structural versatility of polymers enables photochemical tunability and, ultimately, optimisation of photocatalytic performance. Owing to their general chemical inertness and non-metallic nature, porous organic

polymers are of particular interest in the design of new photocatalysts. Yang et al. reported triazine-based conjugated microporous polymers (CMPs) for CO₂ photoconversion to CO using visible light.^[13] The optical band gap of the materials was engineered by the inclusion of various electron-withdrawing and electron-donating groups. Yu et al. employed Pd-catalysed Sonogashira–Hagihara coupling to produce Eosin Y-functionalised porous polymers, able to photoreduce CO₂ to CO with 92% selectivity, using visible light and sacrificial H₂O.^[14] More recently, Fu et al. reported rhenium-doped covalent-organic frameworks (COFs), with high CO₂ photoreduction rates in the presence of acetonitrile and sacrificial triethanolamine.^[12] Furthermore, a metal-free COF produced using solvothermal condensation reactions was reported as a visible-light-driven photocatalyst for CO₂ photoreduction in the presence of water.^[12, 15] While demonstrating the potential of porous organic polymers for CO₂ photoreduction, the synthesis of porous organic polymer photocatalysts generally requires the use of rare-earth metals, or specifically polymerisable monomeric units, presenting implementation barriers due to relatively high-costs and poor sustainability.

Hypercrosslinked polymers (HCPs) represent a class of materials with excellent tunability and relatively low costs. HCPs are densely crosslinked amorphous networks, produced using simple Friedel-Crafts chemistry. Non-functional aromatic compounds (*i.e.* without specifically polymerisable groups) can be ‘knitted’ together using an external crosslinker, requiring only iron(III) chloride as catalyst.^[16] The employment of external crosslinkers means a large array of aromatic compounds can be considered as monomeric material, providing substantial scope for the design of HCPs. Owing to their low cost and chemical versatility, HCPs are being developed for many different applications such as gas separation and storage,^[17-18] solid-state extraction,^[19-20] and in catalysis.^[21] Recently, Wang et al. used an HCP-TiO₂-graphene composite for the photoreduction of CO₂, with the HCP component aiding CO₂ adsorption and diffusion.^[22] The ability of HCPs alone to catalyse solar fuel production, however, remains unknown.

Herein, we present HCPs as a new class of photocatalyst capable of selectively reducing CO₂ to CO. Photocatalytic conversion was achieved using only visible light in the presence of sacrificial H₂O, without additional sacrificial agents or co-catalysts, significantly out-performing TiO₂ P25 (x7.5 times). The influence of the reducing agent was investigated (*i.e.* H₂ vs. H₂O). Surprisingly, employing sacrificial H₂O led to significant improvements in photoconversion rates. We hypothesise that the

preferential adsorption of H₂O concentrates the sacrificial agent at the HCP's surface, driving photocatalytic performance. Owing to their lack of requirement for precious-metal catalysts, as well as their easily scaled chemistry, HCPs present an exciting platform for the further design and discovery of high-performance organic photocatalysts.

Results and Discussion

Hypercrosslinked polymer synthesis and characterisation. We synthesised three HCPs of varied chemical structure, **HCP-1**, **HCP-2**, and **HCP-3** *via* a Friedel-Crafts alkylation reaction using external crosslinkers to 'knit' together aromatic monomers. A general reaction scheme and representative HCP structures are shown in Figure 1a,b. HCP-1 was produced *via* the crosslinking of benzene, using an aliphatic dimethoxymethane external crosslinker, one of the most widely-studied HCPs in recent years.^[23] HCP-2 is comprised of aniline crosslinked using the benzyl ether compound 4,4-bis(methoxymethane)biphenyl, as the analogous polymer produced using dimethoxymethane was non-porous.^[24] Finally, HCP-3 consisted of 2,4-diamino-6-phenyl-1,3,5-triazine crosslinked using 4,4-bis(methoxymethane)biphenyl. We chose the chemistries of HCP-2 and HCP-3 to try to improve the CO₂ adsorption selectivity *via* the inclusion of amino groups. Photographic images of the networks (Figure S1) reveal a colour gradient from dark to light brown from HCP-1 to HCP-3.

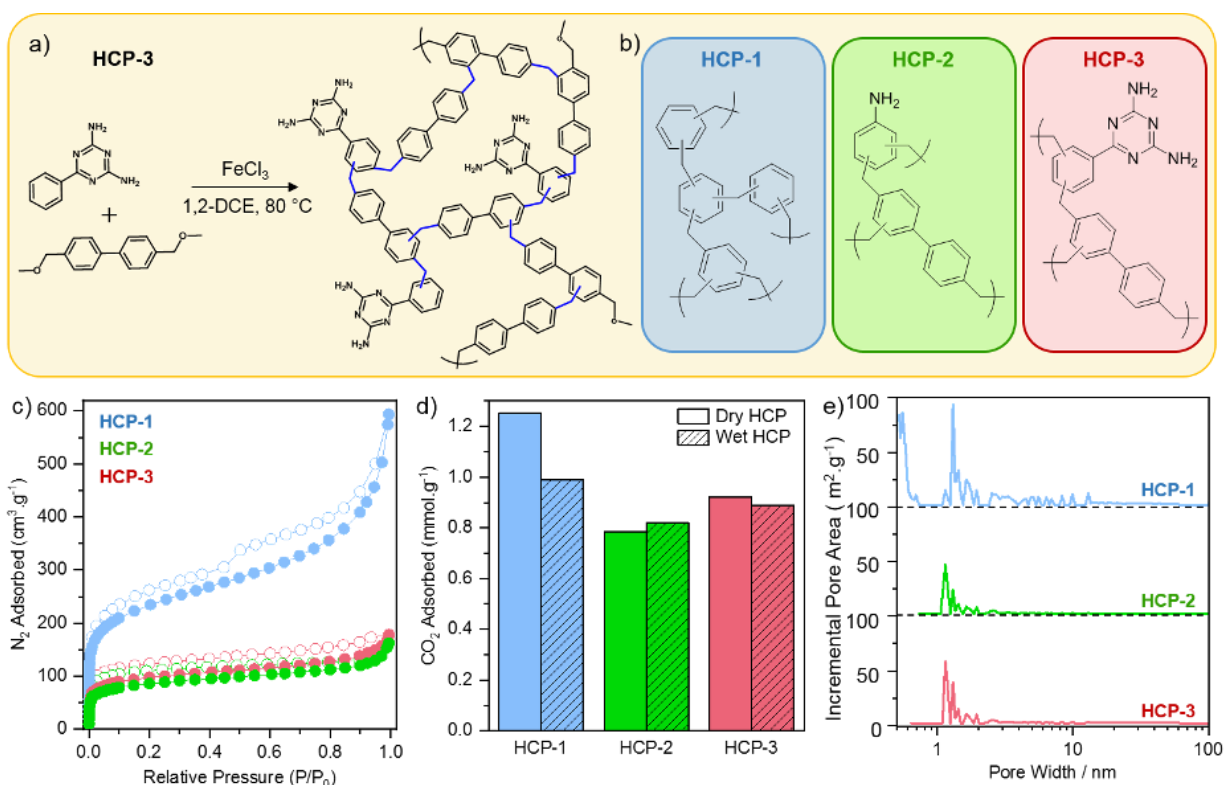


Figure 1. a) Reaction scheme for the production of HCP-3 by Friedel-Crafts alkylation, b) representative chemical structures of HCP repeat units, c) N_2 adsorption isotherms at -196°C , filled symbols represent adsorption and empty symbols represent desorption, d) CO_2 uptake at 1 bar and 25°C for HCPs in both 'dry' and 'wet' states, i.e. HCPs exposed to humid atmospheres before measurement, e) pore size distributions of HCPs, calculated using DFT method.

We successfully incorporated the aromatic monomers into the networks, as confirmed using Fourier-transfer infrared spectroscopy (FTIR), which showed distinct stretches for primary amines in HCP-2 and HCP-3, and the triazine tertiary amines in HCP-3 (Figure S2). HCP-2 and HCP-3 contain 1.3 and 7.9 at% N, respectively, as determined *via* X-ray photoelectron spectroscopy (XPS) survey spectra (Figure S4 and Table S2). These values correspond to final polymer compositions of roughly 1:4 and 1:3 monomer to crosslinker ratios for HCP-2 and HCP-3, respectively. Scanning electron micrographs revealed HCP-1 and HCP-3 as agglomerated spherical particles, whereas HCP-2 shows a more fibrous structure (Figure S4). Thermogravimetric analysis demonstrated the high thermal stability of all HCPs, with decomposition temperatures of $>300^\circ\text{C}$ in both N_2 and air atmospheres (Figure S5-6). Char yields in N_2 at 900°C were $> 60\%$ in all HCPs, while complete

degradation was observed in air at > 550 °C. Powder X-ray diffraction confirmed the amorphous nature of all HCP networks (Figure S7).

We used N₂ sorption measurements at -196 °C to assess the porous nature of the networks. HCP-1, HCP-2, and HCP-3 exhibited BET surface areas of 951, 311, and 357 m²/g, respectively (Figure 1c and Table S3). All HCPs displayed a combination of type I and type IV isotherms,^[25] with significant microporosity, as indicated by the steep N₂ uptake at low relative pressures, as well as meso/macroporosity. Micropore volume was highest in HCP-1 (0.46 cm³/g), dropping to 0.13 and 0.16 cm³/g for HCP-2 and HCP-3, respectively, reflecting trends seen in the polymer's BET surface areas. Figure 1e highlights a multimodal pore size distribution for all networks, predominantly concentrated in the micropore region. Pores of around 0.5 nm in size contribute noticeably to HCP-1's surface area, whereas both HCP-2 and HCP-3 do not show any significant area derived from pores smaller than 1 nm in diameter.

To assess the CO₂ uptake ability of HCPs, we collected adsorption isotherms at 25 °C up to 1 bar (full isotherms are shown in Figure S8). Although the HCPs followed the expected trend, *i.e.* higher surface area polymers adsorbed more CO₂, the CO₂ capacities did not reflect the large differences in surface areas (Table S3). The presence of the amino groups in HCP-2 and HCP-3, which are known to impart CO₂ selectivity to hypercrosslinked polymers,^[26] increased uptake density per unit of surface area due to more attractive interactions with the adsorbate CO₂.^[27-28]

The presence of adsorbed water was shown to impede CO₂ uptake in polar HCPs, due to competitive adsorption.^[29] Therefore, we investigated the effect of H₂O and CO₂ co-adsorption, since we used sacrificial H₂O vapour in CO₂ photoreduction (see below). We exposed the samples to humid air (>99 % humidity) for at least 48 h before collecting CO₂ adsorption isotherms at 25 °C up to 1 bar. Crucially, samples were not degassed prior to CO₂ adsorption measurements (details in ESI), *i.e.* adsorbed H₂O was not removed. These conditions are close to those in photoreduction experiments. The CO₂ sorption capacities at 1 bar are given in Figure 1d. The full isotherms of both degassed, “dry”, and humidity-exposed, “wet”, HCPs are shown in Figure S8. Wet HCP-1 showed a 21% decrease in CO₂ capacity in comparison to its dry equivalent, while the amine-containing HCP-2 and HCP-3 showed negligible difference in CO₂ uptake between the wet and dry networks. These uptake capacities demonstrate the minimal impact of water co-adsorption, emphasising the selective

adsorption of CO₂ by the polymers, particularly HCP-2 and HCP-3. During photoreduction experiments, we did not expose HCPs to water vapour prior to CO₂ reduction, but rather a stream of CO₂ containing water vapour. As such, the effect of co-adsorption is likely to be less significant *in-situ*.

CO₂ photoreduction activity of hypercrosslinked polymers

To evaluate the potential of HCPs for CO₂ photoreduction, we investigated their optoelectronic properties using UV-visible diffuse reflectance spectroscopy (UV-vis DRS). The UV-vis spectra show all HCPs absorb light in both the UV and visible range, with absorption onsets of 348, 350, and 389 nm for HCP-1, HCP-2 and HCP-3, respectively (Figure 2a). All three HCPs exhibited photoluminescence above 550 nm (Figure S9), and as shown in Figure 2b we probed their photoluminescence lifetimes at 700 nm using time-correlated single photon counting (TCSPC) upon 282 nm excitation. The time at which the photoluminescence signal has decayed to half its initial amplitude (half-lifetime) was 1.9 ns, 2.2 ns, and 3.2 ns for HCP-1, HCP-2, and HCP-3, respectively, which demonstrates that HCP-3 has a substantially longer excited state lifetime than HCP-1 or HCP-2. We estimated the HCP's valence band (VB) and conduction band (CB) positions by complementing our UV-vis DRS data with XPS measurements (Figure 2c). First, valence band XPS measurements allowed us to ascertain the distance between the Fermi level (E_F) and the VB onset, also known as VB offset (Figure S10). Placing the VB offset on the absolute energy scale requires knowledge of the position of the Fermi level, which was determined by measuring the secondary electron cut-off through XPS work function measurements (Figure S11). Finally, we identified the CB position using the UV-vis spectra absorption onset. For all HCPs, the CB is located above the reduction potential of CO₂/CO and the VB below the oxidation potential of both H₂/H₂O and O₂/H₂O. Hence, the band diagrams point towards a sufficient thermodynamic driving force to enable the reduction of CO₂ to CO using either gaseous H₂ or H₂O as a sacrificial agent. The Fermi level of all HCPs lies closer to the CB than the VB, suggesting electrons are the major charge carriers, which is desirable for CO₂ photoreduction. Overall, the narrow band gaps and visible light absorption properties of HCPs, as well as their CO₂ adsorption capacities, make them *a priori* attractive candidates for CO₂ photoreduction.

After establishing their CO₂ adsorption ability and desirable optoelectronic properties, we tested HCPs for the photocatalytic reduction of gaseous CO₂. We conducted the tests in a heterogeneous gas/solid photoreactor at ambient temperature, using either H₂ or H₂O as a sacrificial agent under UV-vis or visible irradiation alone (Xe arc lamp, 300 W, Figure S12). No co-catalyst or photosensitiser was required, but some residual iron is present from the HCP synthesis and may play a role in the photoreduction activity (Table S1) as shown with Pd for other organic materials in the context of H₂ evolution.^[30-31] A representative sample of HCP-2 was found to contain 246 ppm of Fe. Under the same conditions, digestion of HCP-1 and HCP-3 was unsuccessful and the iron content could not be estimated. A gas phase reactor was chosen to combine CO₂ capture and CO₂ conversion, avoiding limitations owing to poor CO₂ solubility in some liquid phase reactions (Figure S13). In each experimental set, we compared HCP performance to that of the benchmark TiO₂ P25. For all HCPs, after 3 hours of irradiation the primary carbonaceous product observed was CO, with a selectivity of up to 96% and 95% using sacrificial H₂ or H₂O, respectively (Figure 2d and 2e, Table S4, Table S5). Trace CH₄ was also detected, representing the only other carbonaceous product measured. Regardless of the sacrificial agent, HCP-2 exhibited the lowest CO production rate, while HCP-3 displayed the highest. The photocatalytic performance of HCP-3 was comparable to that of TiO₂ P25 under UV-vis light and was up to 7.5 times better when irradiated with only visible light (Figure 2e, Table S4). In fact, we observed photocatalytic activity for all HCPs under visible light alone, a significant finding for organic materials requiring no doping or co-catalyst. The decrease in activity under visible light compared to UV-vis is rationalised using their UV-vis absorption spectra (Figure 2a). As HCP-1 is the network that shows the highest light absorption in the visible region, its photoactivity is the least affected by the absence of UV light.

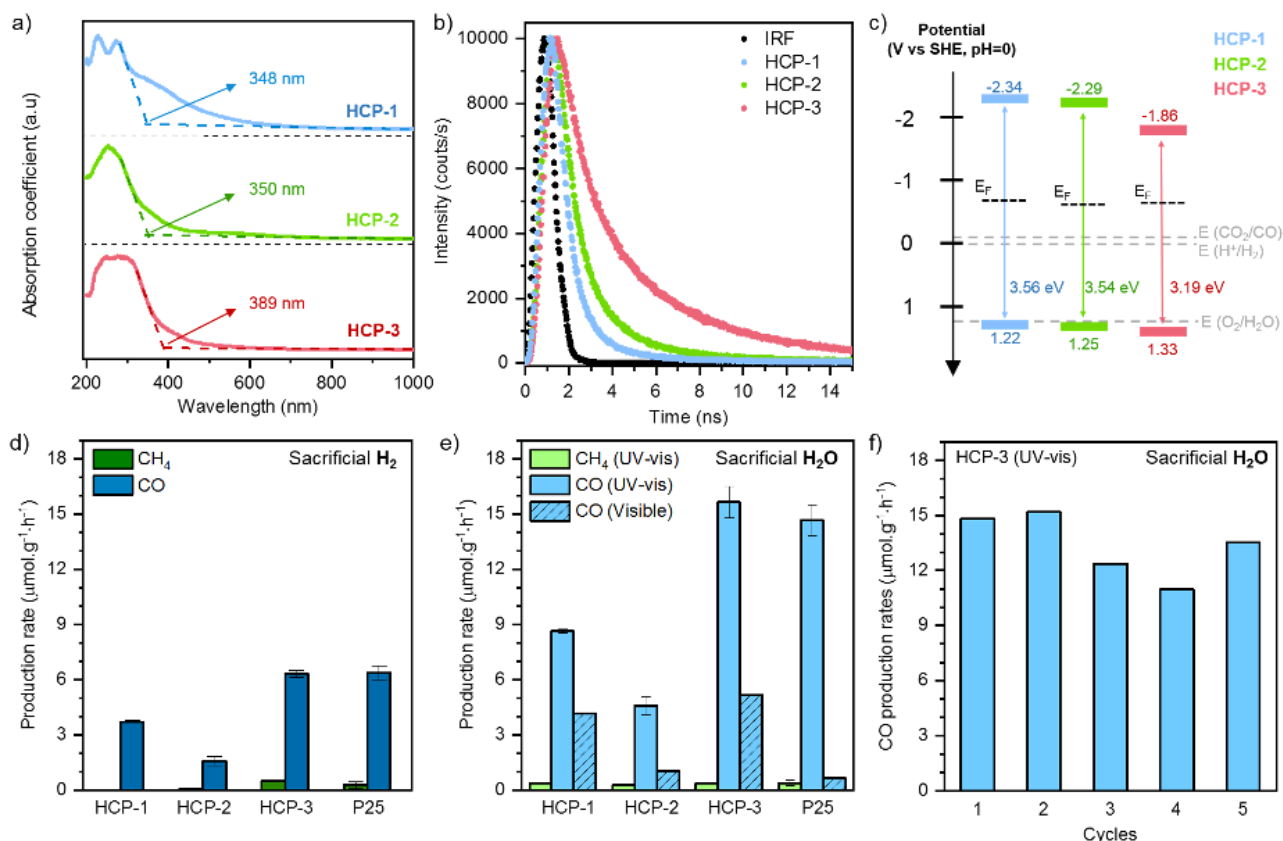


Figure 2. a) UV-vis absorption coefficient spectra with absorption onsets indicated, b) photoluminescence decay kinetics probed at 700 nm following excitation at 282 nm, along with the instrument response function (IRF) probed at the excitation wavelength, c) band gap position, d) photocatalytic production rates using sacrificial H_2 in UV-vis, e) photocatalytic production rates using sacrificial H_2O in both UV-vis and visible light alone, f) HCP-3 recyclability test over 5 cycles of 3 h irradiation using UV-vis light and sacrificial H_2O .

Activity in the visible range is promising for the future of HCP photocatalysts in real-world applications as visible light comprises a large portion of the sun's output reaching the Earth's surface. Targeted network modifications might allow further optimisation of this visible light activity. The high photocatalytic activity of HCP-3 likely arises from the presence of triazine groups. Lee et al. reported stronger electrostatic CO_2 interactions in triazines when compared to benzene and amino groups, as are present in HCP-1 and HCP-2, respectively.^[32] Triazine groups may also offer an additional delocalisation of the electrons, favouring lower electron-hole recombination.^[33-34] Time-resolved photoluminescence showed that HCP-3 displayed the lowest electron-hole recombination rates (Figure 2b), offering more opportunity

for charges to migrate to the surface of the photocatalyst for CO₂ photoconversion. To gain further insights on the key parameters influencing CO₂ adsorption and photoconversion, a systematic HCPs screening is required.

Interestingly, CO₂ photoreduction performance of HCPs improved by up to 2.5 times when replacing H₂ with sacrificial H₂O (Figure 2 d,e). From a thermodynamic standpoint, such behaviour is intriguing as H₂O oxidation requires a higher driving force than H₂ oxidation. We hypothesised that the increased photoactivity in the presence of H₂O is due to HCPs displaying significantly improved adsorption capacities for H₂O when compared to H₂. This leads to an increased availability of the sacrificial agent at the photoactive sites on the HCPs' surface, improving photoreduction rates. To investigate this hypothesis, we collected pure H₂ and H₂O adsorption isotherms for all HCPs (Figure 3). From the pure adsorption isotherms, under operating conditions (atmospheric pressure, 25 °C) HCPs adsorbed <0.1 mmol/g of H₂, in comparison to between 2 and 9.4 mmol/g for H₂O, an increase of 2 orders of magnitude. A higher concentration of sacrificial agent at the HCP's surface should favour high CO₂ photoreduction rates, explaining the increase of photoactivity when using H₂O as reducing agent.

To further investigate the importance of H₂O adsorption on the photoactivity, we decreased the humidity inside the photoreactor by decreasing the temperature of the H₂O vapour saturator to ~ 1 °C. At 1 °C, the partial pressure of H₂O at saturation is reduced (6.6 mbar), dramatically reducing the concentration of H₂O introduced into the system. After sealing the reactor, we conducted CO₂ photoreduction measurements at 25 °C, under atmospheric pressure. The decreased humidity of the stream resulted in a 38% decrease in activity for HCP-3 (Figure S14). Indeed, H₂O uptake in this network is reduced to around 0.4 mmol/g at 6.6 mbar, as estimated from the pure water sorption isotherm (Figure 3b).

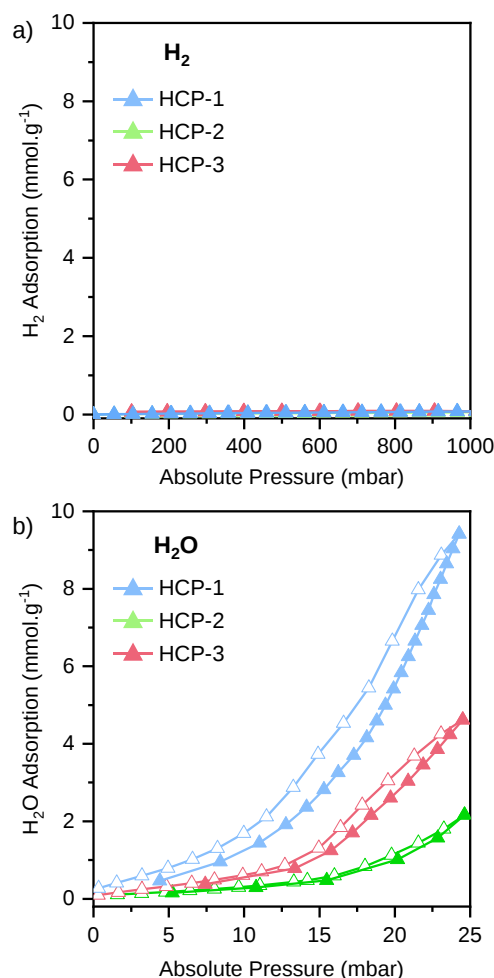


Figure 3. a) H₂ and b) H₂O adsorption isotherms at 25 °C. Filled symbols represent adsorption and empty symbols represent desorption.

This further corroborates the importance of the adsorption of the sacrificial agents to the photocatalyst surface. TiO₂ also showed improvements when employing sacrificial H₂O in place of H₂. Sorescu et al. outlined how co-adsorbed water on TiO₂ can positively affect the adsorption capacities of CO₂ through the formation of hydrogen bonds.^[35] Other materials such as ZrO and coal also exhibit increased CO₂ adsorption and/or activation in the presence of co-adsorbed H₂O.^[36-38] In addition to ensuring the presence of H₂O molecules close to active sites, we speculate that co-adsorbed water may also favour CO₂ activation and/or the formation of bicarbonate species and facilitate its photoreduction, as suggested elsewhere for other photocatalysts.^[39-40] Nonetheless, further studies are required to understand the influence of H₂O on CO₂ adsorption.

We examined further the photocatalytic properties under UV-vis irradiation of HCP-3, the most active photocatalyst of this study. Kinetic studies point to a relatively linear production of CO up to 3 h of

irradiation (Figure S15). Recyclability tests were also performed. As shown in Figure 2f, after 5 cycles the photoactivity decreased by 9%, which may be due to the formation of surface products or mild degradation of the polymer. We also probed the structural and chemical stability of HCP-3 by collecting N_2 sorption isotherms and XPS and FTIR spectra before and after UV-vis irradiation. Elemental composition, porosity and chemical bonds were maintained without significant alteration, with the exception of a change in the shape of the N_2 isotherm (Figure S3, S16 and Table S2). To verify the evolution of CO from CO_2 conversion over HCPs photocatalysts, we conducted a series of control experiments, i.e.: in an inert atmosphere (N_2/H_2 or N_2/H_2O); without catalyst; without light; isotopic labelling of $^{13}CO_2$ (control experiments details are outlined in Table S4). In the absence of CO_2 , the activity decreased by 77% to 88% depending on the atmosphere (N_2/H_2O vs N_2/H_2). We attribute the trace CO detected under inert atmosphere arises from the degradation of the residual oxygen-containing functional groups of the HCP crosslinkers. To verify the photocatalytic production of CO from CO_2 , we conducted isotopic labelled $^{13}CO_2$ tests using H_2O as a sacrificial agent under UV-visible light irradiation. We observe a ^{13}CO peak ($m/z = 29$) after light irradiation, confirming the ability of HCPs to photoconvert CO_2 to CO (Figure S17).

Conclusion

We report hypercrosslinked polymers for the first time as a photocatalytic platform for CO_2 photoreduction under both UV-vis and visible light irradiation. HCPs show promising photocatalytic activity using only sacrificial H_2O , without the requirement of any co-catalyst or photosensitiser, significantly outperforming the benchmark material TiO_2 P25 under visible light illumination. This was rationalised by new insights into the concentration of sacrificial agents at the surface of HCPs *via* selective adsorption, as networks showed significantly higher H_2O adsorption capacity in comparison to negligible H_2 adsorption. The performance disparity between these reducing agents outlines a key consideration when producing photocatalysts for yield efficient solar-energy conversion. Their lack of requirement for precious-metal catalysts, as well as their simple engineering, good general stabilities and low costs, make HCPs an exciting and promising platform for the design of organic photocatalysts.

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Supporting information for this article is given via a link at the end of the document.

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Supporting Information

Hypercrosslinked polymers as a photocatalytic platform for visible-light-driven CO₂ photoreduction using H₂O

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Table of Contents

1. Experimental Section.....	S2
2. Characterisation.....	S3
3. Supplementary figures and tables	S9
4. References.....	S34

1. Experimental Section

Materials

TiO₂ P25 (>99.5%, 21 nm primary particle size), benzene, dimethoxymethane, 2,4-diamino-6-phenyl-1,3,5-triazine, aniline, 1,2-dichloroethane, N,N-dimethylformamide and iron(III) chloride were all purchased from Sigma-Aldrich. 4,4'-bis(methoxymethyl)biphenyl was purchased from Tokyo Chemical Industry (TCI) UK and methanol (reagent grade) was purchased from VWR. All reagents were used as received. All gases were purchased from BOC.

Hypercrosslinked Polymer Synthesis

HCP-1: Anhydrous 1,2-dichloroethane (20 mL) was added to benzene (0.78 g, 10 mmol) and dimethoxymethane (2.28 g, 30 mmol) under N₂, before the solution was purged with N₂ for at least a further 30 minutes. After purging, iron(III) chloride (4.87 g, 30 mmol) was quickly added to the solution and the mixture was heated to 80 °C for a further 24 h, during which the reaction was kept under an inert atmosphere. The resulting solid was allowed to cool before it was filtrated using a Buchner funnel and washed with methanol until the filtrate was almost colourless. The polymer was then further washed by Soxhlet extraction in methanol for 24 h. Finally, the polymer was dried in a vacuum oven overnight at 70 °C.

HCP-2: The overall procedure remained the same as HCP-1 with 1,2-dichloroethane (20 mL) added to aniline (0.28 g, 3 mmol) and 4,4'-bis(methoxymethyl)biphenyl (1.45 g, 6 mmol) before iron(III) chloride (0.98 g, 6 mmol) was added.

HCP-3: Again, the overall procedure remained the same as HCP-1 with 1,2-dichloroethane (20 mL) added to 2,4-diamino-6-phenyl-1,3,5-triazine (0.37 g, 2 mmol) and 4,4'-

bis(methoxymethyl)biphenyl (0.97 g, 4 mmol) before iron(III) chloride (0.65 g, 4 mmol) was added. After synthesis, a step was added in which HCP-3 was washed in chloroform by Soxhlet extraction, to ensure the removal of any unreacted 2,4-diamino-6-phenyl-1,3,5-triazine. Yields for HCP-1, HCP-2 and HCP-3 were 84 %, 66 % and 91%, respectively, based on hypothetical 100% polycondensation.

2. Characterisation

Chemical and structural properties

Fourier-transform infrared (FTIR) spectroscopy was performed in the range of 500 – 4000 cm^{-1} on finely ground samples using a PerkinElmer Spectrum 100 FT-IR spectrometer equipped with an attenuated total reflectance (ATR) accessory.

Thermal analyses were performed using a Netzsch TG209 F1 Libra thermogravimetric analyser. At least 10 mg of sample was heated from room temperature to 900 °C at a rate of 10 °C min^{-1} under either air or N_2 gas flow (flow rate 100 mL min^{-1}). An initial isothermal step of 1 h was included at 120 °C to ensure removal of adsorbates before heating continued.

X-ray photoelectron spectroscopy (XPS) measurements were carried out on a Thermo Scientific K-Alpha+ X-ray photoelectron spectrometer equipped with a MXR3 Al $\text{K}\alpha$ monochromated X-ray source ($h\nu = 1486.6 \text{ eV}$). Samples were ground and mounted on the XPS holder using a conductive carbon tape. The X-ray gun power was set to 72 W (6 mA and 12 kV). Survey scans were acquired using 200 eV pass energy, 0.5 eV step size, and 100 ms (50 ms x 2 scans) dwell times. Data analysis was performed using the Thermo Advantage data analysis program.

Nitrogen isotherms were measured using a porosity analyser (Micromeritics 3Flex) at -196 °C. Prior to measurement, all samples were degassed overnight at 393 K at around 0.2 mbar pressure. Samples underwent a further degas step at 393 K *in-situ* on the porosity analyser for 4 h, this time at around 0.003 mbar. Surface areas were calculated using the Brunauer–Emmett–Teller (BET) method.^[1] The total volume of pores (V_{TOT}) was calculated from the volume of N₂ adsorbed at $P/P_0 = 0.97$ and micropore volume (V_{MICRO}) was determined using the Dubinin–Astakhov method.^[2] The pore size distribution was derived from the adsorption isotherms by using an built-in software from Micromeritics and selecting the DFT model for carbon slit shape pores (N₂@77 on Carbon Slit Pores by NLDFT).

Powder X-ray diffraction (PXRD) measurements were recorded at room temperature on a BRUKER 2D PHASE diffractometer operating at 30 kV and 10 mA with monochromatised Cu K α radiation ($\lambda = 0.15418$ nm).

The morphology of the samples was imaged using a scanning electron microscope (SEM, Leo Gemini 1525, Zeiss) in secondary electron mode (InLens detector) at 5 kV. The samples were ground, deposited on carbon tape, and coated with 20 nm of chromium to reduce charging.

For determination of Iron content in HCP-2, samples were first digested (~5 mg sample) using 4 mL conc. nitric acid (4 mL) and H₂O₂ (200 μ L) using an open vessel graphite digestion system (Labter, ODLAB; Distributor: AHF Analysentechnik AG; Germany). Samples were twice heated to 150 °C and held at the target temperature for 1 h before cooling to 50 °C, however this was not sufficient for sample digestion. Samples were then twice heated to 200 °C and held for 45 h before again cooling to 50 °C. After digestion the sample was diluted in ultrapure water (18.2 M Ω cm, Milli-Q Advantage, Darmstadt, Germany). Digested samples were analysed using an ICP-MS (an Agilent 7800, Agilent Technologies, Tokyo, Japan) equipped with an Agilent SPS 4 autosampler (Agilent Technologies, Tokyo, Japan) and a

MicroMist nebulizer at a sample uptake rate of approx. 0.2 ml/min. The Agilent MassHunter software package (Workstation Software, Version C.01.04, 2018) was used for data evaluation. The instrumental parameters for the ICP-MS are summarized in Table S1. A representation sample of HCP-2 was found to contain 246 ppm of Fe, however under the above describe conditions digestion of HCP-1 and HCP-3 was unsuccessful.

Table S1: Instrumental parameters for the ICP-MS measurements

RF power	1550 W
Sampling depth	8 mm
Nebulizer	MicroMist
Spray chamber	Scott double-pass
Spraying chamber temp.	2°C
Monitored Isotopes	⁵⁶ Fe, ⁵⁷ Fe, ¹¹⁵ In, ¹⁸⁵ Re,
Measurement mode	He, 5 L min ⁻¹
Plasma gas	15 L min ⁻¹
Nebulizer gas	1.09 L min ⁻¹
Auxiliary gas	0.90 L min ⁻¹
Cones	Ni
Integration time	0.3 s

Optoelectronic properties

Valence band X-ray photoelectron spectroscopy (XPS) and work function measurements were carried out on a Thermo Scientific K-Alpha⁺ X-ray photoelectron spectrometer equipped with a MXR3 Al K α monochromated X-ray source ($h\nu = 1486.6$ eV). Samples were ground and mounted on the XPS holder using a conductive carbon tape. The X-ray gun power was set to 72 W (6 mA and 12 kV). Valence band spectra were obtained using 15 eV pass energy and 0.05 eV step size. Data analysis was performed using the software Thermo Advantage. The work functions of the polymers were determined by measuring the secondary electron cut-off in the low kinetic energy region. The sample holder contained a clean gold standard sample, which was used as a reference material to ensure correct calibration. A sample bias of -29.47 V was

applied to the samples using an ion gun and the cut-off spectra were obtained using a pass energy of 10 eV. To account for potential variations across the surface of the material, the work function was measured at three different locations and the average was taken. To convert the valence band position and the work function to the absolute energy scale vs. vacuum with the redox potential scale vs. SHE, a factor of 4.44 was required, as 4.44 eV on the former corresponds to 0.00 V on the latter, at 25 °C.

Diffuse reflectance ultraviolet-visible (DR-UV-Vis) spectra were obtained using a Perkin-Elmer Spectrum 100 Spectrometer equipped with an integrating sphere. Spectral band width was set to 2 nm, with Spectralon as a standard.

Time-correlated single photon counting (TCSPC) experiments were carried out using a commercial TCSPC setup (Horiba DeltaFlex) equipped with a pulsed LED excitation source (Horiba NanoLED series) and a fast rise-time photomultiplier detector (Horiba PPD-650 and PPD-900). The instrument response function (IRF) was measured at the wavelength of the excitation source (282 nm). During all other measurements, a suitable long pass filter was inserted between sample and detector to block off scattered excitation light.

Gas and water sorption

Water vapor, CO₂ and H₂ adsorption isotherms were collected at 25 °C using a Micromeritics 3Flex instrument, equipped with a liquid container in the case of H₂O. HCPs were degassed overnight at 120 °C at around 0.2 mbar pressure and again *in-situ* on the porosity analyser (Micromeritics 3Flex) for 4 h down to around 0.003 mbar. Research grade (99.999%) CO₂ and H₂ (99.9995%, Peak Scientific PH200 hydrogen generator) were used for CO₂ and H₂ isotherms. For H₂O isotherms, miliQ water with a resistance > 18.2 micro-ohms was purified by 4 freeze pump thaw cycles. Water isotherms were collected up to a relative pressure of 0.8

to avoid condensation. For “wet” CO₂ uptake, i.e. investigating CO₂ uptake on HCPs pre-exposed to H₂O, HCPs were exposed to humid air (>99 % humidity) by placing HCPs in a sealed vessel containing liquid water and a hygrometer for at least 48 hours at room temperature. HCPs were not in contact with the liquid water during this process. After removal, CO₂ adsorption isotherms were performed at 25 °C up to 1 bar, skipping all prior degas steps. The first pressure CO₂ adsorption point was collected at around 10 mbar (~2 orders of magnitude higher than a standard ‘dry’ measurement) to minimise water desorption. Resulting isotherms for wet polymers gave negative adsorption values at low absolute pressures due to some water desorption in the initial stages of measurement. Therefore, to allow comparison to dry samples, a factor was applied to the isotherm, raising the lowest absolute pressure measurement to 0 mmol/g adsorbed CO₂. It is worth noting that some subsequent uptake may be due to re-adsorption of desorbed water.

Photocatalytic properties

A gas/solid photoreactor was assembled to conduct CO₂ photocatalytic measurements (Figure S13). Tests were conducted at ambient temperature. The photocatalysts were deposited on a stainless-steel plate with a fixed area of 9.6 cm². To do so, 10-15 mg of the ground photocatalyst was dispersed in DI water (1.2 mL), sonicated for 30 seconds and drop cast onto the sample holder. Research grade (99.999%) CO₂ and H₂ (99.9995%, Peak Scientific PH200 hydrogen generator) were flowed at controlled rates using mass flow controllers (Omega Engineering, 0–50 mL min⁻¹). For experiments using H₂ as sacrificial agent, the photoreactor (35 cm³) was vacuumed and replenished with a gas mixture of CO₂ and H₂ (1.5 vol/vol ratio) six times. The same gas mixture of CO₂ and H₂ was subsequently passed over the catalyst bed in the photoreactor for 15 residence times before it was sealed at 1.25 bar and irradiated for 3 h. For experiments using water as sacrificial agent, H₂O vapour was generated from a saturator at

room temperature (25°C), unless stated otherwise, providing a gas mixture of CO₂ and H₂O (1.4 wt% H₂O). The photoreactor was vacuumed and replenished with a gas mixture of CO₂ and H₂O at least six times prior to measurement. A xenon arc lamp (300 W, $\lambda > 325$ nm, LOT Quantum Design) equipped with a water filter was used as the irradiation source. The distance from the lamp to the sample was 9.5 cm with a broadband irradiance at the sample surface of 1830 W.m⁻². For visible light measurements a long pass UV filter ($\lambda < 400$ nm) (LOT Quantum Design) was used.

Evolved gases were analysed by a gas chromatograph mass spectrometer (GC-MS) with gas sampling valves connected directly to the photoreactor. The GC (Agilent Technologies, 7890B) was equipped with HayeSep (Agilent J&W 6 foot, 1/8 inch, 2mm, HayeSep Q Column 80/100 SST) and molecular sieve (Agilent J&W 6 foot, 1/8 inch, 2 mm, MolSieve 5A, 60/80, preconditioned) packed columns in series, a thermal conductivity detector (TCD) and a flame ionisation detector (FID). The MS was equipped with a GS-GASPRO capillary column (Agilent J&W HP-5ms GC Column, 30 m, 0.25 mm, 0.25 μ m). For recyclability tests, the aforementioned process was repeated after each 3 h irradiation cycle without opening the photoreactor. In addition, isotopic tracing experiments were performed with ¹³CO₂ (BOC, >98% atom ¹³CO₂ compared to ¹²CO₂, >99%). The photocatalytic CO₂ reduction tests were repeated 3 times for each material under the same reaction conditions.

3. Supplementary Figures and Tables



Figure S1. Photographic images of: HCP-1, HCP-2 and HCP-3 (from left to right, respectively).

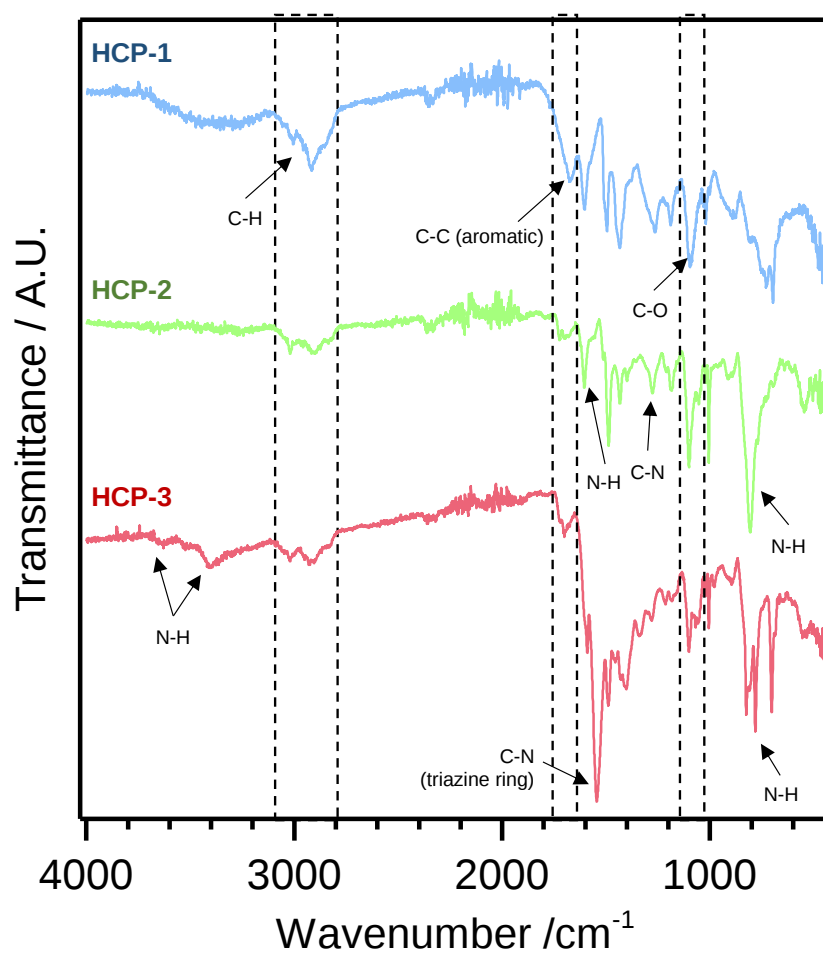


Figure S2. FTIR spectra of HCP-1 (blue), HCP-2 (green) and HCP-3 (red). Signals present in all spectra are highlighted by dashed lines.

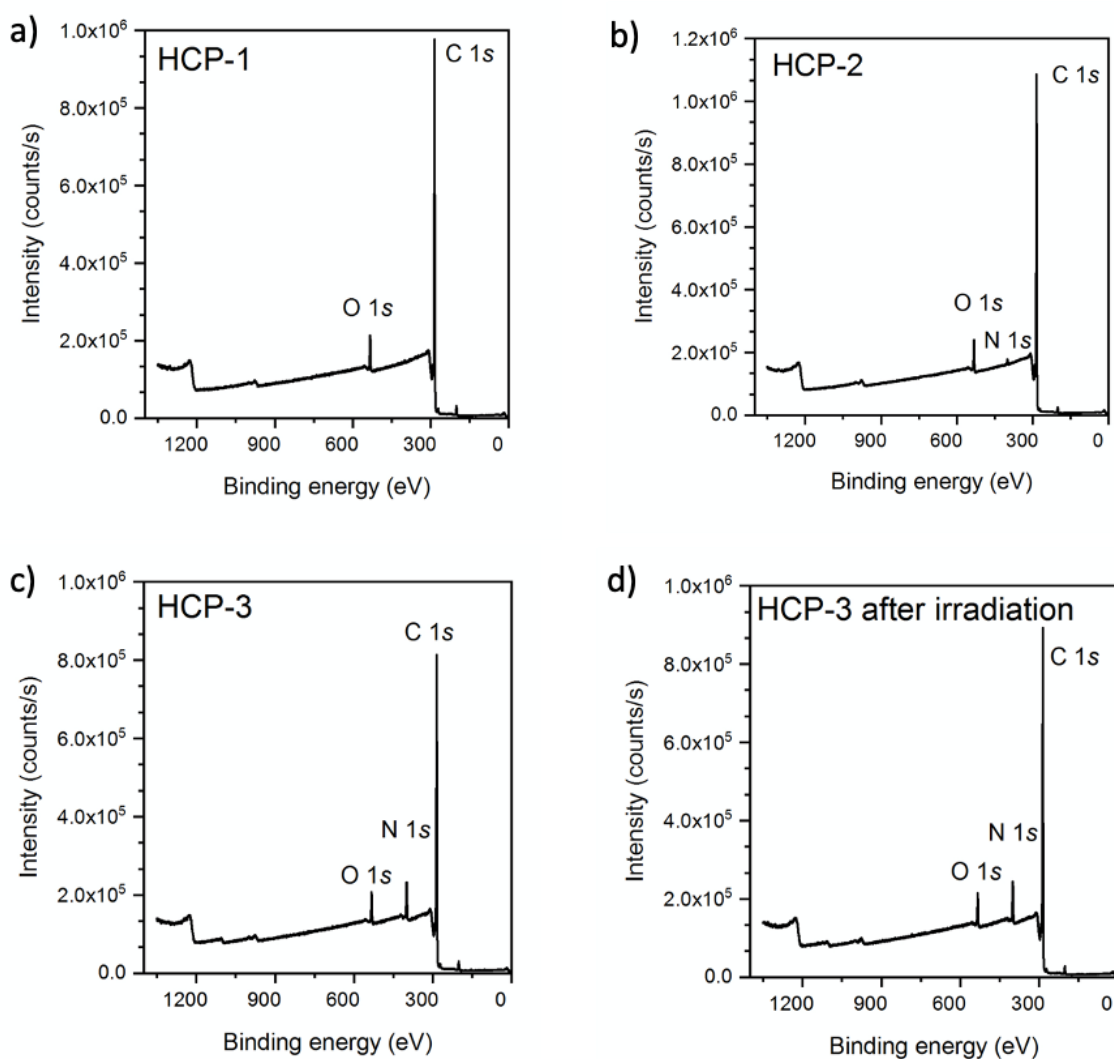


Figure S3. X-ray photoelectron spectroscopy survey spectra of: a) HCP-1, b) HCP-2, c) HCP-3, and d) HCP-3 after 3 h of UV-vis light irradiation.

Table S2. Atomic composition of HCP-1, HCP-2, HCP-3 and HCP-3 after irradiation, determined using XPS survey spectra. The Fe content of HCP-2 determined using ICP-MS is also included.

	Atomic % of O	Atomic % of N	Atomic % of C	Fe content (ppm)
HCP-1	4.5	-	95.5	-
HCP-2	4.2	1.3	94.5	246
HCP-3	4.5	7.9	87.6	-
HCP-3 after irradiation	4.7	8.3	87.0	-

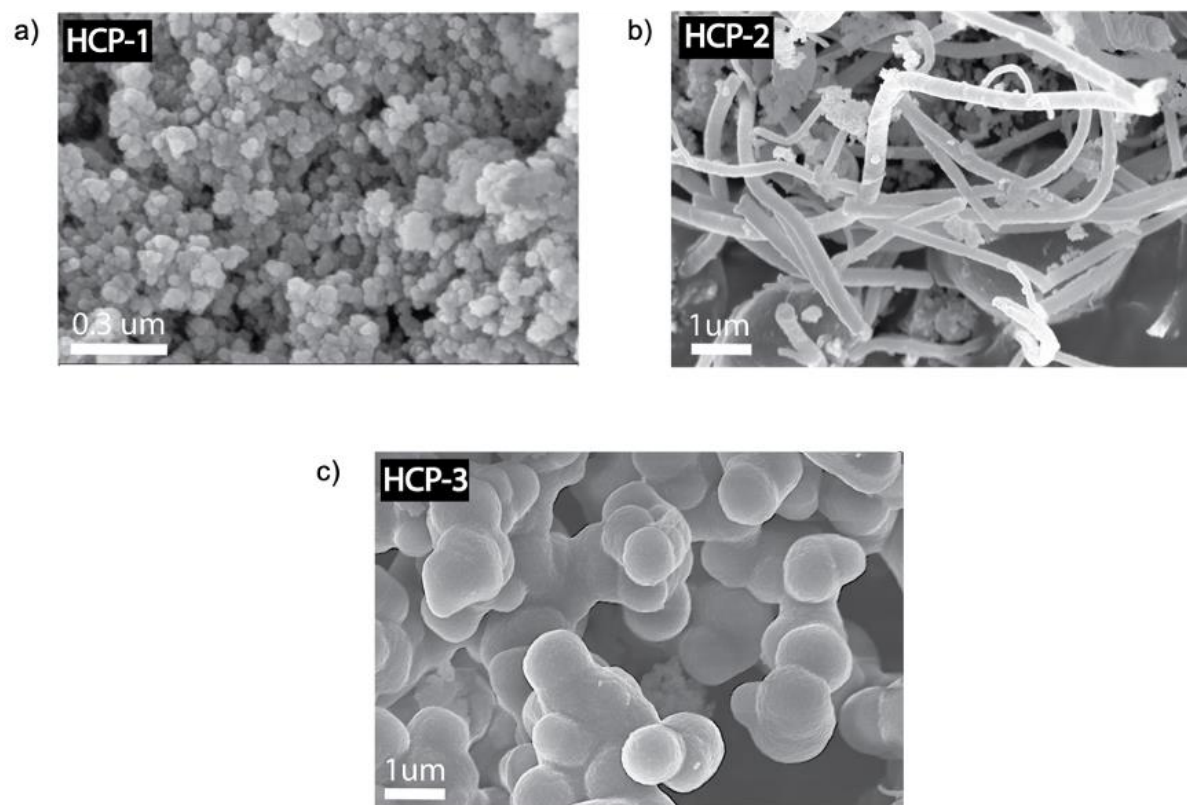


Figure S4. SEM images of a) HCP-1, b) HCP-2, and c) HCP-3.

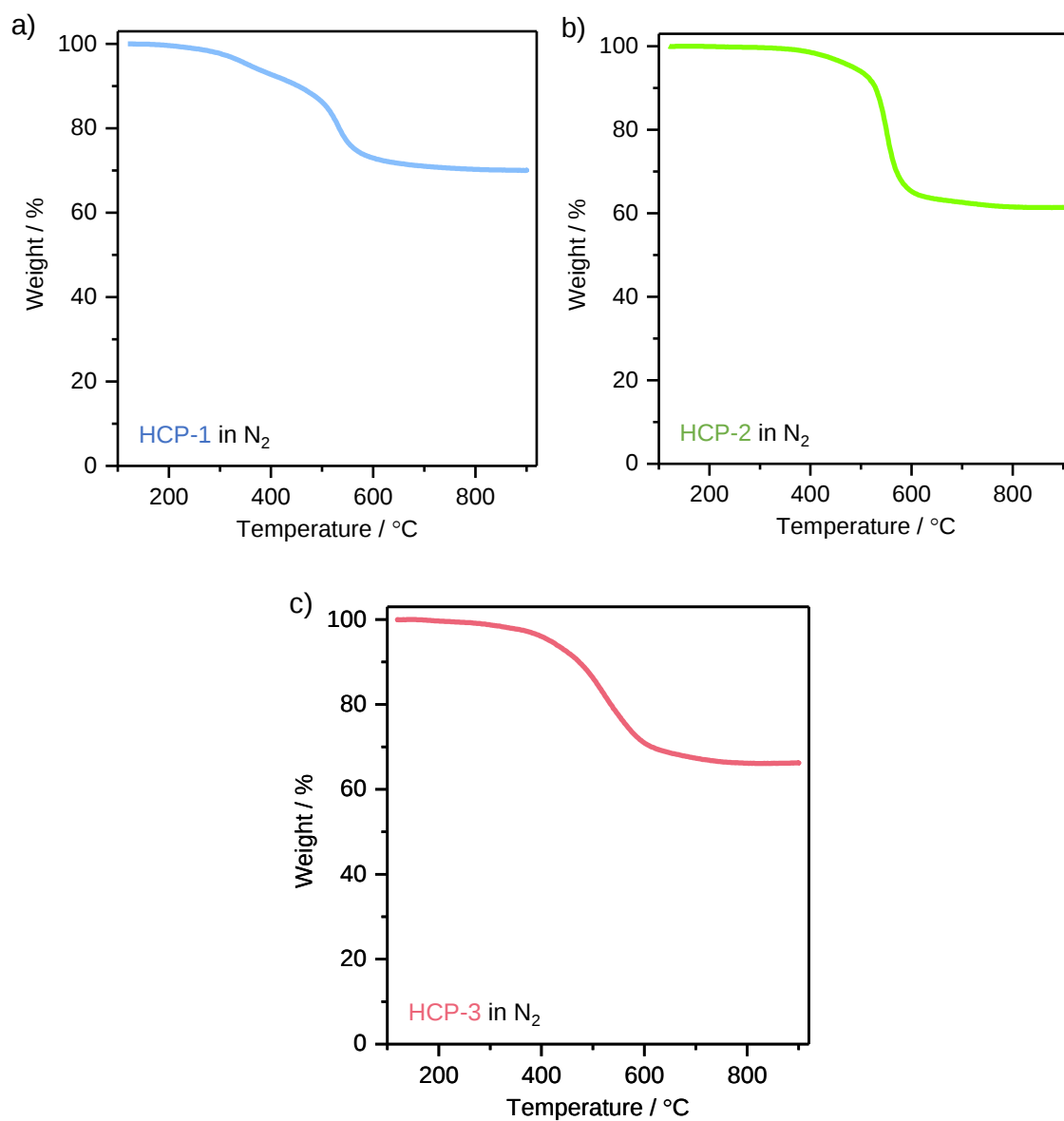


Figure S5. TGA thermograms up to 900 °C in a N₂ atmosphere, heated at a ramp rate of 10 °C/min with a N₂ flow rate of 100 mL/min. a) HCP-1, b) HCP-2, and c) HCP-3.

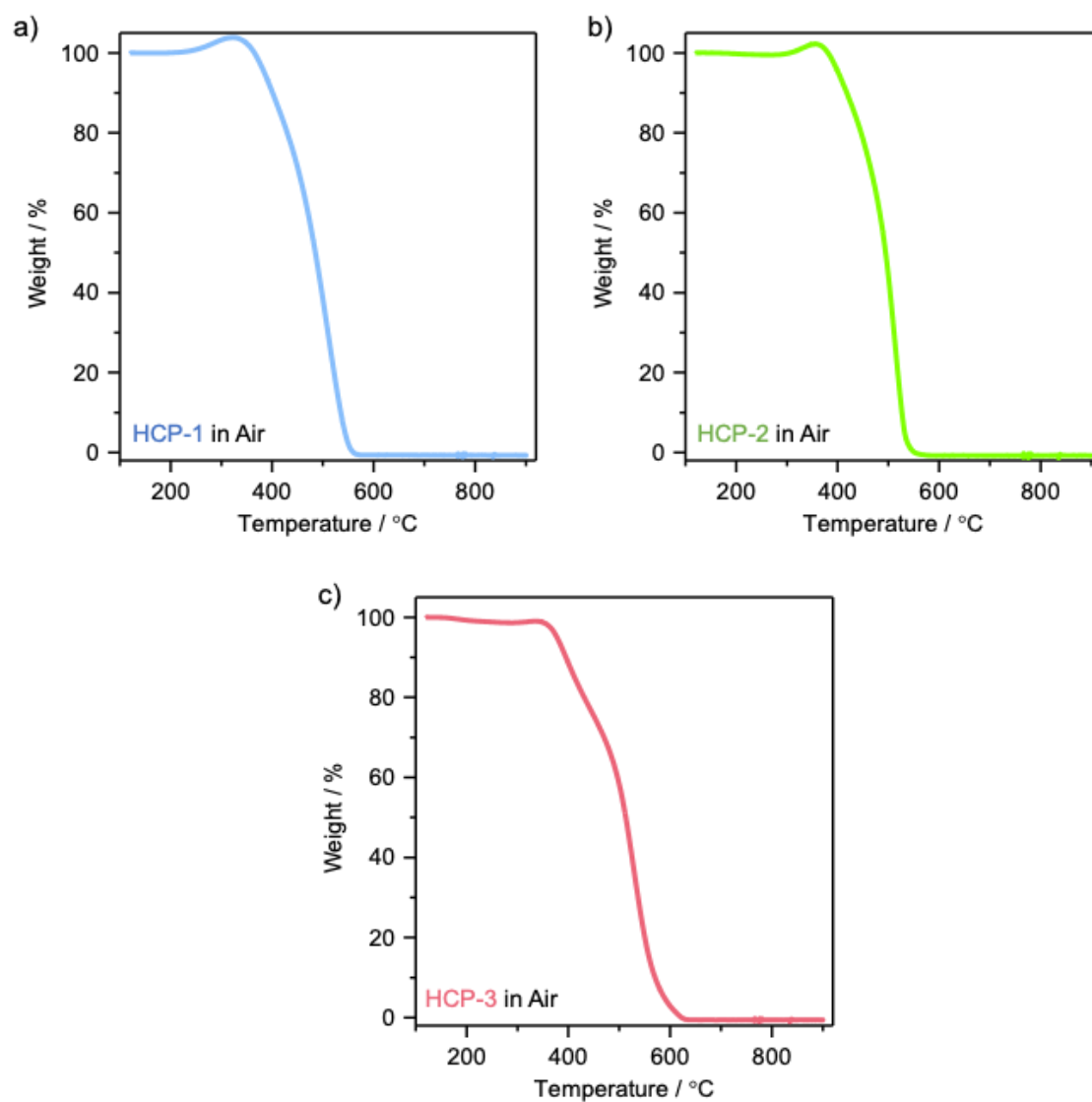


Figure S6. TGA thermograms up to 900 °C in air, heated at a ramp rate of 10 °C/min with an air flow rate of 100 mL/min. a) HCP-1, b) HCP-2, and c) HCP-3.

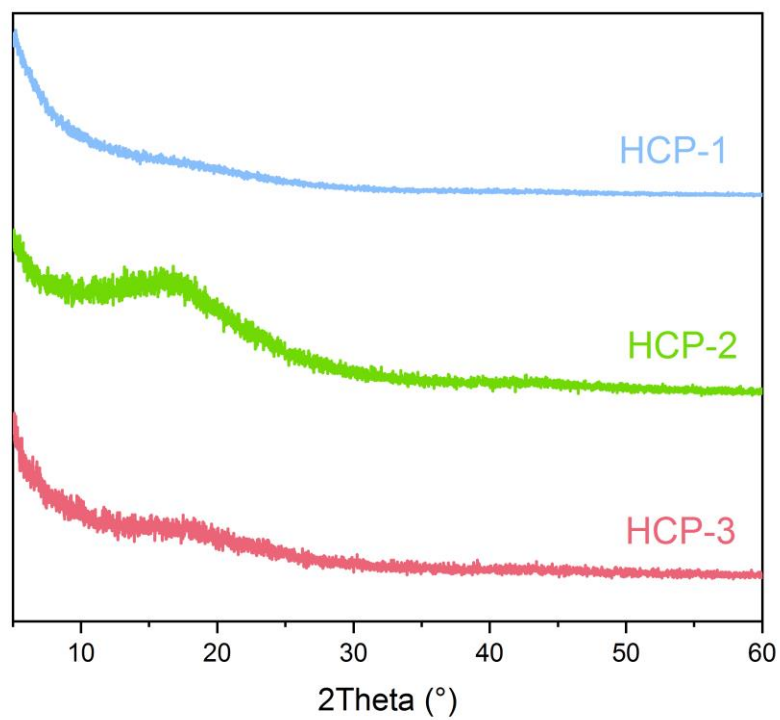


Figure S7. PXRD patterns of a) HCP-1, b) HCP-2, and c) HCP-3.

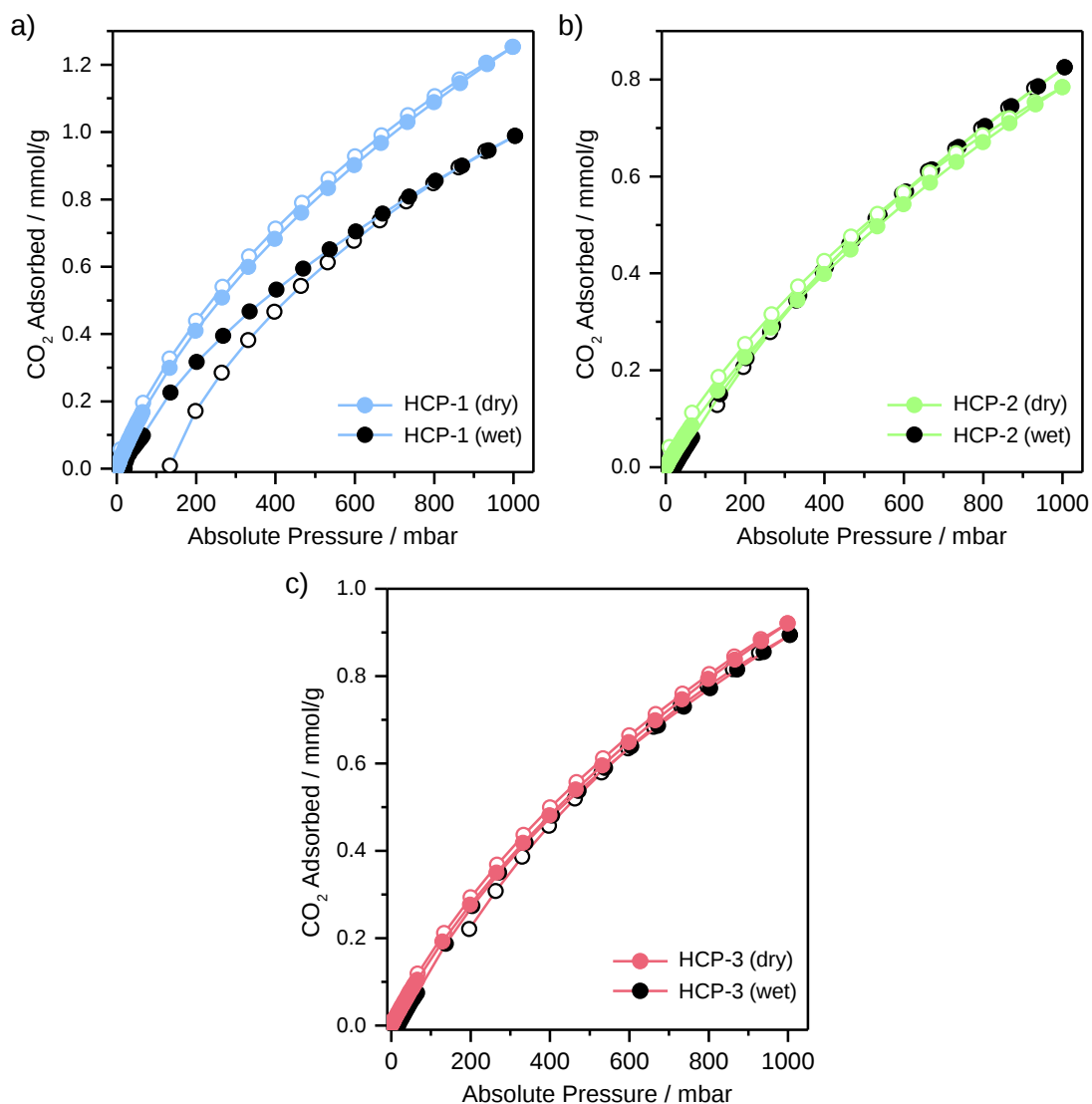


Figure S8. CO₂ adsorption isotherms at 298 K of both dry and wet (i.e. exposed to humid air for at least 48 h before measurement, 99% humidity) networks. a) HCP-1, b) HCP-2, and c) HCP-3. Filled symbols represent adsorption, empty symbols represent desorption.

Table S3. Textural parameters derived from N₂ sorption isotherms at –196 °C and CO₂ adsorption capacities at 25 °C.

Sample	V _{MICRO} (cm ³ /g) ^a	V _{TOT} (cm ³ /g) ^a	SA _{BET} (m ² /g) ^a	CO ₂ ad. (mmol/g)	
				Dry ^b	Wet ^c
HCP-1	0.46	1.07	950	1.25	0.99
HCP-2	0.13	0.21	310	0.78	0.82
HCP-3	0.16	0.25	360	0.92	0.89
HCP-3 after irradiation	0.11	-	300	-	-

^aDerived from N₂ sorption isotherms at – 196 °C .

^bCapacity of degassed HCP at 25 °C and 1 bar

^cCapacity of non-degassed HCP at 25 °C and 1 bar after 48 h exposure to humid atmosphere

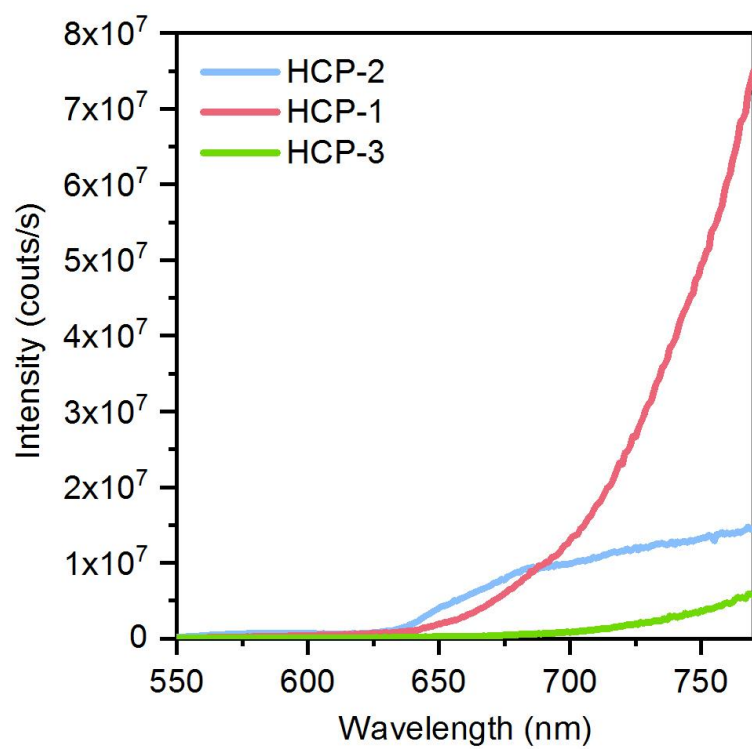


Figure S9. Photoluminescence emission spectra

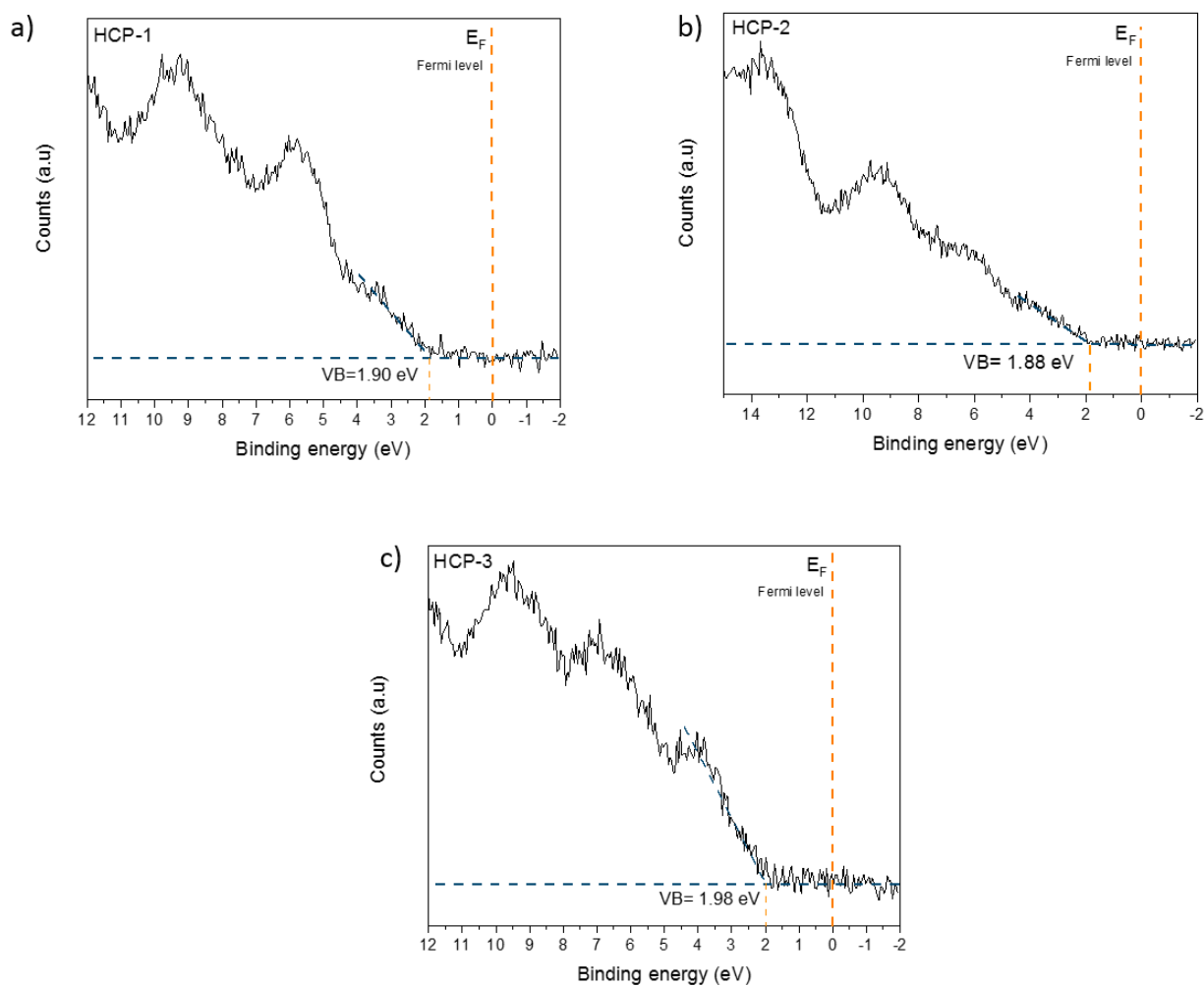


Figure S10. Valence band XPS spectra of a) HCP-1, b) HCP-2, and HCP-3.

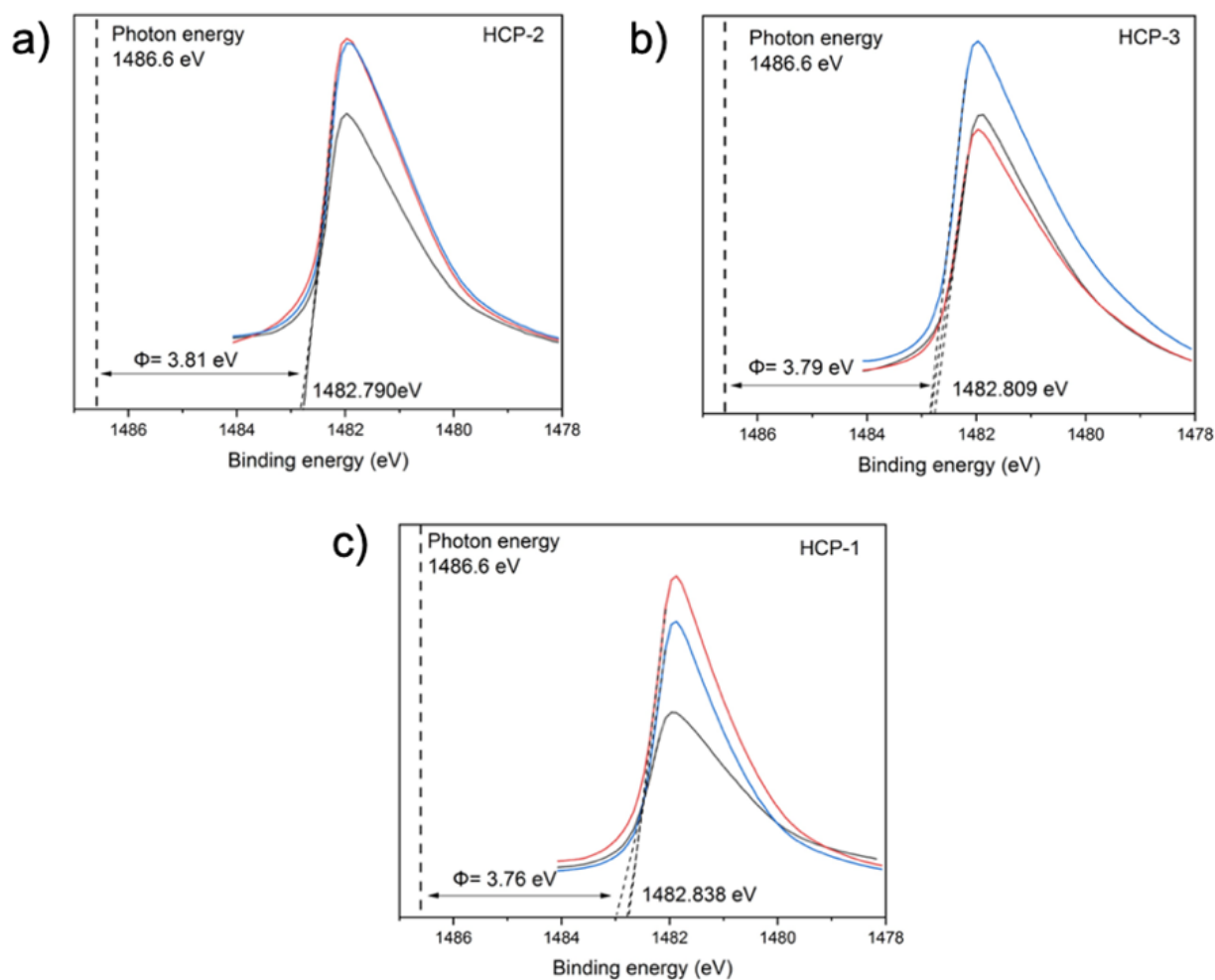


Figure S11. Work function measurements at three different locations on a) HCP-2, b) HCP-3, and c) HCP-1 to account for potential variations across the surface.

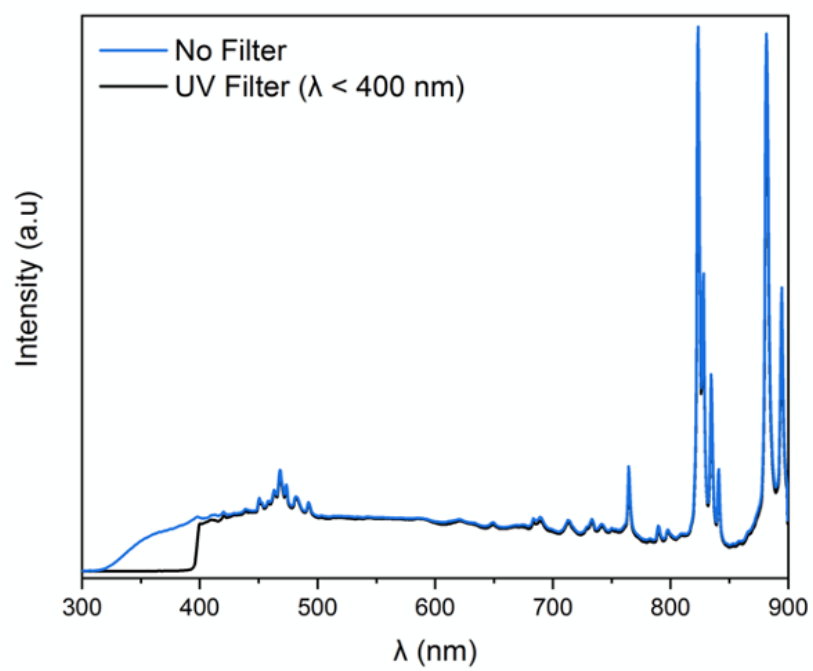


Figure S12. Xenon arc lamp emission spectra, (300W, LOT Quantum Design), equipped with a water filter.

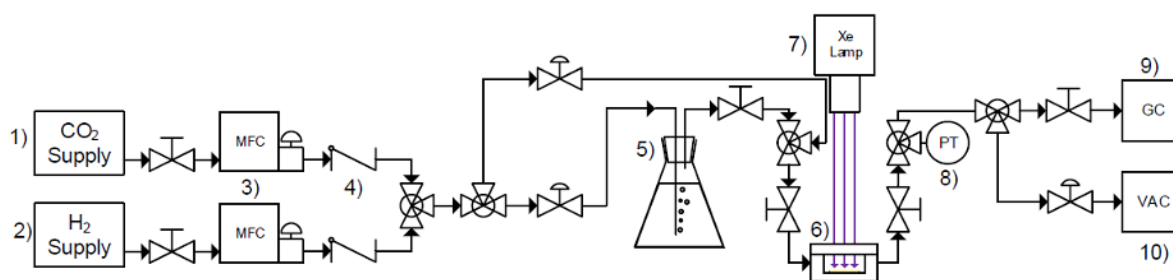


Figure S13. Photocatalytic gas-solid reactor setup used to evaluate photocatalytic CO₂ reduction: 1) CO₂ cylinder, 2) H₂ generator, 3) mass flow controllers, 4) non-return valves, 5) H₂O saturator, 6) photoreactor, 7) Xe arc lamp, 8) pressure transducer, 9) gas chromatograph, 10) vacuum pump.^[3]

Table S4. Photocatalytic evolution rates of HCP-1, HCP-2, HCP-3, and TiO₂ P25 and control experiments

Sample	UV-vis (Sacrificial H ₂)		UV-vis (Sacrificial H ₂ O)		Visible (Sacrificial H ₂ O)	
	CO*	CH ₄ *	CO*	CH ₄ *	CO*	CH ₄ *
HCP-1	3.7 ± 0.1	0	8.6 ± 0.1	0.4 ± 0.1	4.2	0.1
HCP-2	1.6 ± 0.3	0.1 ± 0.1	4.6 ± 0.5	0.4 ± 0.2	1	0
HCP-3	6.3 ± 0.2	0.5 ± 0.1	15.6 ± 0.9	0.4 ± 0.1	5.2	0.1
P25 (TiO ₂)	6.4 ± 0.4	0.3 ± 0.2	14.7 ± 0.9	0.3 ± 0.1	0.69	0.2
N ₂ /H ₂ O, no catalyst	-	-	0	-	-	-
N ₂ /H ₂ O ^a	-	-	3.58 (23% ^c)	-	-	-
N ₂ /H ₂ O repeat ^{a,b}	-	-	3.78 (24% ^c)	-	-	-
N ₂ /H ₂ O ^a	-	-	-	-	0.82 (15% ^c)	-
N ₂ /H ₂ O repeat ^{a,b}	-	-	-	-	1.06 (20% ^c)	-
N ₂ /H ₂ ^a	0.74 (12% ^c)	-	-	-	-	-
N ₂ /H ₂ repeat ^{a,b}	0.61 (10% ^c)	-	-	-	-	-
CO ₂ / H ₂ O, no light ^a	-	-	0.16 (1% ^c)	-	-	-
CO ₂ / H ₂ O, no catalyst	-	-	10 ppm	-	-	-

* All data are given in $\mu\text{mol.g}^{-1}\cdot\text{h}^{-1}$

^a tests were performed on HCP-3, the leading material of this study

^b repeat samples were done on the same sample as the first one, without opening the photo-reactor

^c percentage compared to the total activity of HCP-3

Apparent quantum yield (AQY) calculations

The apparent quantum yield at a given wavelength λ is defined as:

$$AQY = \frac{N_e}{N_p} = \frac{\text{no.of reacted electrons}}{\text{no.of absorbed photons}} \times 100 \quad (\text{Equation S1})$$

Based on the stoichiometry of the CO evolution redox reaction:

$$AQY = \frac{2N_{CO}}{N_p} = \frac{(2)(\text{no.of evolved CO molecules})}{\text{no.of absorbed photons}} \times 100 \quad (\text{Equation S2})$$

For a polychromatic light source, we must consider the total number of absorbed photons across the wavelength range (270 – 900 nm for UV-vis and 400 – 900 nm for visible irradiation) and the corresponding total moles of CO evolved during the irradiation time:

$$AQY = \frac{2N_{CO}(\text{total})}{N_p} = \frac{(2)(\text{total no.of evolved CO molecules})}{\text{no.of absorbed photons}} \times 100 \quad (\text{Equation S3})$$

The number of photons absorbed by the photocatalyst at a given wavelength λ is given by:

$$N_{P,absorbed} = \frac{(P_{abs})(\lambda)(t)}{(hc)} \quad (\text{Equation S4})$$

where λ denotes the wavelength, P denotes the power of the irradiation source, t denotes the irradiation time, h denotes Planck's constant and c the speed of light.

Equation S4 can be written in terms of the intensity of the irradiation as a function of the irradiation absorbed at wavelength λ , $[I_{abs}(\lambda)]$, and irradiation area (S) as:

$$N_{P,absorbed} = \frac{[I_{abs}(\lambda)](S)(\lambda)(t)}{(hc)} \quad (\text{Equation S5})$$

To account for the number of photons absorbed by the photocatalyst at a given wavelength λ , we need to consider the absorbance (Abs) of the material at that wavelength and apply the Beer-Lambert law:

$$Abs(\lambda) = -\log \left[\frac{I_F(\lambda)}{I_I(\lambda)} \right] \quad (\text{Equation S6})$$

where $I_I(\lambda)$ denotes the intensity emitted from the irradiation source at a given wavelength λ and $I_F(\lambda)$ denotes the intensity after passing through the photocatalyst at the same wavelength λ .

The intensity of irradiation absorbed by the photocatalyst at a given wavelength λ is given by:

$$I_{abs}(\lambda) = I_I(\lambda) - I_F(\lambda) \quad (\text{Equation S7})$$

which, using equation (S6), can be written as:

$$I_{abs}(\lambda) = I_I(\lambda) - I_I(\lambda)10^{-Abs(\lambda)} = I_I(\lambda)[1 - 10^{-Abs(\lambda)}] \quad (\text{Equation S8})$$

Substituting equation (S8) into equation (S5) gives

$$N_{P,absorbed} = \frac{I_I(\lambda)[1-10^{-Abs(\lambda)}](S)(\lambda)(t)}{(hc)} \quad (\text{Equation S9})$$

The total number of photons absorbed by the photocatalyst across the entire wavelength range of the irradiation source is then given by:

$$N_{P,absorbed (total)} = \sum_{\lambda_{start}}^{\lambda_{end}} \frac{I_I(\lambda)[1-10^{-Abs(\lambda)}](S)(\lambda)(t)}{(hc)} \quad (\text{Equation S10})$$

$$N_{P,absorbed (total)} = \frac{(S)(t)}{(hc)} \sum_{\lambda_{start}}^{\lambda_{end}} I_I(\lambda)[1 - 10^{-Abs(\lambda)}](\lambda) \quad (\text{Equation S11})$$

The total number of evolved CO molecules during a given reaction cycle can be written as

$$N_{CO(total)} = (N_a)(n_{CO,total}) \quad (\text{Equation S12})$$

where N_a denotes Avagadro's constant and $n_{CO,total}$ denotes the total moles of CO evolved during the irradiation time.

Substituting equations (S11) and (S12) to (S3) gives us the final expression for the apparent quantum yield for CO evolution:

$$AQY = \frac{(2) N_{CO (total)}}{N_P} = \frac{(2)(N_a)(n_{CO,total})}{\frac{(S)(t)}{(hc)} \sum_{\lambda_{start}}^{\lambda_{end}} I_I(\lambda) [1 - 10^{-abs(\lambda)}](\lambda)} \times 100 \quad (\text{Equation S13})$$

Table S5. Apparent quantum yield calculation of HCP-3

Sample	UV-vis irradiation (sacrificial H ₂ O)	Visible irradiation (sacrificial H ₂ O)
HCP-3	0.002 %	0.0005 %

*The apparent quantum yield was calculated from a polychromatic light source. The total number of absorbed photons across the wavelength range (270 – 900 nm for UV-Vis and 400 – 900 nm for visible irradiation) was taken into consideration.

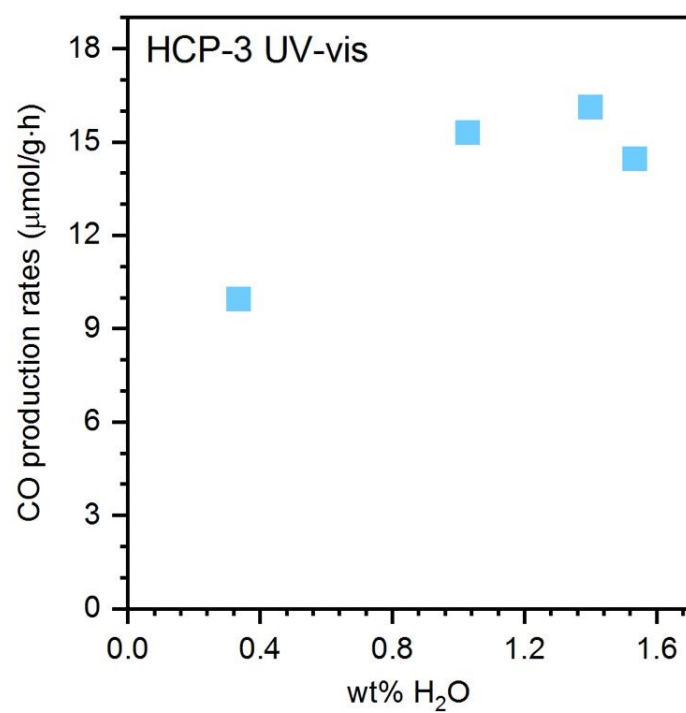


Figure S14. CO production rates of HCP-3 under UV-vis irradiation using different water vapour contents.

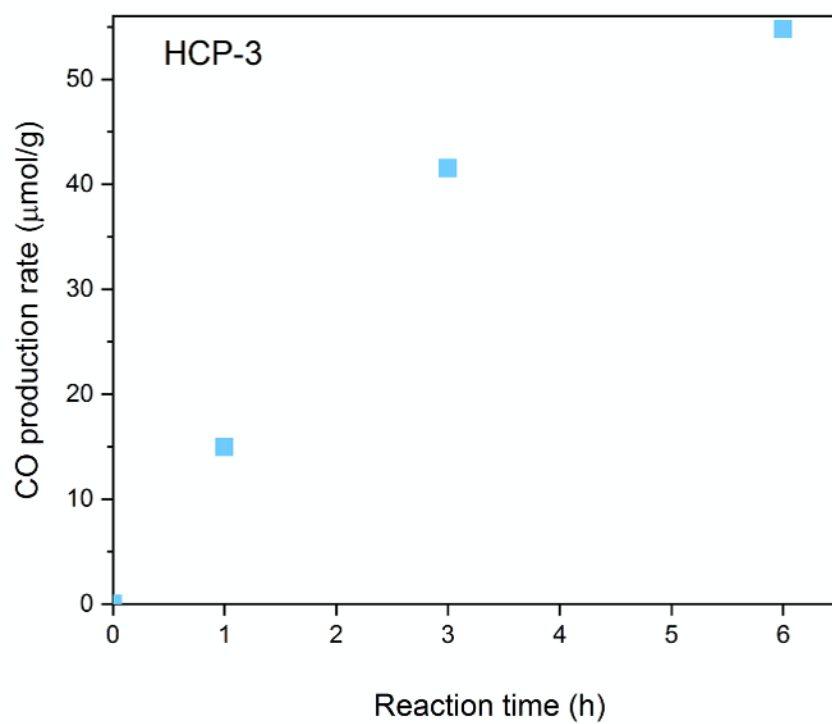


Figure S15. Photocatalytic CO evolution from HCP-3 under UV-vis irradiation as a function of time.

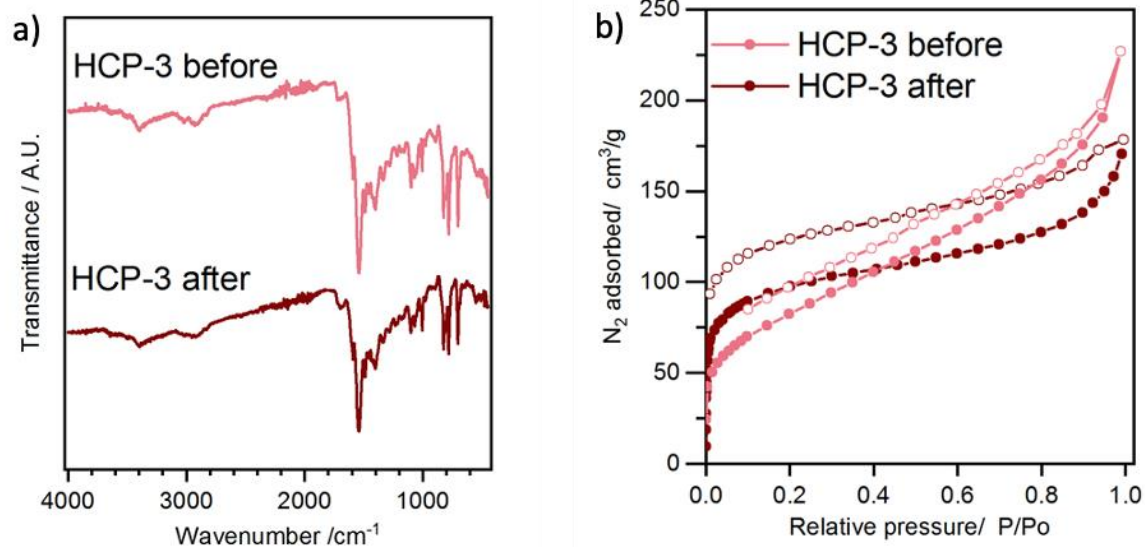


Figure S16. a) FTIR and b) N_2 adsorption isotherms at 77 K of HCP-3 before and after 3h UV-vis irradiation.

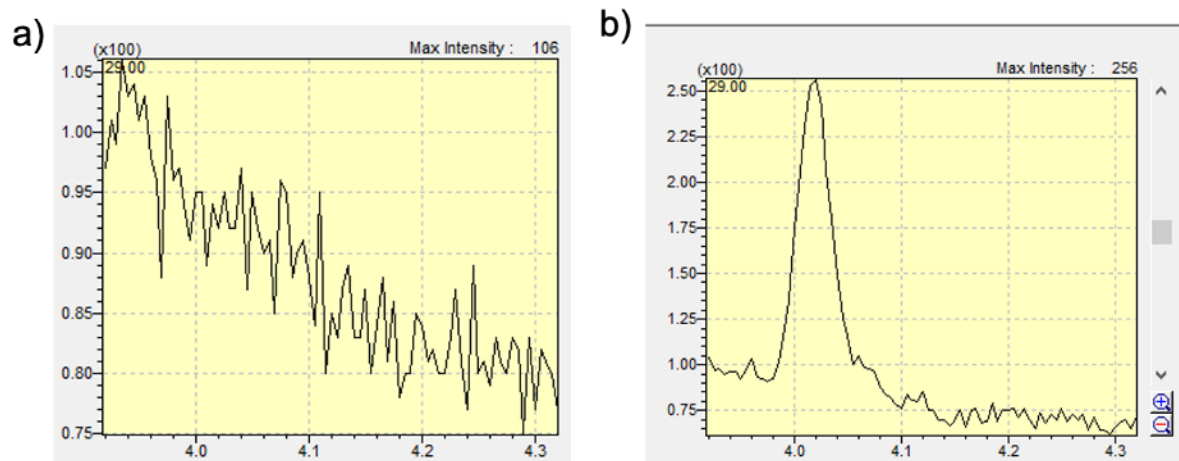


Figure S17. Isotopic $^{13}\text{CO}_2$ measurements. Mass spectrum chromatogram of HCP-3 illustrating the ^{13}CO ($m/z = 29$) peak observed with the photocatalytic $^{13}\text{CO}_2$ reduction system after a) 0 min and b) 4h UV-vis irradiation.

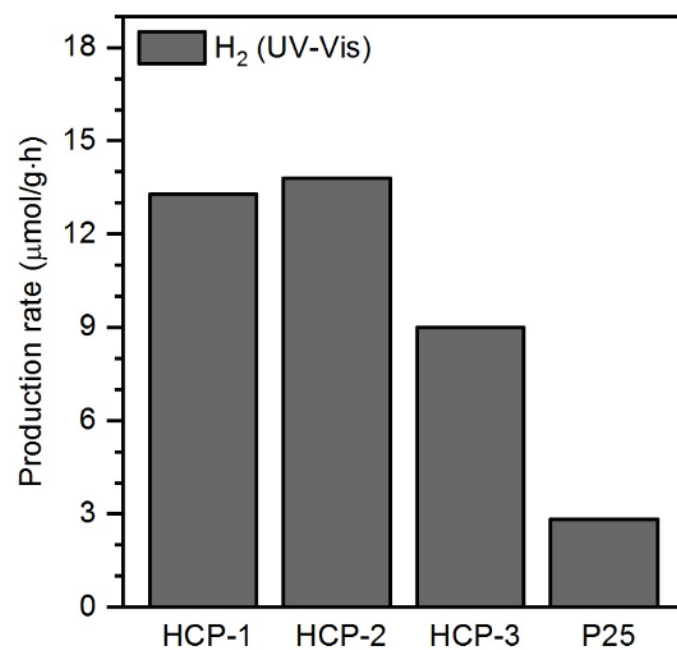


Figure S18. H₂ production rates of HCPs under UV-vis irradiation using H₂O as sacrificial agent.

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Hypercrosslinked polymers as a photocatalytic platform for visible-light-driven CO₂ photoreduction using H₂O

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Abstract: The design of robust, high-performance photocatalysts is key for the success of solar fuel production via CO₂ conversion. Herein, we present hypercrosslinked polymer (HCP) photocatalysts for the selective reduction of CO₂ to CO, combining excellent CO₂ sorption capacities, good general stabilities, and low production costs. HCPs are active photocatalysts in the visible light range, significantly out-performing the benchmark material, TiO₂ P25, using only sacrificial H₂O. We hypothesise that superior H₂O adsorption capacities led to concentration at photoactive sites, improving photocatalytic conversion rates when compared to sacrificial H₂. These polymers are an intriguing set of organic photocatalysts, displaying no long-range order or extended pi-conjugation. The as-synthesised networks are the sole photocatalytic component, requiring no co-catalyst doping or photosensitiser, representing a highly versatile and exciting platform for solar-energy conversion.

Keywords: Carbon dioxide photoreduction • Hypercrosslinked polymers • Photocatalysis • Porous organic polymers • Solar fuels

Introduction

The ever-increasing global energy demand requires a significant overhaul of current production processes if humanity is to address climate change. Carbon management and renewable energy must play a key role in our energy outlook, challenging researchers to reshape our energy portfolio. Research efforts are focused on the development of efficient carbon capture, utilisation, and storage (CCUS) technologies, as well as the improvement of methods to harness renewable energy.^[1] The use of sunlight shows promise towards the building of a sustainable chemical industry. Solar fuels are synthetic fuels produced *via* the conversion of solar energy into chemical energy, namely H_2 from H_2O , and C_1 and C_{1+} chemicals from CO_2 . This conversion can be done by a variety of processes, including photochemical (often named artificial photosynthesis), thermochemical, and electrochemical reactions. However, overcoming the high thermodynamic and kinetic barriers to conversion is challenging, and so a catalyst is required to improve energy efficiency and, ultimately, render these processes viable.^[2-3]

Here, we focus on a photochemical route to solar fuel production, namely photocatalysis, whose main advantage lies in the simplicity of its implementation. To date, 'traditional' semiconductors, *e.g.* metal oxide/sulfides and transition metal complexes, such as TiO_2 , CdS , ZnO , WO_3 , Ru-, Re- and Pd-based complexes have received much attention as photocatalysts, owing to their ability to generate charge carriers under light irradiation.^[4-7] However, a lack of structural versatility and notoriously difficult to tune frontier energy levels in inorganic materials often limit their performance, while the requirement of rare-earth metals presents significant sustainability issues. Moreover, traditional semiconductors are often predominantly active at ultraviolet wavelengths, constituting just ~4% of the solar spectrum, prompting great interest in the development of visible light-active photocatalysts for improved efficiency.

The development of new classes of photoactive materials, including inorganic-organic hybrids, such as metal-organic frameworks (MOFs), or organic-based materials, such as porous organic polymers, have emerged as promising alternatives to traditional photocatalysts.^[8-12] The structural versatility of polymers enables photochemical tunability and, ultimately, optimisation of

photocatalytic performance. Owing to their general chemical inertness and non-metallic nature, porous organic polymers are of particular interest in the design of new photocatalysts. Yang et al. reported triazine-based conjugated microporous polymers (CMPs) for CO₂ photoconversion to CO using visible light.^[13] The optical band gap of the materials was engineered by the inclusion of various electron-withdrawing and electron-donating groups. Yu et al. employed Pd-catalysed Sonogashira–Hagihara coupling to produce Eosin Y-functionalised porous polymers, able to photoreduce CO₂ to CO with 92% selectivity, using visible light and sacrificial H₂O.^[14] More recently, Fu et al. reported rhenium-doped covalent-organic frameworks (COFs), with high CO₂ photoreduction rates in the presence of acetonitrile and sacrificial triethanolamine.^[12] Furthermore, a metal-free COF produced using solvothermal condensation reactions was reported as a visible-light-driven photocatalyst for CO₂ photoreduction in the presence of water.^[12, 15] While demonstrating the potential of porous organic polymers for CO₂ photoreduction, the synthesis of porous organic polymer photocatalysts generally requires the use of rare-earth metals, or specifically polymerisable monomeric units, presenting implementation barriers due to relatively high-costs and poor sustainability.

Hypercrosslinked polymers (HCPs) represent a class of materials with excellent tunability and relatively low costs. HCPs are densely crosslinked amorphous networks, produced using simple Friedel-Crafts chemistry. Non-functional aromatic compounds (*i.e.* without specifically polymerisable groups) can be ‘knitted’ together using an external crosslinker, requiring only iron(III) chloride as catalyst.^[16] The employment of external crosslinkers means a large array of aromatic compounds can be considered as monomeric material, providing substantial scope for the design of HCPs. Owing to their low cost and chemical versatility, HCPs are being developed for many different applications such as gas separation and storage,^[17-18] solid-state extraction,^[19-20] and in catalysis.^[21] Recently, Wang et al. used an HCP-TiO₂-graphene composite for the photoreduction of CO₂, with the HCP component aiding CO₂ adsorption and diffusion.^[22] The ability of HCPs alone to catalyse solar fuel production, however, remains unknown.

Herein, we present HCPs as a new class of photocatalyst capable of selectively reducing CO₂ to CO. Photocatalytic conversion was achieved using only visible light in the presence of sacrificial H₂O, without additional sacrificial agents or co-catalysts, significantly out-performing TiO₂ P25 (x7.5

times). The influence of the reducing agent was investigated (i.e. H_2 vs. H_2O). Surprisingly, employing sacrificial H_2O led to significant improvements in photoconversion rates. We hypothesise that the preferential adsorption of H_2O concentrates the sacrificial agent at the HCP's surface, driving photocatalytic performance. Owing to their lack of requirement for precious-metal catalysts, as well as their easily scaled chemistry, HCPs present an exciting platform for the further design and discovery of high-performance organic photocatalysts.

Results and Discussion

Hypercrosslinked polymer synthesis and characterisation. We synthesised three HCPs of varied chemical structure, **HCP-1**, **HCP-2**, and **HCP-3** *via* a Friedel-Crafts alkylation reaction using external crosslinkers to 'knit' together aromatic monomers. A general reaction scheme and representative HCP structures are shown in Figure 1a,b. HCP-1 was produced *via* the crosslinking of benzene, using an aliphatic dimethoxymethane external crosslinker, one of the most widely-studied HCPs in recent years.^[23] HCP-2 is comprised of aniline crosslinked using the benzyl ether compound 4,4-bis(methoxymethane)biphenyl, as the analogous polymer produced using dimethoxymethane was non-porous.^[24] Finally, HCP-3 consisted of 2,4-diamino-6-phenyl-1,3,5-triazine crosslinked using 4,4-bis(methoxymethane)biphenyl. We chose the chemistries of HCP-2 and HCP-3 to try to improve the CO_2 adsorption selectivity *via* the inclusion of amino groups. Photographic images of the networks (Figure S1) reveal a colour gradient from dark to light brown from HCP-1 to HCP-3.

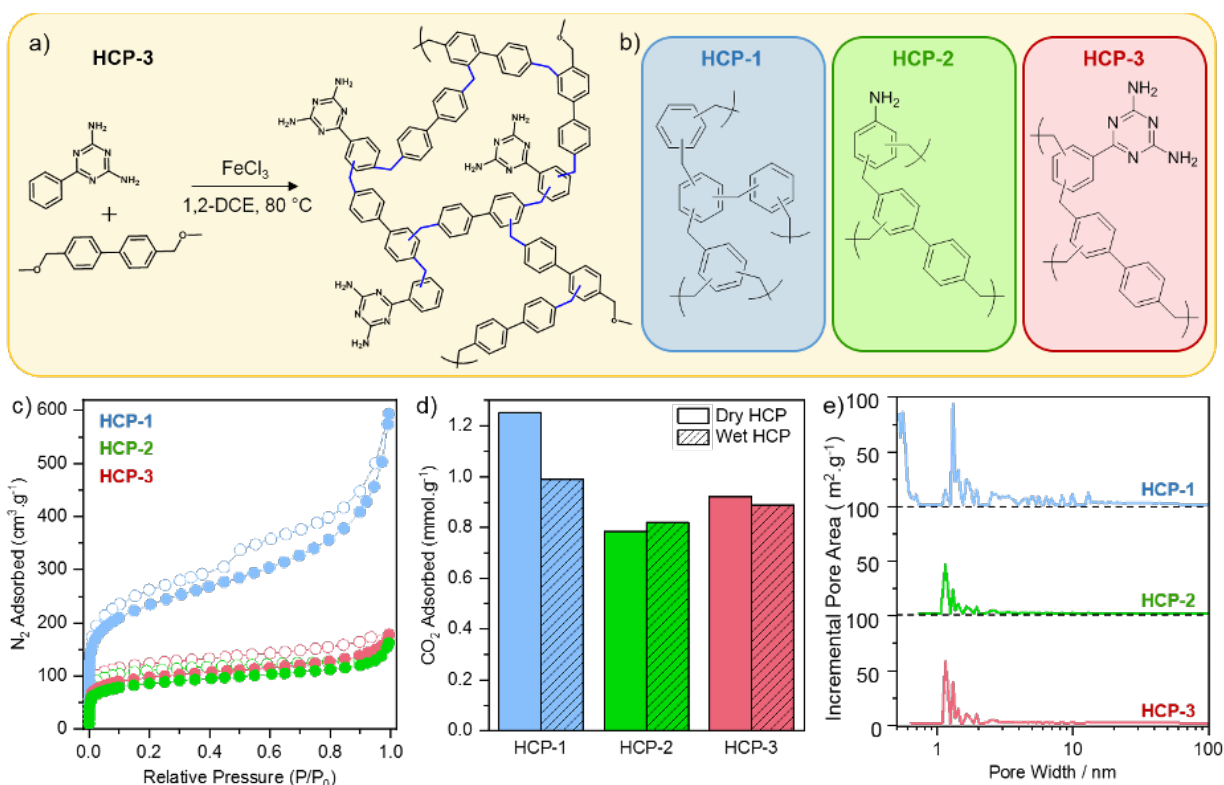


Figure 1. a) Reaction scheme for the production of HCP-3 by Friedel-Crafts alkylation, b) representative chemical structures of HCP repeat units, c) N_2 adsorption isotherms at -196°C , filled symbols represent adsorption and empty symbols represent desorption, d) CO_2 uptake at 1 bar and 25°C for HCPs in both 'dry' and 'wet' states, i.e. HCPs exposed to humid atmospheres before measurement, e) pore size distributions of HCPs, calculated using DFT method.

We successfully incorporated the aromatic monomers into the networks, as confirmed using Fourier-transfer infrared spectroscopy (FTIR), which showed distinct stretches for primary amines in HCP-2 and HCP-3, and the triazine tertiary amines in HCP-3 (Figure S2). HCP-2 and HCP-3 contain 1.3 and 7.9 at% N, respectively, as determined via X-ray photoelectron spectroscopy (XPS) survey spectra (Figure S4 and Table S2). These values correspond to final polymer compositions of roughly 1:4 and 1:3 monomer to crosslinker ratios for HCP-2 and HCP-3, respectively. Scanning electron micrographs revealed HCP-1 and HCP-3 as agglomerated spherical particles, whereas HCP-2 shows a more fibrous structure (Figure S4). Thermogravimetric analysis demonstrated the high thermal stability of all HCPs, with decomposition temperatures of $>300^\circ\text{C}$ in both N_2 and air atmospheres (Figure S5-6). Char yields in N_2 at 900°C were $> 60\%$ in

all HCPs, while complete degradation was observed in air at $> 550\text{ }^{\circ}\text{C}$. Powder X-ray diffraction confirmed the amorphous nature of all HCP networks (Figure S7).

We used N_2 sorption measurements at $-196\text{ }^{\circ}\text{C}$ to assess the porous nature of the networks. HCP-1, HCP-2, and HCP-3 exhibited BET surface areas of 951, 311, and $357\text{ m}^2/\text{g}$, respectively (Figure 1c and Table S3). All HCPs displayed a combination of type I and type IV isotherms,^[25] with significant microporosity, as indicated by the steep N_2 uptake at low relative pressures, as well as meso/macroporosity. Micropore volume was highest in HCP-1 ($0.46\text{ cm}^3/\text{g}$), dropping to 0.13 and $0.16\text{ cm}^3/\text{g}$ for HCP-2 and HCP-3, respectively, reflecting trends seen in the polymer's BET surface areas. Figure 1e highlights a multimodal pore size distribution for all networks, predominantly concentrated in the micropore region. Pores of around 0.5 nm in size contribute noticeably to HCP-1's surface area, whereas both HCP-2 and HCP-3 do not show any significant area derived from pores smaller than 1 nm in diameter.

To assess the CO_2 uptake ability of HCPs, we collected adsorption isotherms at $25\text{ }^{\circ}\text{C}$ up to 1 bar (full isotherms are shown in Figure S8). Although the HCPs followed the expected trend, *i.e.* higher surface area polymers adsorbed more CO_2 , the CO_2 capacities did not reflect the large differences in surface areas (Table S3). The presence of the amino groups in HCP-2 and HCP-3, which are known to impart CO_2 selectivity to hypercrosslinked polymers,^[26] increased uptake density per unit of surface area due to more attractive interactions with the adsorbate CO_2 .^[27-28]

The presence of adsorbed water was shown to impede CO_2 uptake in polar HCPs, due to competitive adsorption.^[29] Therefore, we investigated the effect of H_2O and CO_2 co-adsorption, since we used sacrificial H_2O vapour in CO_2 photoreduction (see below). We exposed the samples to humid air ($>99\%$ humidity) for at least 48 h before collecting CO_2 adsorption isotherms at $25\text{ }^{\circ}\text{C}$ up to 1 bar. Crucially, samples were not degassed prior to CO_2 adsorption measurements (details in ESI), *i.e.* adsorbed H_2O was not removed. These conditions are close to those in photoreduction experiments. The CO_2 sorption capacities at 1 bar are given in Figure 1d. The full isotherms of both degassed, "dry", and humidity-exposed, "wet", HCPs are shown in Figure S8. Wet HCP-1 showed a 21% decrease in CO_2 capacity in comparison to its dry equivalent, while the amine-containing HCP-2 and HCP-3 showed negligible difference in CO_2 uptake between the wet and dry networks. These uptake capacities demonstrate the minimal impact of water co-adsorption, emphasising the

selective adsorption of CO₂ by the polymers, particularly HCP-2 and HCP-3. During photoreduction experiments, we did not expose HCPs to water vapour prior to CO₂ reduction, but rather a stream of CO₂ containing water vapour. As such, the effect of co-adsorption is likely to be less significant *in-situ*.

CO₂ photoreduction activity of hypercrosslinked polymers

To evaluate the potential of HCPs for CO₂ photoreduction, we investigated their optoelectronic properties using UV-visible diffuse reflectance spectroscopy (UV-vis DRS). The UV-vis spectra show all HCPs absorb light in both the UV and visible range, with absorption onsets of 348, 350, and 389 nm for HCP-1, HCP-2 and HCP-3, respectively (Figure 2a). All three HCPs exhibited photoluminescence above 550 nm (Figure S9), and as shown in Figure 2b we probed their photoluminescence lifetimes at 700 nm using time-correlated single photon counting (TCSPC) upon 282 nm excitation. The time at which the photoluminescence signal has decayed to half its initial amplitude (half-lifetime) was 1.9 ns, 2.2 ns, and 3.2 ns for HCP-1, HCP-2, and HCP-3, respectively, which demonstrates that HCP-3 has a substantially longer excited state lifetime than HCP-1 or HCP-2. We estimated the HCP's valence band (VB) and conduction band (CB) positions by complementing our UV-vis DRS data with XPS measurements (Figure 2c). First, valence band XPS measurements allowed us to ascertain the distance between the Fermi level (E_F) and the VB onset, also known as VB offset (Figure S10). Placing the VB offset on the absolute energy scale requires knowledge of the position of the Fermi level, which was determined by measuring the secondary electron cut-off through XPS work function measurements (Figure S11). Finally, we identified the CB position using the UV-vis spectra absorption onset. For all HCPs, the CB is located above the reduction potential of CO₂/CO and the VB below the oxidation potential of both H₂/H₂O and O₂/H₂O. Hence, the band diagrams point towards a sufficient thermodynamic driving force to enable the reduction of CO₂ to CO using either gaseous H₂ or H₂O as a sacrificial agent. The Fermi level of all HCPs lies closer to the CB than the VB, suggesting electrons are the major charge carriers, which is desirable for CO₂ photoreduction. Overall, the narrow band gaps and visible light absorption properties of HCPs, as well as their CO₂ adsorption capacities, make them *a priori* attractive candidates for CO₂ photoreduction.

After establishing their CO₂ adsorption ability and desirable optoelectronic properties, we tested HCPs for the photocatalytic reduction of gaseous CO₂. We conducted the tests in a heterogeneous gas/solid photoreactor at ambient temperature, using either H₂ or H₂O as a sacrificial agent under UV-vis or visible irradiation alone (Xe arc lamp, 300 W, Figure S12). No co-catalyst or photosensitiser was required, but some residual iron is present from the HCP synthesis and may play a role in the photoreduction activity (Table S1) as shown with Pd for other organic materials in the context of H₂ evolution.^[30-31] A representative sample of HCP-2 was found to contain 246 ppm of Fe. Under the same conditions, digestion of HCP-1 and HCP-3 was unsuccessful and the iron content could not be estimated. A gas phase reactor was chosen to combine CO₂ capture and CO₂ conversion, avoiding limitations owing to poor CO₂ solubility in some liquid phase reactions (Figure S13). In each experimental set, we compared HCP performance to that of the benchmark TiO₂ P25. For all HCPs, after 3 hours of irradiation the primary carbonaceous product observed was CO, with a selectivity of up to 96% and 95% using sacrificial H₂ or H₂O, respectively (Figure 2d and 2e, Table S4, Table S5). Trace CH₄ was also detected, representing the only other carbonaceous product measured. Regardless of the sacrificial agent, HCP-2 exhibited the lowest CO production rate, while HCP-3 displayed the highest. The photocatalytic performance of HCP-3 was comparable to that of TiO₂ P25 under UV-vis light and was up to 7.5 times better when irradiated with only visible light (Figure 2e, Table S4). In fact, we observed photocatalytic activity for all HCPs under visible light alone, a significant finding for organic materials requiring no doping or co-catalyst. The decrease in activity under visible light compared to UV-vis is rationalised using their UV-vis absorption spectra (Figure 2a). As HCP-1 is the network that shows the highest light absorption in the visible region, its photoactivity is the least affected by the absence of UV light.

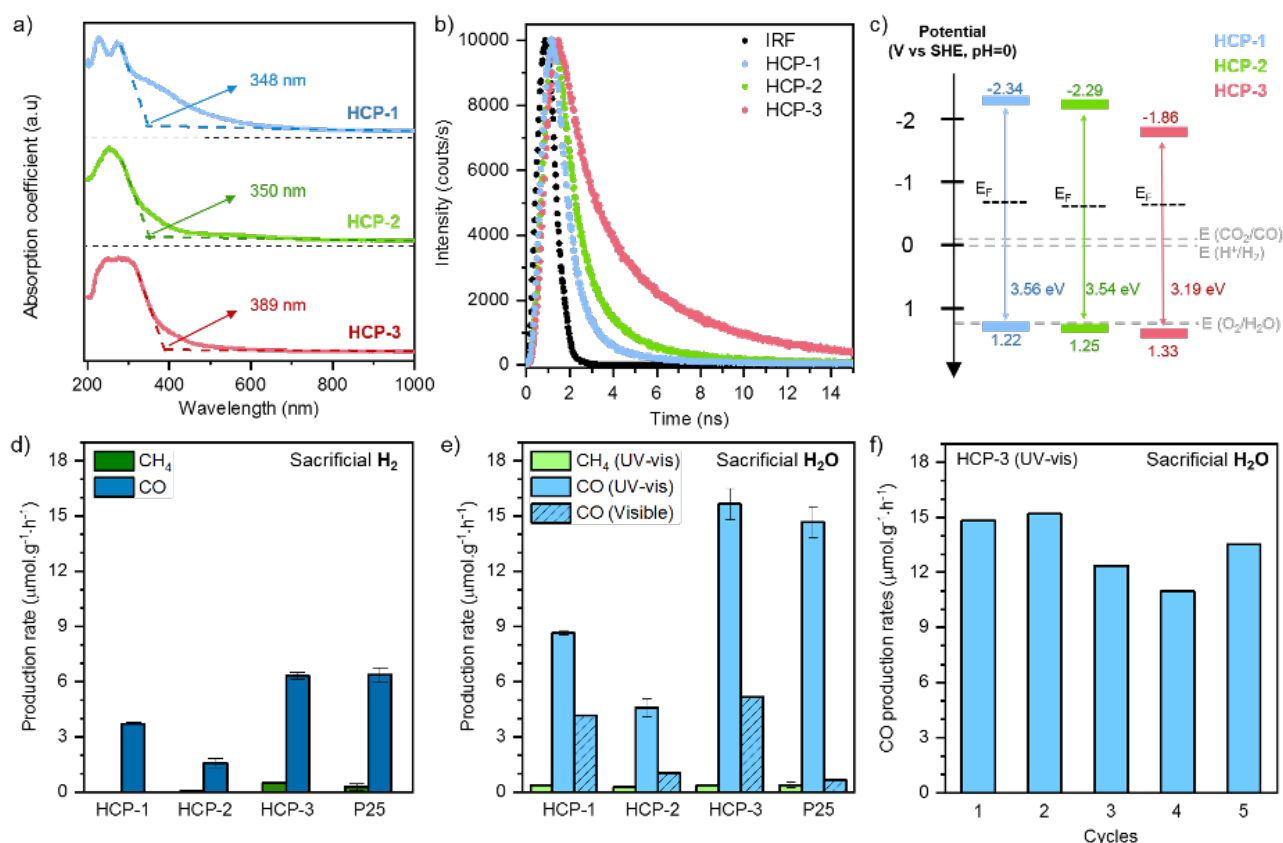


Figure 2. a) UV-vis absorption coefficient spectra with absorption onsets indicated, b) photoluminescence decay kinetics probed at 700 nm following excitation at 282 nm, along with the instrument response function (IRF) probed at the excitation wavelength, c) band gap position, d) photocatalytic production rates using sacrificial H_2 in UV-vis, e) photocatalytic production rates using sacrificial H_2O in both UV-vis and visible light alone, f) HCP-3 recyclability test over 5 cycles of 3 h irradiation using UV-vis light and sacrificial H_2O .

Activity in the visible range is promising for the future of HCP photocatalysts in real-world applications as visible light comprises a large portion of the sun's output reaching the Earth's surface. Targeted network modifications might allow further optimisation of this visible light activity. The high photocatalytic activity of HCP-3 likely arises from the presence of triazine groups. Lee et al. reported stronger electrostatic CO_2 interactions in triazines when compared to benzene and amino groups, as are present in HCP-1 and HCP-2, respectively.^[32] Triazine groups may also offer an additional delocalisation of the electrons, favouring lower electron-hole recombination.^[33-34] Time-resolved photoluminescence showed that HCP-3 displayed the lowest electron-hole recombination rates (Figure

2b), offering more opportunity for charges to migrate to the surface of the photocatalyst for CO₂ photoconversion. To gain further insights on the key parameters influencing CO₂ adsorption and photoconversion, a systematic HCPs screening is required.

Interestingly, CO₂ photoreduction performance of HCPs improved by up to 2.5 times when replacing H₂ with sacrificial H₂O (Figure 2 d,e). From a thermodynamic standpoint, such behaviour is intriguing as H₂O oxidation requires a higher driving force than H₂ oxidation. We hypothesised that the increased photoactivity in the presence of H₂O is due to HCPs displaying significantly improved adsorption capacities for H₂O when compared to H₂. This leads to an increased availability of the sacrificial agent at the photoactive sites on the HCPs' surface, improving photoreduction rates. To investigate this hypothesis, we collected pure H₂ and H₂O adsorption isotherms for all HCPs (Figure 3). From the pure adsorption isotherms, under operating conditions (atmospheric pressure, 25 °C) HCPs adsorbed <0.1 mmol/g of H₂, in comparison to between 2 and 9.4 mmol/g for H₂O, an increase of 2 orders of magnitude. A higher concentration of sacrificial agent at the HCP's surface should favour high CO₂ photoreduction rates, explaining the increase of photoactivity when using H₂O as reducing agent.

To further investigate the importance of H₂O adsorption on the photoactivity, we decreased the humidity inside the photoreactor by decreasing the temperature of the H₂O vapour saturator to ~ 1 °C. At 1 °C, the partial pressure of H₂O at saturation is reduced (6.6 mbar), dramatically reducing the concentration of H₂O introduced into the system. After sealing the reactor, we conducted CO₂ photoreduction measurements at 25 °C, under atmospheric pressure. The decreased humidity of the stream resulted in a 38% decrease in activity for HCP-3 (Figure S14). Indeed, H₂O uptake in this network is reduced to around 0.4 mmol/g at 6.6 mbar, as estimated from the pure water sorption isotherm (Figure 3b).

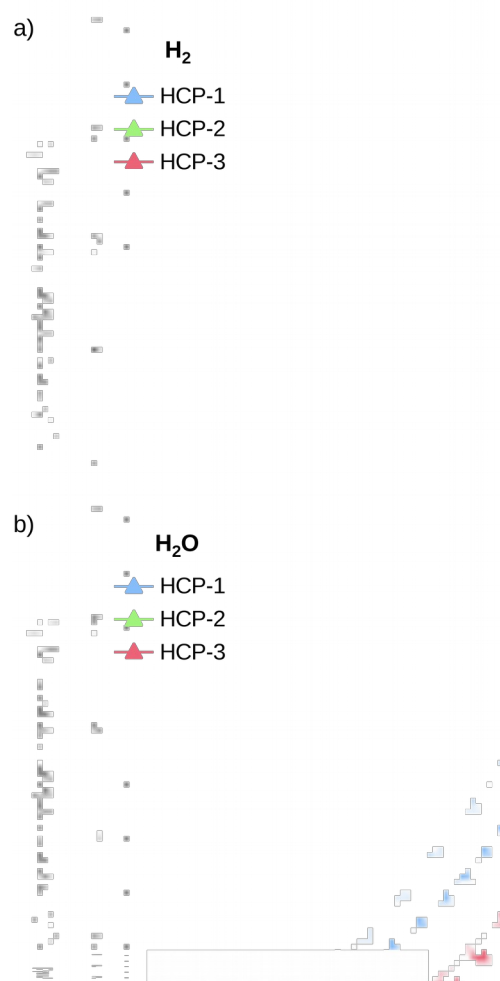


Figure 3. a) H_2 and b) H_2O adsorption isotherms at 25 °C. Filled symbols represent adsorption and empty symbols represent desorption.

This further corroborates the importance of the adsorption of the sacrificial agents to the photocatalyst surface. TiO_2 also showed improvements when employing sacrificial H_2O in place of H_2 . Sorescu et al. outlined how co-adsorbed water on TiO_2 can positively affect the adsorption capacities of CO_2 through the formation of hydrogen bonds.^[35] Other materials such as ZrO and coal also exhibit increased CO_2 adsorption and/or activation in the presence of co-adsorbed H_2O .^[36-38] In addition to ensuring the presence of H_2O molecules close to active sites, we speculate that co-adsorbed water may also favour CO_2 activation and/or the formation of bicarbonate species and facilitate its photoreduction, as suggested elsewhere for other photocatalysts.^[39-40] Nonetheless, further studies are required to understand the influence of H_2O on CO_2 adsorption.

We examined further the photocatalytic properties under UV-vis irradiation of HCP-3, the most active photocatalyst of this study. Kinetic studies point to a relatively linear production of CO up to 3 h

of irradiation (Figure S15). Recyclability tests were also performed. As shown in Figure 2f, after 5 cycles the photoactivity decreased by 9%, which may be due to the formation of surface products or mild degradation of the polymer. We also probed the structural and chemical stability of HCP-3 by collecting N₂ sorption isotherms and XPS and FTIR spectra before and after UV-vis irradiation. Elemental composition, porosity and chemical bonds were maintained without significant alteration, with the exception of a change in the shape of the N₂ isotherm (Figure S3, S16 and Table S2). To verify the evolution of CO from CO₂ conversion over HCPs photocatalysts, we conducted a series of control experiments, i.e.: in an inert atmosphere (N₂/H₂ or N₂/H₂O); without catalyst; without light; isotopic labelling of ¹³CO₂ (control experiments details are outlined in Table S4). In the absence of CO₂, the activity decreased by 77% to 88% depending on the atmosphere (N₂/H₂O vs N₂/H₂). We attribute the trace CO detected under inert atmosphere arises from the degradation of the residual oxygen-containing functional groups of the HCP crosslinkers. To verify the photocatalytic production of CO from CO₂, we conducted isotopic labelled ¹³CO₂ tests using H₂O as a sacrificial agent under UV-visible light irradiation. We observe a ¹³CO peak (m/z= 29) after light irradiation, confirming the ability of HCPs to photoconvert CO₂ to CO (Figure S17).

Conclusion

We report hypercrosslinked polymers for the first time as a photocatalytic platform for CO₂ photoreduction under both UV-vis and visible light irradiation. HCPs show promising photocatalytic activity using only sacrificial H₂O, without the requirement of any co-catalyst or photosensitiser, significantly outperforming the benchmark material TiO₂ P25 under visible light illumination. This was rationalised by new insights into the concentration of sacrificial agents at the surface of HCPs *via* selective adsorption, as networks showed significantly higher H₂O adsorption capacity in comparison to negligible H₂ adsorption. The performance disparity between these reducing agents outlines a key consideration when producing photocatalysts for yield efficient solar-energy conversion. Their lack of requirement for precious-metal catalysts, as well as their simple engineering, good general stabilities and low costs, make HCPs an exciting and promising platform for the design of organic photocatalysts.

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Supporting information for this article is given via a link at the end of the document.

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Supporting Information

Hypercrosslinked polymers as a photocatalytic platform for visible-light-driven CO₂ photoreduction using H₂O

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Table of Contents

1.Experimental Section.....	2
2.Characterisation.....	3
3.Supplementary Figures and Tables.....	9
4.References.....	35

1. Experimental Section

Materials

TiO₂ P25 (>99.5%, 21 nm primary particle size), benzene, dimethoxymethane, 2,4-diamino-6-phenyl-1,3,5-triazine, aniline, 1,2-dichloroethane, N,N-dimethylformamide and iron(III) chloride were all purchased from Sigma-Aldrich. 4,4'-bis(methoxymethyl)biphenyl was purchased from Tokyo Chemical Industry (TCI) UK and methanol (reagent grade) was purchased from VWR. All reagents were used as received. All gases were purchased from BOC.

Hypercrosslinked Polymer Synthesis

HCP-1: Anhydrous 1,2-dichloroethane (20 mL) was added to benzene (0.78 g, 10 mmol) and dimethoxymethane (2.28 g, 30 mmol) under N₂, before the solution was purged with N₂ for at least a further 30 minutes. After purging, iron(III) chloride (4.87 g, 30 mmol) was quickly added to the solution and the mixture was heated to 80 °C for a further 24 h, during which the reaction was kept under an inert atmosphere. The resulting solid was allowed to cool before it was filtrated using a Buchner funnel and washed with methanol until the filtrate was almost colourless. The polymer was then further washed by Soxhlet extraction in methanol for 24 h. Finally, the polymer was dried in a vacuum oven overnight at 70 °C.

HCP-2: The overall procedure remained the same as HCP-1 with 1,2-dichloroethane (20 mL) added to aniline (0.28 g, 3 mmol) and 4,4'-bis(methoxymethyl)biphenyl (1.45 g, 6 mmol) before iron(III) chloride (0.98 g, 6 mmol) was added.

HCP-3: Again, the overall procedure remained the same as HCP-1 with 1,2-dichloroethane (20 mL) added to 2,4-diamino-6-phenyl-1,3,5-triazine (0.37 g, 2 mmol) and 4,4'-

bis(methoxymethyl)biphenyl (0.97 g, 4 mmol) before iron(III) chloride (0.65 g, 4 mmol) was added. After synthesis, a step was added in which HCP-3 was washed in chloroform by Soxhlet extraction, to ensure the removal of any unreacted 2,4-diamino-6-phenyl-1,3,5-triazine. Yields for HCP-1, HCP-2 and HCP-3 were 84 %, 66 % and 91%, respectively, based on hypothetical 100% polycondensation.

2. Characterisation

Chemical and structural properties

Fourier-transform infrared (FTIR) spectroscopy was performed in the range of 500 – 4000 cm^{-1} on finely ground samples using a PerkinElmer Spectrum 100 FT-IR spectrometer equipped with an attenuated total reflectance (ATR) accessory.

Thermal analyses were performed using a Netzsch TG209 F1 Libra thermogravimetric analyser. At least 10 mg of sample was heated from room temperature to 900 °C at a rate of 10 °C min^{-1} under either air or N_2 gas flow (flow rate 100 mL min^{-1}). An initial isothermal step of 1 h was included at 120 °C to ensure removal of adsorbates before heating continued.

X-ray photoelectron spectroscopy (XPS) measurements were carried out on a Thermo Scientific K-Alpha+ X-ray photoelectron spectrometer equipped with a MXR3 Al $\text{K}\alpha$ monochromated X-ray source ($h\nu = 1486.6 \text{ eV}$). Samples were ground and mounted on the XPS holder using a conductive carbon tape. The X-ray gun power was set to 72 W (6 mA and 12 kV). Survey scans were acquired using 200 eV pass energy, 0.5 eV step size, and 100 ms (50 ms x 2 scans) dwell times. Data analysis was performed using the Thermo Advantage data analysis program.

Nitrogen isotherms were measured using a porosity analyser (Micromeritics 3Flex) at -196 °C. Prior to measurement, all samples were degassed overnight at 393 K at around 0.2 mbar pressure. Samples underwent a further degas step at 393 K *in-situ* on the porosity analyser for 4 h, this time at around 0.003 mbar. Surface areas were calculated using the Brunauer–Emmett–Teller (BET) method.^[1] The total volume of pores (V_{TOT}) was calculated from the volume of N₂ adsorbed at $P/P_0 = 0.97$ and micropore volume (V_{MICRO}) was determined using the Dubinin–Astakhov method.^[2] The pore size distribution was derived from the adsorption isotherms by using an built-in software from Micromeritics and selecting the DFT model for carbon slit shape pores (N₂@77 on Carbon Slit Pores by NLDFT).

Powder X-ray diffraction (PXRD) measurements were recorded at room temperature on a BRUKER 2D PHASE diffractometer operating at 30 kV and 10 mA with monochromatised Cu K α radiation ($\lambda = 0.15418$ nm).

The morphology of the samples was imaged using a scanning electron microscope (SEM, Leo Gemini 1525, Zeiss) in secondary electron mode (InLens detector) at 5 kV. The samples were ground, deposited on carbon tape, and coated with 20 nm of chromium to reduce charging.

For determination of Iron content in HCP-2, samples were first digested (~5 mg sample) using 4 mL conc. nitric acid (4 mL) and H₂O₂ (200 μ L) using an open vessel graphite digestion system (Labter, ODLAB; Distributor: AHF Analysentechnik AG; Germany). Samples were twice heated to 150 °C and held at the target temperature for 1 h before cooling to 50 °C, however this was not sufficient for sample digestion. Samples were then twice heated to 200 °C and held for 45 h before again cooling to 50 °C. After digestion the sample was diluted in ultrapure water (18.2 M Ω cm, Milli-Q Advantage, Darmstadt, Germany). Digested samples were analysed using an ICP-MS (an Agilent 7800, Agilent Technologies,

Tokyo, Japan) equipped with an Agilent SPS 4 autosampler (Agilent Technologies, Tokyo, Japan) and a MicroMist nebulizer at a sample uptake rate of approx. 0.2 ml/min. The Agilent MassHunter software package (Workstation Software, Version C.01.04, 2018) was used for data evaluation. The instrumental parameters for the ICP-MS are summarized in Table S1. A representation sample of HCP-2 was found to contain 246 ppm of Fe, however under the above describe conditions digestion of HCP-1 and HCP-3 was unsuccessful.

Table S1: Instrumental parameters for the ICP-MS measurements

RF power	1550 W
Sampling depth	8 mm
Nebulizer	MicroMist
Spray chamber	Scott double-pass
Spraying chamber temp.	2°C
Monitored Isotopes	⁵⁶ Fe, ⁵⁷ Fe, ¹¹⁵ In, ¹⁸⁵ Re,
Measurement mode	He, 5 L min ⁻¹
Plasma gas	15 L min ⁻¹
Nebulizer gas	1.09 L min ⁻¹
Auxiliary gas	0.90 L min ⁻¹
Cones	Ni
Integration time	0.3 s

Optoelectronic properties

Valence band X-ray photoelectron spectroscopy (XPS) and work function measurements were carried out on a Thermo Scientific K-Alpha⁺ X-ray photoelectron spectrometer equipped with a MXR3 Al K α monochromated X-ray source ($h\nu = 1486.6$ eV). Samples were ground and mounted on the XPS holder using a conductive carbon tape. The X-ray gun power was set to 72 W (6 mA and 12 kV). Valence band spectra were obtained using 15 eV pass energy and 0.05 eV step size. Data analysis was performed using the software Thermo Avantage. The work functions of the polymers were determined by measuring the secondary electron cut-off in the low kinetic energy region. The sample holder contained a clean gold

standard sample, which was used as a reference material to ensure correct calibration. A sample bias of -29.47 V was applied to the samples using an ion gun and the cut-off spectra were obtained using a pass energy of 10 eV. To account for potential variations across the surface of the material, the work function was measured at three different locations and the average was taken. To convert the valence band position and the work function to the absolute energy scale vs. vacuum with the redox potential scale vs. SHE, a factor of 4.44 was required, as 4.44 eV on the former corresponds to 0.00 V on the latter, at 25 °C.

Diffuse reflectance ultraviolet-visible (DR-UV-Vis) spectra were obtained using a Perkin-Elmer Spectrum 100 Spectrometer equipped with an integrating sphere. Spectral band width was set to 2 nm, with Spectralon as a standard.

Time-correlated single photon counting (TCSPC) experiments were carried out using a commercial TCSPC setup (Horiba DeltaFlex) equipped with a pulsed LED excitation source (Horiba NanoLED series) and a fast rise-time photomultiplier detector (Horiba PPD-650 and PPD-900). The instrument response function (IRF) was measured at the wavelength of the excitation source (282 nm). During all other measurements, a suitable long pass filter was inserted between sample and detector to block off scattered excitation light.

Gas and water sorption

Water vapor, CO₂ and H₂ adsorption isotherms were collected at 25 °C using a Micromeritics 3Flex instrument, equipped with a liquid container in the case of H₂O. HCPs were degassed overnight at 120 °C at around 0.2 mbar pressure and again *in-situ* on the porosity analyser (Micromeritics 3Flex) for 4 h down to around 0.003 mbar. Research grade (99.999%) CO₂ and H₂ (99.9995%, Peak Scientific PH200 hydrogen generator) were used for CO₂ and H₂ isotherms. For H₂O isotherms, miliQ water with a resistance > 18.2 micro-ohms was purified

by 4 freeze pump thaw cycles. Water isotherms were collected up to a relative pressure of 0.8 to avoid condensation. For “wet” CO₂ uptake, i.e. investigating CO₂ uptake on HCPs pre-exposed to H₂O, HCPs were exposed to humid air (>99 % humidity) by placing HCPs in a sealed vessel containing liquid water and a hygrometer for at least 48 hours at room temperature. HCPs were not in contact with the liquid water during this process. After removal, CO₂ adsorption isotherms were performed at 25 °C up to 1 bar, skipping all prior degas steps. The first pressure CO₂ adsorption point was collected at around 10 mbar (~2 orders of magnitude higher than a standard ‘dry’ measurement) to minimise water desorption. Resulting isotherms for wet polymers gave negative adsorption values at low absolute pressures due to some water desorption in the initial stages of measurement. Therefore, to allow comparison to dry samples, a factor was applied to the isotherm, raising the lowest absolute pressure measurement to 0 mmol/g adsorbed CO₂. It is worth noting that some subsequent uptake may be due to re-adsorption of desorbed water.

Photocatalytic properties

A gas/solid photoreactor was assembled to conduct CO₂ photocatalytic measurements (Figure S13). Tests were conducted at ambient temperature. The photocatalysts were deposited on a stainless-steel plate with a fixed area of 9.6 cm². To do so, 10-15 mg of the ground photocatalyst was dispersed in DI water (1.2 mL), sonicated for 30 seconds and drop cast onto the sample holder. Research grade (99.999%) CO₂ and H₂ (99.9995%, Peak Scientific PH200 hydrogen generator) were flowed at controlled rates using mass flow controllers (Omega Engineering, 0–50 mL min⁻¹). For experiments using H₂ as sacrificial agent, the photoreactor (35 cm³) was vacuumed and replenished with a gas mixture of CO₂ and H₂ (1.5 vol/vol ratio) six times. The same gas mixture of CO₂ and H₂ was subsequently passed over the catalyst bed in the photoreactor for 15 residence times before it was sealed at 1.25 bar and

irradiated for 3 h. For experiments using water as sacrificial agent, H₂O vapour was generated from a saturator at room temperature (25°C), unless stated otherwise, providing a gas mixture of CO₂ and H₂O (1.4 wt% H₂O). The photoreactor was vacuumed and replenished with a gas mixture of CO₂ and H₂O at least six times prior to measurement. A xenon arc lamp (300 W, λ > 325 nm, LOT Quantum Design) equipped with a water filter was used as the irradiation source. The distance from the lamp to the sample was 9.5 cm with a broadband irradiance at the sample surface of 1830 W.m⁻². For visible light measurements a long pass UV filter (λ < 400 nm) (LOT Quantum Design) was used.

Evolved gases were analysed by a gas chromatograph mass spectrometer (GC-MS) with gas sampling valves connected directly to the photoreactor. The GC (Agilent Technologies, 7890B) was equipped with HayeSep (Agilent J&W 6 foot, 1/8 inch, 2mm, HayeSep Q Column 80/100 SST) and molecular sieve (Agilent J&W 6 foot, 1/8 inch, 2 mm, MolSieve 5A, 60/80, preconditioned) packed columns in series, a thermal conductivity detector (TCD) and a flame ionisation detector (FID). The MS was equipped with a GS-GASPRO capillary column (Agilent J&W HP-5ms GC Column, 30 m, 0.25 mm, 0.25 μ m). For recyclability tests, the aforementioned process was repeated after each 3 h irradiation cycle without opening the photoreactor. In addition, isotopic tracing experiments were performed with ¹³CO₂ (BOC, >98% atom ¹³CO₂ compared to ¹²CO₂, >99%). The photocatalytic CO₂ reduction tests were repeated 3 times for each material under the same reaction conditions.

3. Supplementary Figures and Tables



Figure S1. Photographic images of: HCP-1, HCP-2 and HCP-3 (from left to right, respectively).

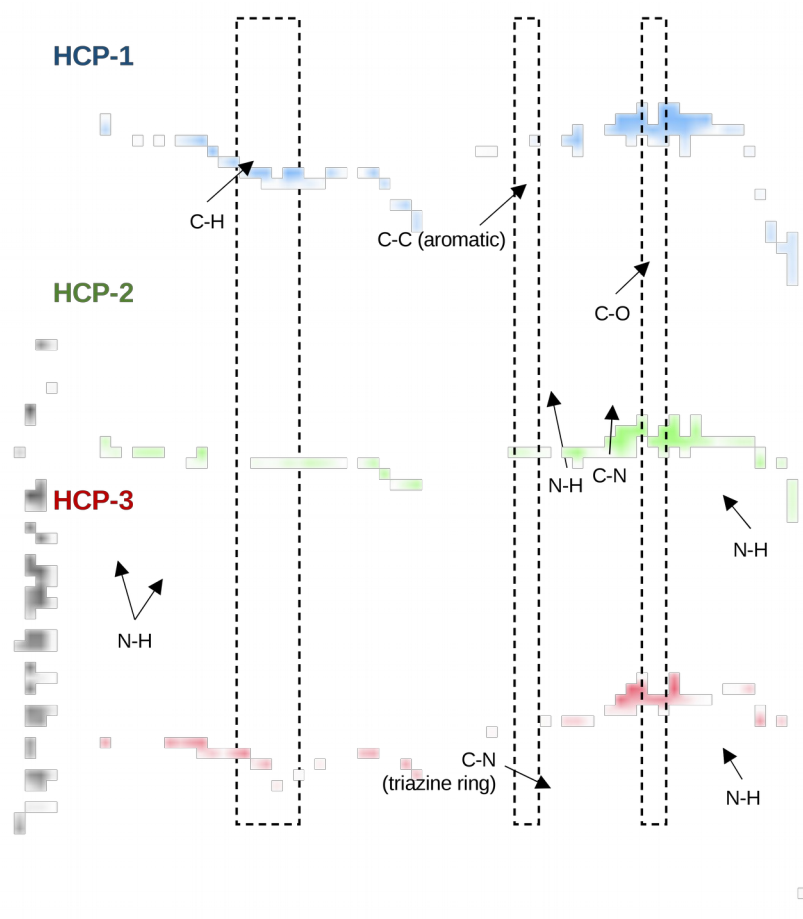


Figure S2. FTIR spectra of HCP-1 (blue), HCP-2 (green) and HCP-3 (red). Signals present in all spectra are highlighted by dashed lines.

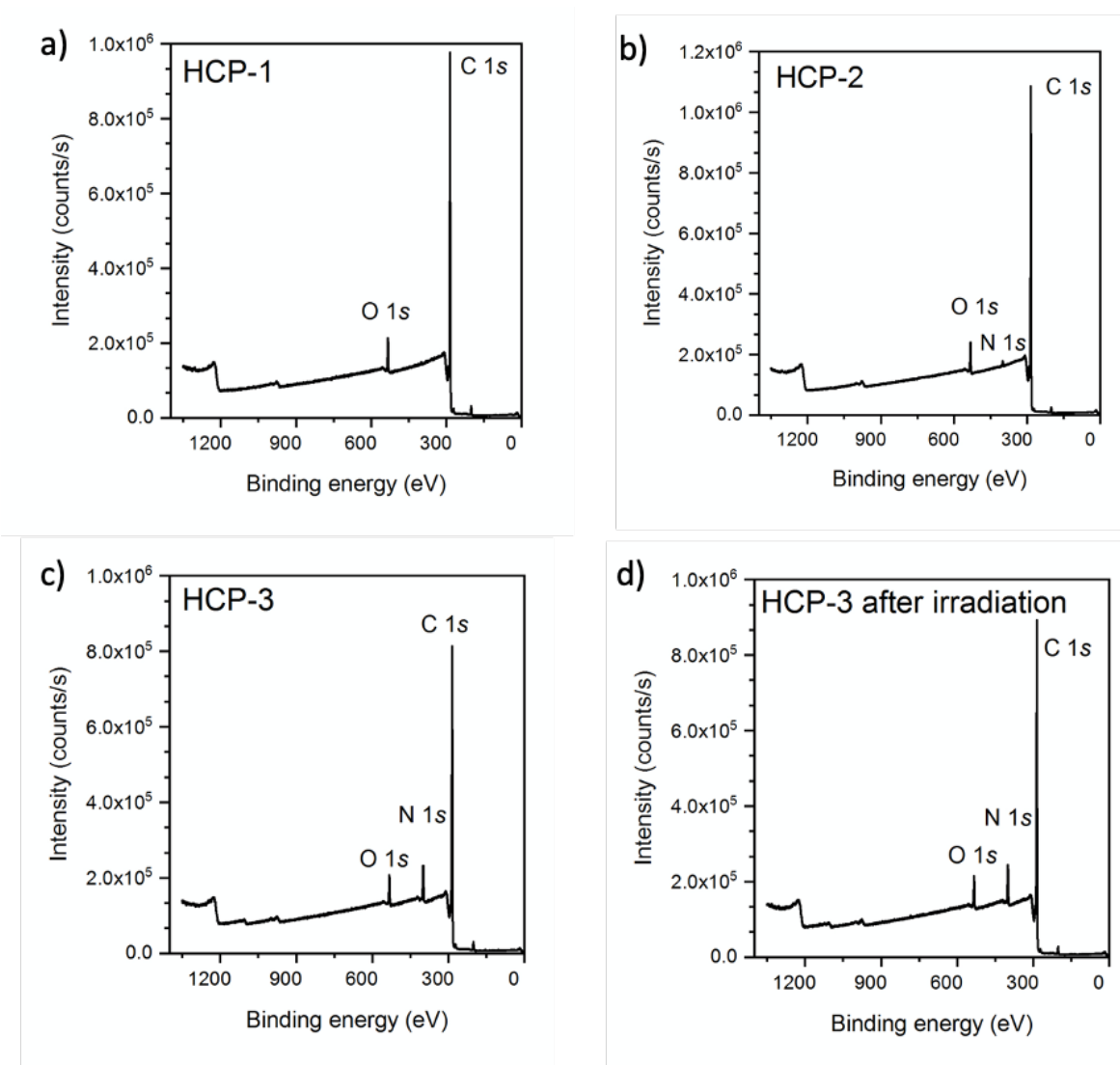


Figure S3. X-ray photoelectron spectroscopy survey spectra of: a) HCP-1, b) HCP-2, c) HCP-3, and d) HCP-3 after 3 h of UV-vis light irradiation.

Table S2. Atomic composition of HCP-1, HCP-2, HCP-3 and HCP-3 after irradiation, determined using XPS survey spectra. The Fe content of HCP-2 determined using ICP-MS is also included.

	Atomic % of O	Atomic % of N	Atomic % of C	Fe content (ppm)
HCP-1	4.5	-	95.5	-
HCP-2	4.2	1.3	94.5	246
HCP-3	4.5	7.9	87.6	-
HCP-3 after irradiation	4.7	8.3	87.0	-

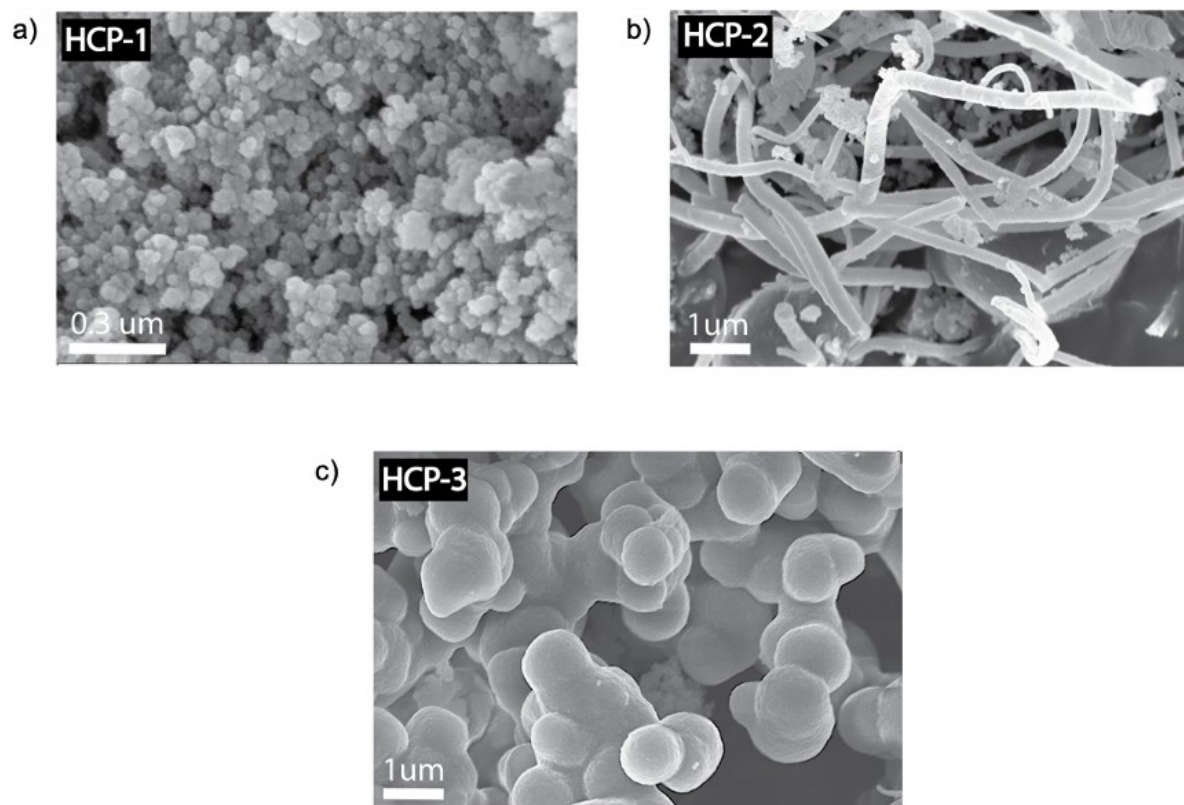


Figure S4. SEM images of a) HCP-1, b) HCP-2, and c) HCP-3.

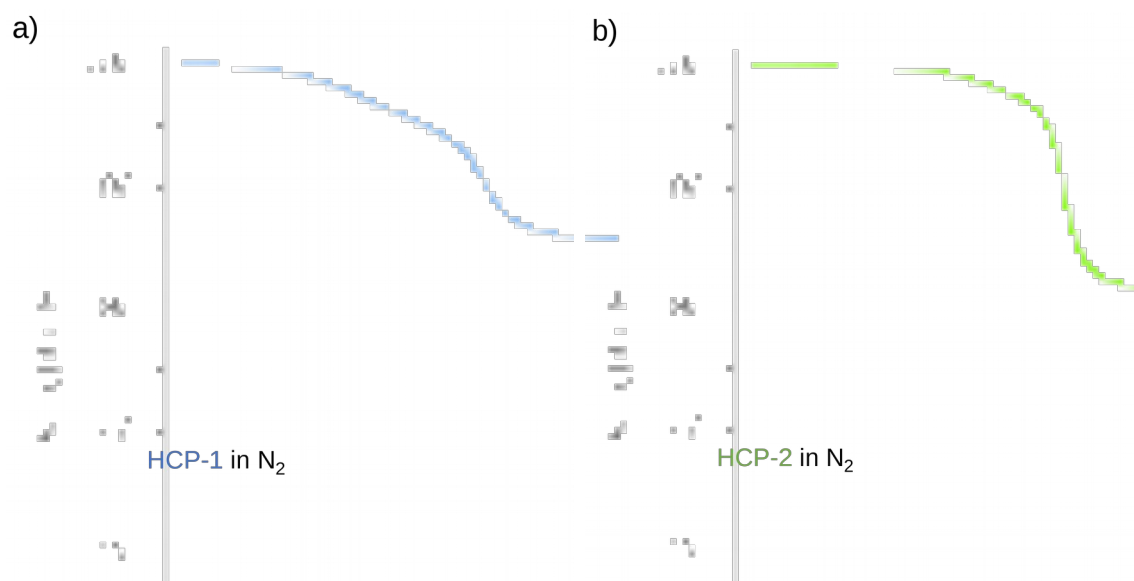
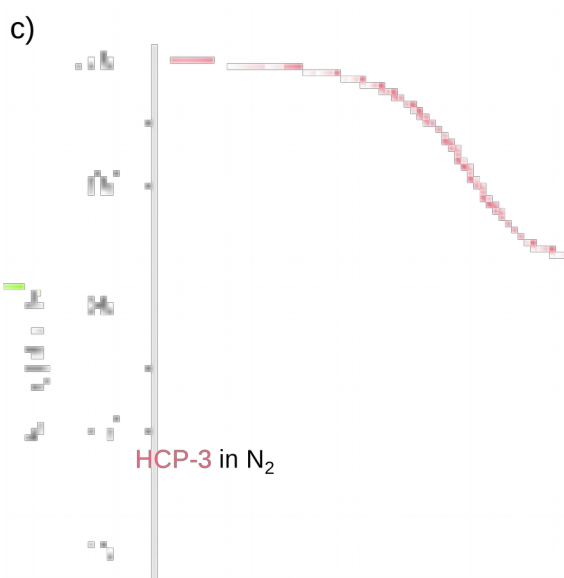


Figure S5. TGA thermograms up to 900 $^{\circ}C$ in a N_2 atmosphere, heated at a ramp rate of 10 $^{\circ}C/min$ with a N_2 flow rate of 100 mL/min. a) HCP-1, b) HCP-2, and c) HCP-3.



thermograms up to 900 $^{\circ}C$ in a N_2 atmosphere, heated at a ramp rate of 10 $^{\circ}C/min$ with a N_2 flow rate of 100 mL/min. a) HCP-1, b) HCP-2,

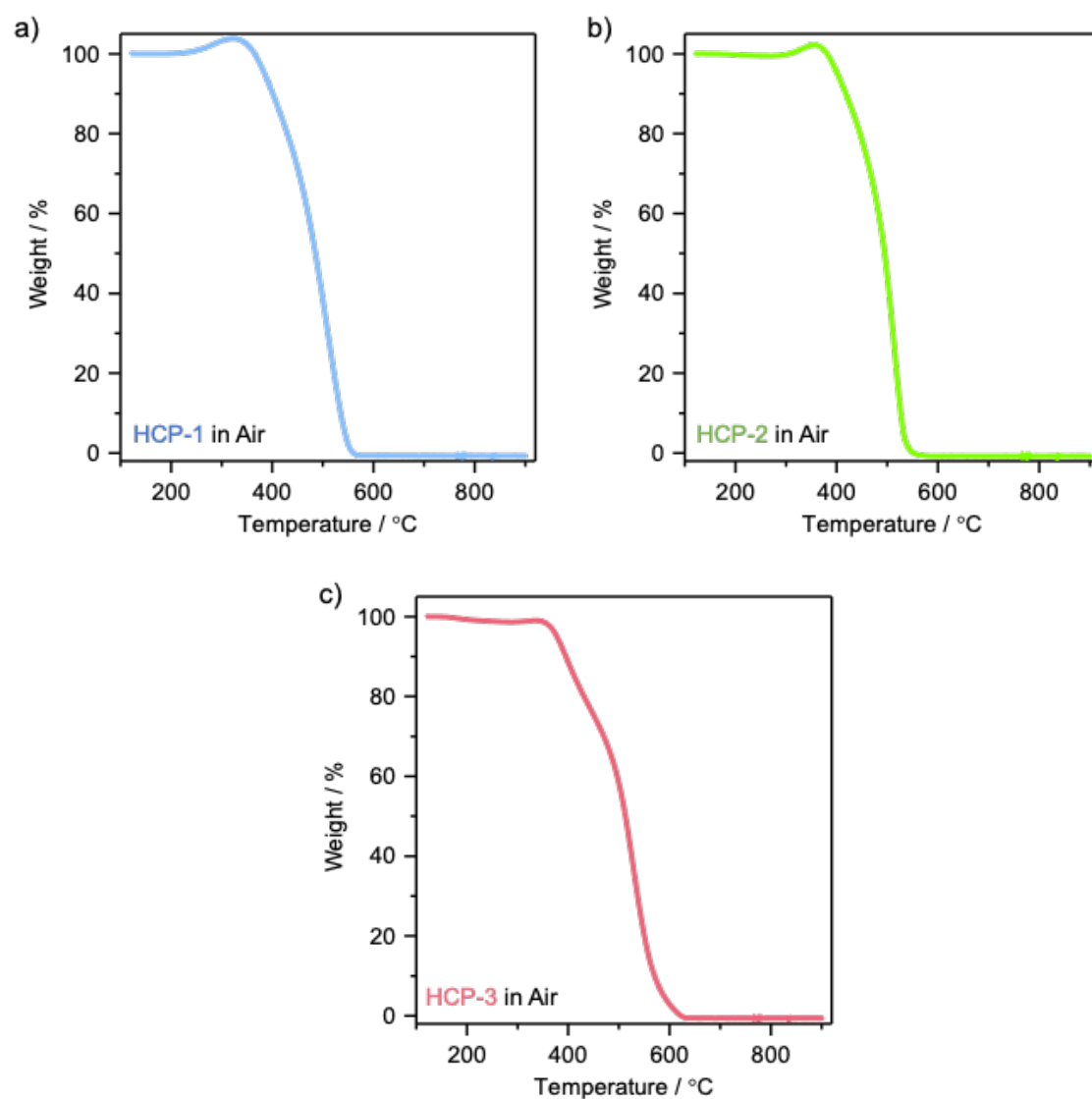


Figure S6. TGA thermograms up to 900 °C in air, heated at a ramp rate of 10 °C/min with an air flow rate of 100 mL/min. a) HCP-1, b) HCP-2, and c) HCP-3.

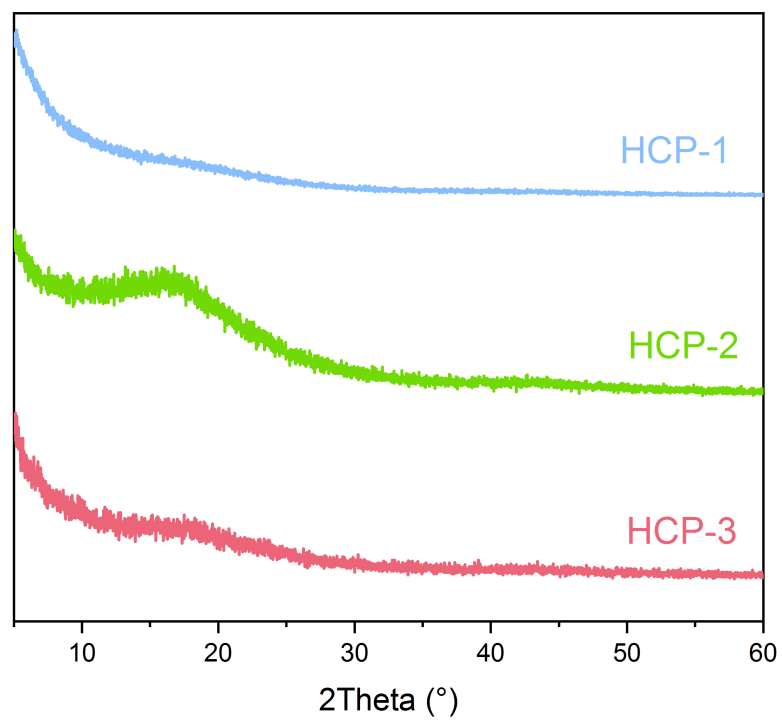


Figure S7. PXRD patterns of a) HCP-1, b) HCP-2, and c) HCP-3.

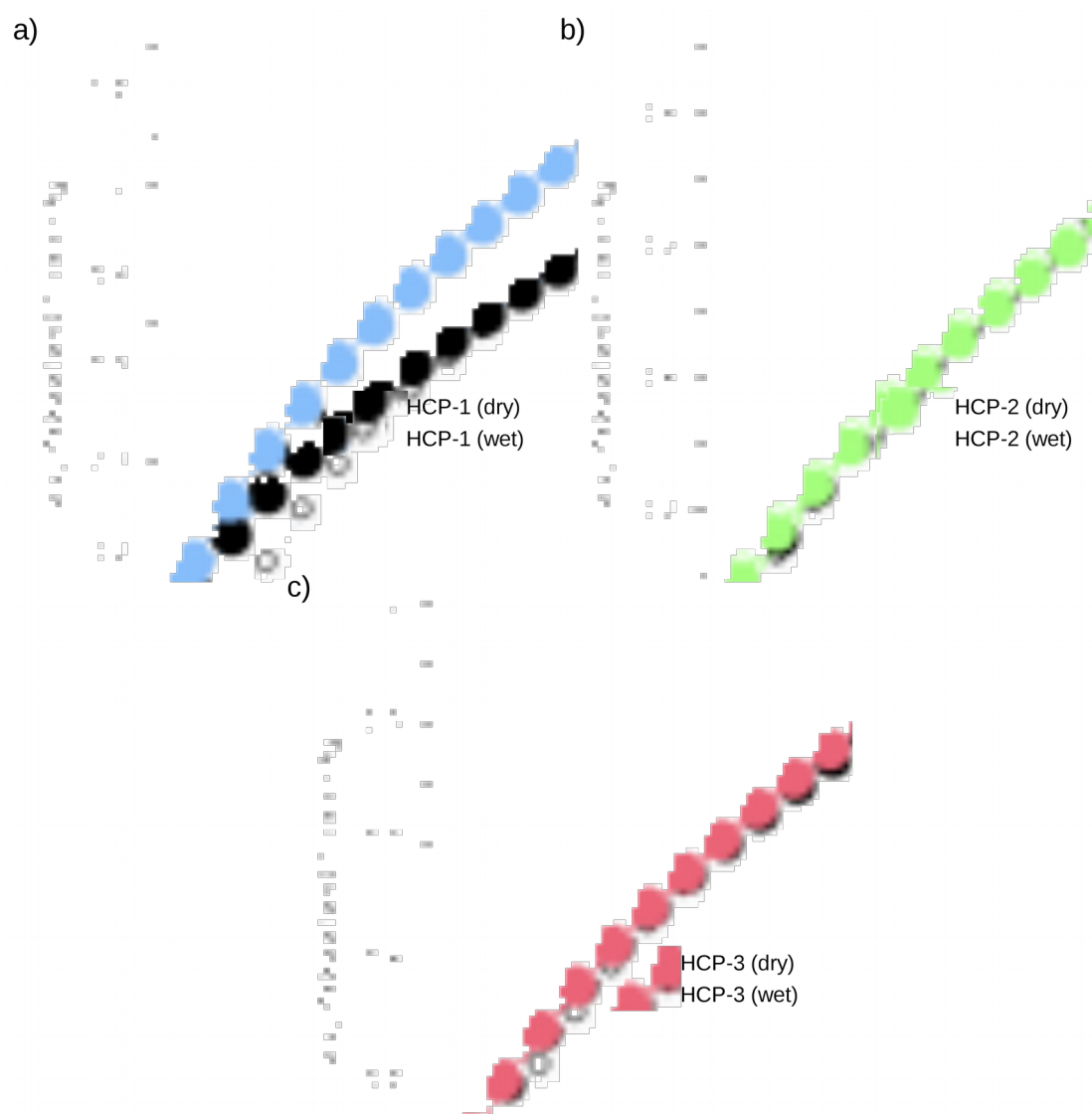


Figure S8. CO₂ adsorption isotherms at 298 K of both dry and wet (i.e. exposed to humid air for at least 48 h before measurement, 99% humidity) networks. a) HCP-1, b) HCP-2, and c) HCP-3. Filled symbols represent adsorption, empty symbols represent desorption.

Table S3. Textural parameters derived from N₂ sorption isotherms at –196 °C and CO₂ adsorption capacities at 25 °C.

Sample	V _{MICRO} (cm ³ /g) ^a	V _{TOT} (cm ³ /g) ^a	S _{BET} (m ² /g) ^a	CO ₂ ad. (mmol/g)	
				Dry ^b	Wet ^c
HCP-1	0.46	1.07	950	1.25	0.99
HCP-2	0.13	0.21	310	0.78	0.82
HCP-3	0.16	0.25	360	0.92	0.89
HCP-3 after irradiation	0.11	-	300	-	-

^aDerived from N₂ sorption isotherms at – 196 °C .
^bCapacity of degassed HCP at 25 °C and 1 bar
^cCapacity of non-degassed HCP at 25 °C and 1 bar after 48 h exposure to humid atmosphere

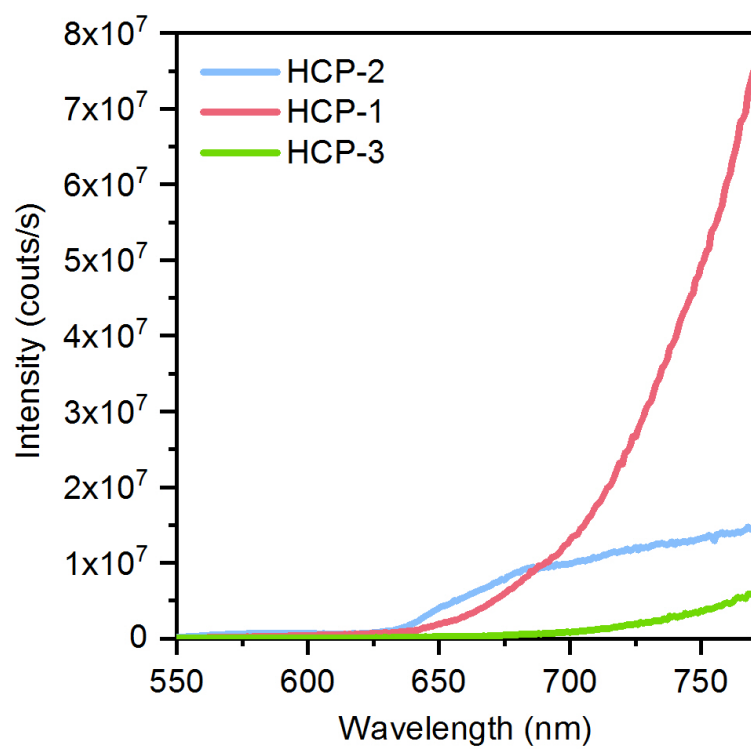


Figure S9. Photoluminescence emission spectra

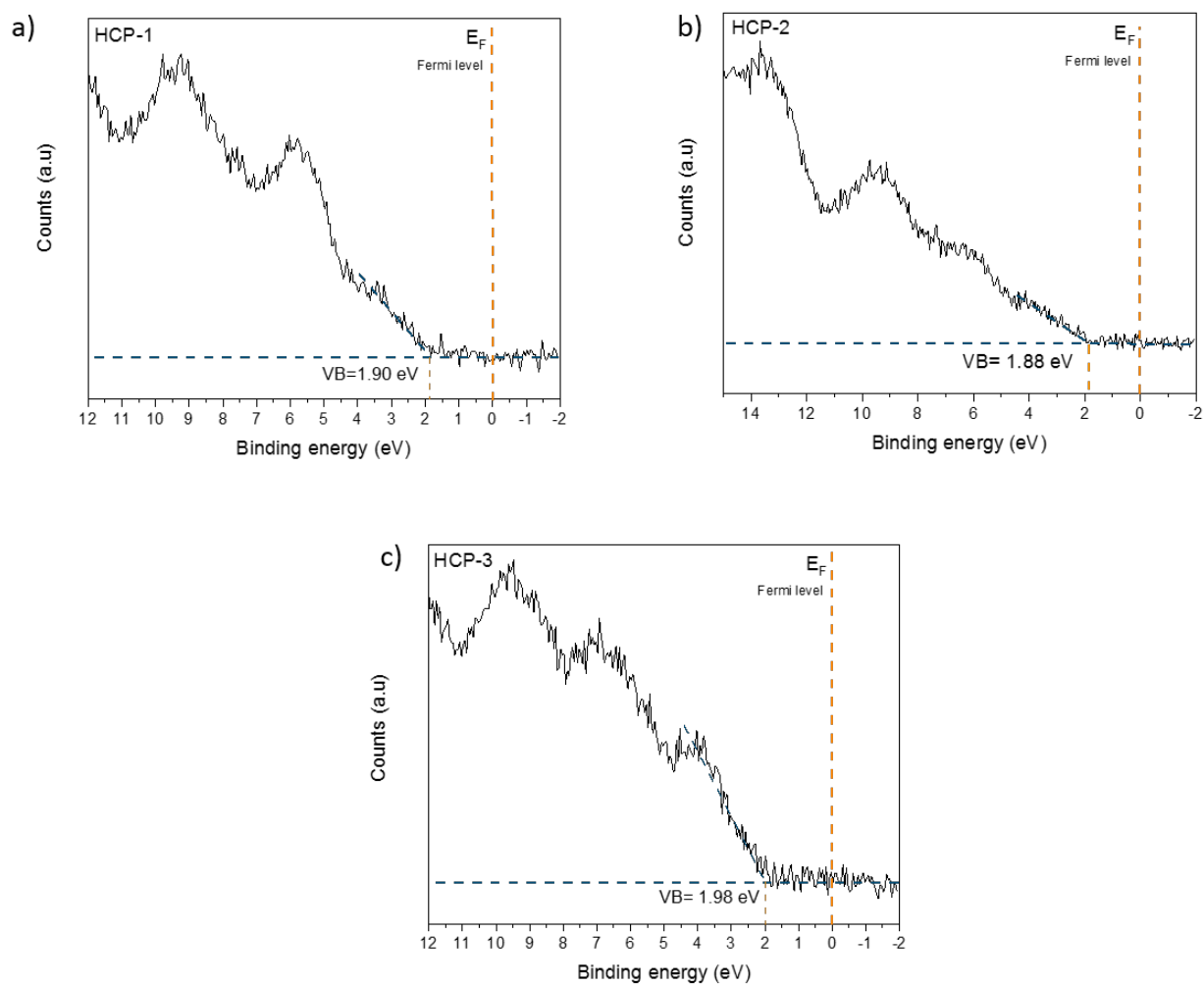


Figure S10. Valence band XPS spectra of a) HCP-1, b) HCP-2, and HCP-3.

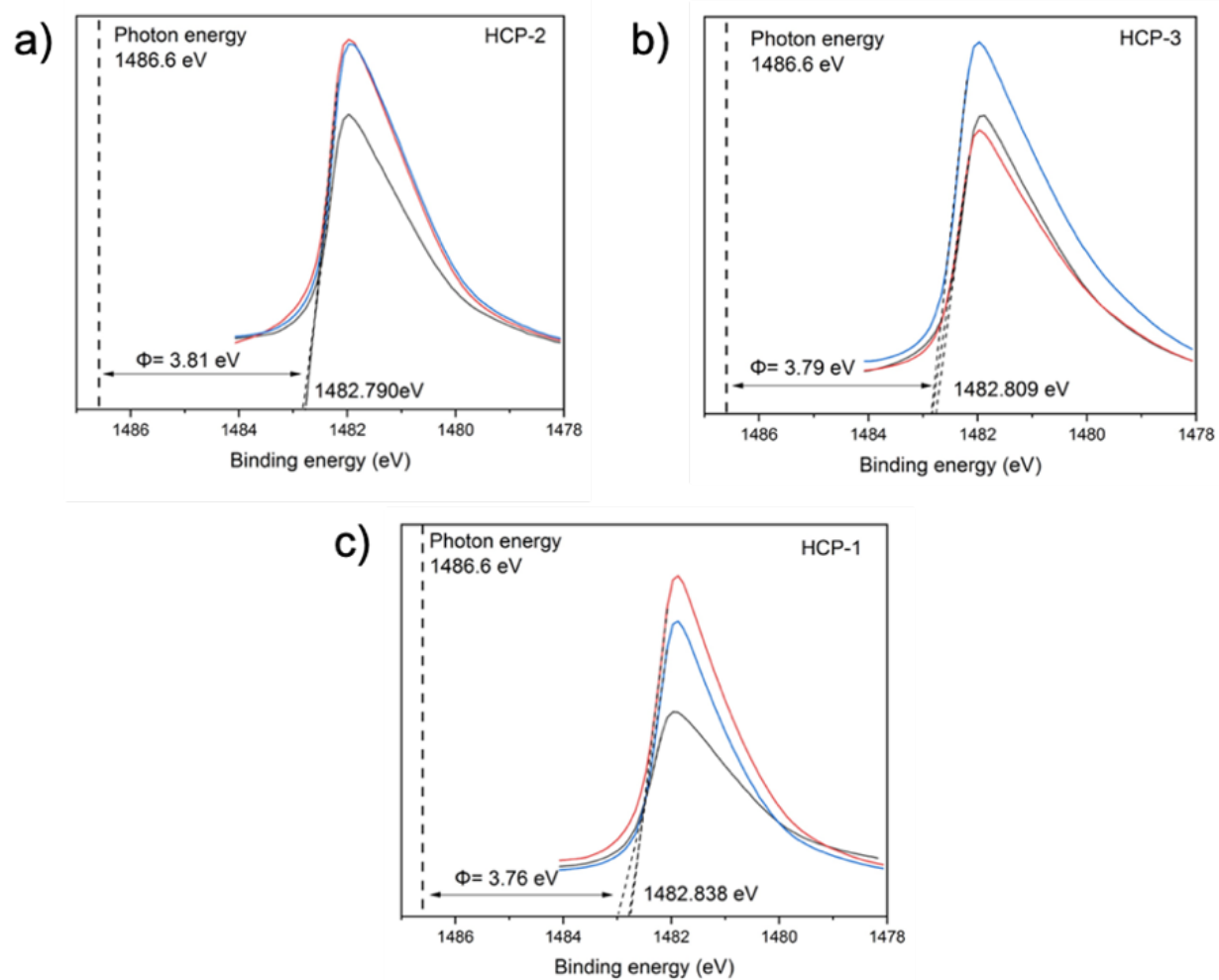


Figure S11. Work function measurements at three different locations on a) HCP-2, b) HCP-3, and c) HCP-1 to account for potential variations across the surface.

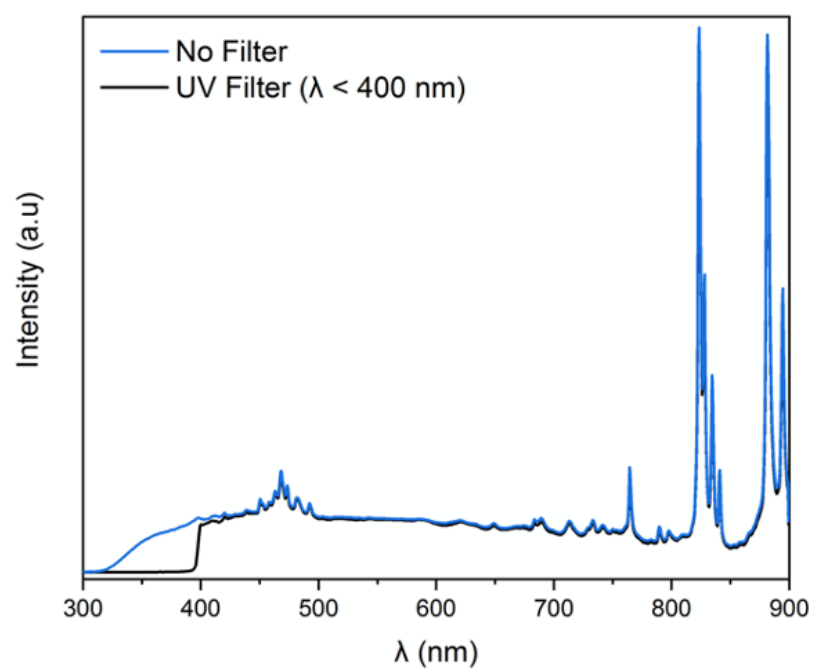


Figure S12. Xenon arc lamp emission spectra, (300W, LOT Quantum Design), equipped with a water filter.

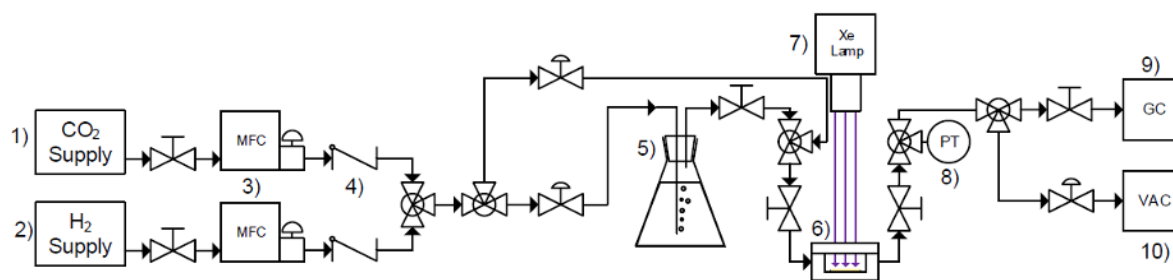


Figure S13. Photocatalytic gas-solid reactor setup used to evaluate photocatalytic CO₂ reduction: 1) CO₂ cylinder, 2) H₂ generator, 3) mass flow controllers, 4) non-return valves, 5) H₂O saturator, 6) photoreactor, 7) Xe arc lamp, 8) pressure transducer, 9) gas chromatograph, 10) vacuum pump.^[3]

Table S4. Photocatalytic evolution rates of HCP-1, HCP-2, HCP-3, and TiO₂ P25 and control experiments

Sample	UV-vis (Sacrificial H ₂)		UV-vis (Sacrificial H ₂ O)		Visible (Sacrificial H ₂ O)	
	CO*	CH ₄ *	CO*	CH ₄ *	CO*	CH ₄ *
HCP-1	3.7 ± 0.1	0	8.6 ± 0.1	0.4 ± 0.1	4.2	0.1
HCP-2	1.6 ± 0.3	0.1 ± 0.1	4.6 ± 0.5	0.4 ± 0.2	1	0
HCP-3	6.3 ± 0.2	0.5 ± 0.1	15.6 ± 0.9	0.4 ± 0.1	5.2	0.1
P25 (TiO ₂)	6.4 ± 0.4	0.3 ± 0.2	14.7 ± 0.9	0.3 ± 0.1	0.69	0.2
N ₂ /H ₂ O, no catalyst	-	-	0	-	-	-
N ₂ /H ₂ O ^a	-	-	3.58 (23% ^c)	-	-	-
N ₂ /H ₂ O repeat ^{a,b}	-	-	3.78 (24% ^c)	-	-	-
N ₂ /H ₂ O ^a	-	-	-	-	0.82 (15% ^c)	-
N ₂ /H ₂ O repeat ^{a,b}	-	-	-	-	1.06 (20% ^c)	-
N ₂ /H ₂ ^a	0.74 (12% ^c)	-	-	-	-	-
N ₂ /H ₂ repeat ^{a,b}	0.61 (10% ^c)	-	-	-	-	-
CO ₂ / H ₂ O, no light ^a	-	-	0.16 (1% ^c)	-	-	-
CO ₂ / H ₂ O, no catalyst	-	-	10 ppm	-	-	-

* All data are given in μmol.g⁻¹.h⁻¹

^a tests were performed on HCP-3, the leading material of this study

^b repeat samples were done on the same sample as the first one, without opening the photo-reactor

^c percentage compared to the total activity of HCP-3

Apparent quantum yield (AQY) calculations

The apparent quantum yield at a given wavelength λ is defined as:

$$AQY = \frac{N_e}{N_p} = \frac{\text{no. of reacted electrons}}{\text{no. of absorbed photons}} \times 100 \quad (\text{Equation S1})$$

Based on the stoichiometry of the CO evolution redox reaction:

$$AQY = \frac{2N_{CO}}{N_p} = \frac{(2)(\text{no. of evolved CO molecules})}{\text{no. of absorbed photons}} \times 100 \quad (\text{Equation S2})$$

For a polychromatic light source, we must consider the total number of absorbed photons across the wavelength range (270 – 900 nm for UV-vis and 400 – 900 nm for visible irradiation) and the corresponding total moles of CO evolved during the irradiation time:

$$AQY = \frac{2N_{CO(\text{total})}}{N_p} = \frac{(2)(\text{total no. of evolved CO molecules})}{\text{no. of absorbed photons}} \times 100 \quad (\text{Equation S3})$$

The number of photons absorbed by the photocatalyst at a given wavelength λ is given by:

$$N_{P, \text{absorbed}} = \frac{P(\lambda)t}{hc} \quad (\text{Equation S4})$$

where λ denotes the wavelength, P denotes the power of the irradiation source, t denotes the irradiation time, h denotes Planck's constant and c the speed of light.

Equation S4 can be written in terms of the intensity of the irradiation as a function of the

irradiation absorbed at wavelength λ , $I_{\lambda}(\lambda)$, and irradiation area (S) as:

$$N_{P,absorbed} = \frac{I_{\lambda}(\lambda)}{(S)(\lambda)(t)} \quad (\text{Equation S5})$$

To account for the number of photons absorbed by the photocatalyst at a given wavelength λ , we need to consider the absorbance (*Abs*) of the material at that wavelength and apply the Beer-Lambert law:

$$||\lambda|| = -\log \left[\frac{I_F(\lambda)}{I_I(\lambda)} \right] \quad (\text{Equation S6})$$

where $I_I(\lambda)$ denotes the intensity emitted from the irradiation source at a given wavelength λ and $I_F(\lambda)$ denotes the intensity after passing through the photocatalyst at the same wavelength λ .

The intensity of irradiation absorbed by the photocatalyst at a given wavelength λ is given by:

$$I_{\lambda}(\lambda) = I_I(\lambda) - I_F(\lambda) \quad (\text{Equation S7})$$

which, using equation (S6), can be written as:

$$I_{\lambda}(\lambda) - I_F(\lambda) = I_I(\lambda) \left[1 - 10^{-||\lambda||} \right] \quad (\text{Equation S8})$$

Substituting equation (S8) into equation (S5) gives

$$N_{P,absorbed} = \frac{I_I(\lambda)[1 - 10^{-|\lambda|}](S)(\lambda)(t)}{(hc)} \quad (\text{Equation S9})$$

The total number of photons absorbed by the photocatalyst across the entire wavelength range of the irradiation source is then given by:

$$N_{P,absorbed(total)} = \sum_{\lambda_{start}}^{\lambda_{end}} \frac{I_I(\lambda)[1 - 10^{-|\lambda|}](S)(\lambda)(t)}{(hc)} \quad (\text{Equation S10})$$

$$N_{P,absorbed(total)} = \frac{(S)(t)}{(hc)} \sum_{\lambda_{start}}^{\lambda_{end}} I_I(\lambda)[1 - 10^{-|\lambda|}](\lambda) \quad (\text{Equation S11})$$

The total number of evolved CO molecules during a given reaction cycle can be written as

$$N_{CO(total)} = (N_a)(n_{CO,total}) \quad (\text{Equation S12})$$

where N_a denotes Avagadro's constant and $n_{CO,total}$ denotes the total moles of CO evolved during the irradiation time.

Substituting equations (S11) and (S12) to (S3) gives us the final expression for the apparent quantum yield for CO evolution:

$$AQY = \frac{(2)N_{CO(total)}}{N_P} = \frac{(2)(N_a)(n_{CO,total})}{\frac{(S)(t)}{(hc)} \sum_{\lambda_{start}}^{\lambda_{end}} I_I(\lambda)[1 - 10^{-|\lambda|}](\lambda)} \times 100 \quad (\text{Equation S13})$$

Table S5. Apparent quantum yield calculation of HCP-3

Sample	UV-vis irradiation (sacrificial H ₂ O)	Visible irradiation (sacrificial H ₂ O)
HCP-3	0.002 %	0.0005 %

*The apparent quantum yield was calculated from a polychromatic light source. The total number of absorbed photons across the wavelength range (270 – 900 nm for UV-Vis and 400 – 900 nm for visible irradiation) was taken into consideration.

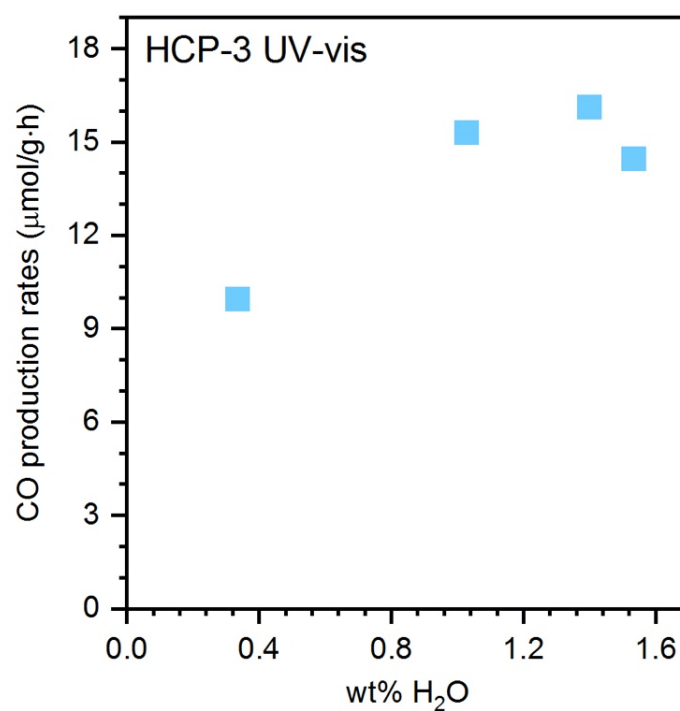


Figure S14. CO production rates of HCP-3 under UV-vis irradiation using different water vapour contents.

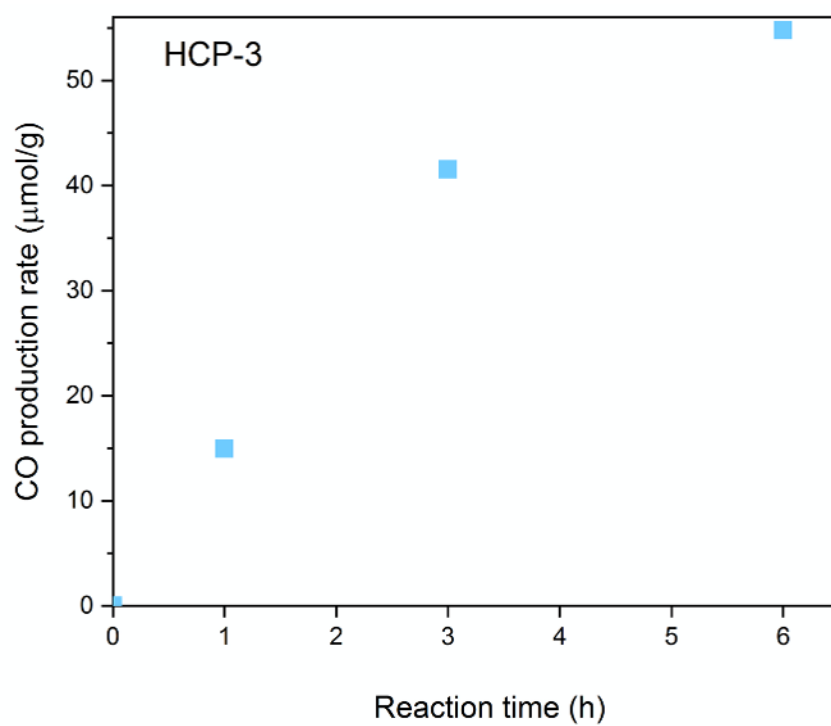


Figure S15. Photocatalytic CO evolution from HCP-3 under UV-vis irradiation as a function of time.

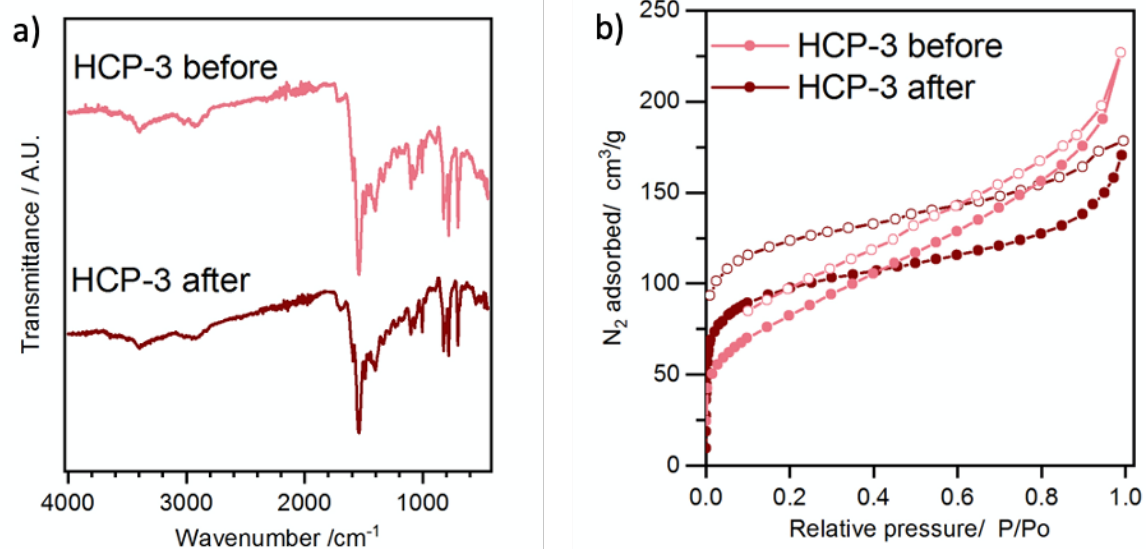


Figure S16. a) FTIR and b) N_2 adsorption isotherms at 77 K of HCP-3 before and after 3h UV-vis irradiation.

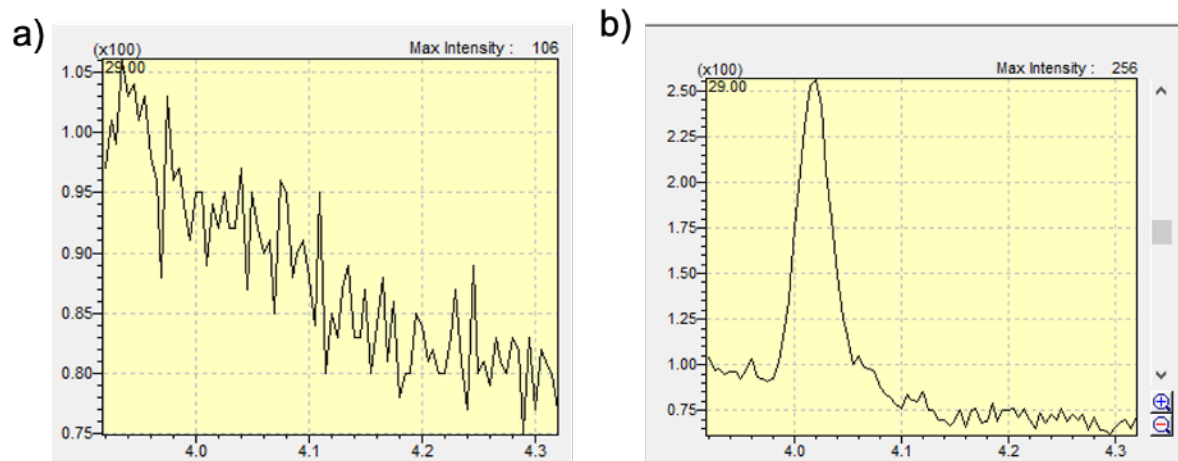


Figure S17. Isotopic $^{13}\text{CO}_2$ measurements. Mass spectrum chromatogram of HCP-3 illustrating the ^{13}CO ($m/z = 29$) peak observed with the photocatalytic $^{13}\text{CO}_2$ reduction system after a) 0 min and b) 4h UV-vis irradiation.

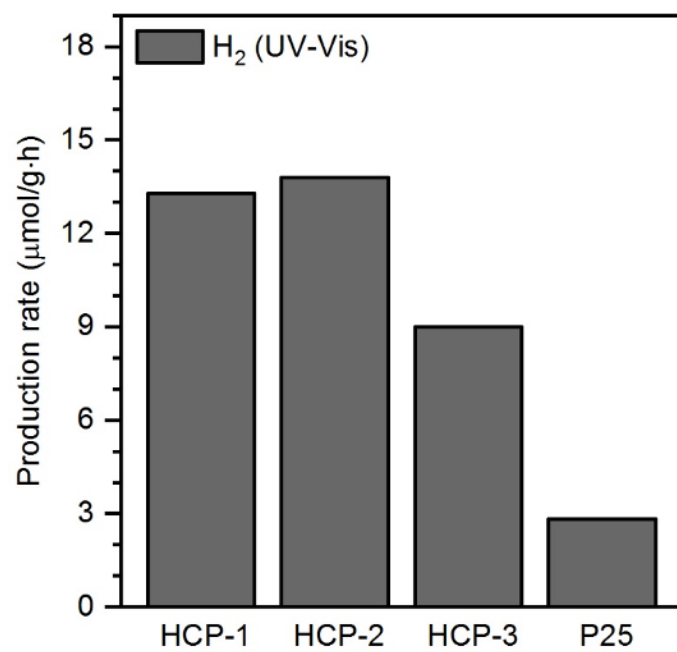


Figure S18. H₂ production rates of HCPs under UV-vis irradiation using H₂O as sacrificial agent.

4. References

1. Brunauer, S.; Emmett, P. H.; Teller, E., Adsorption of gases in multimolecular layers. *Journal of the American chemical society* **1938**, *60* (2), 309-319.
2. Chen, S.; Yang, R., Theoretical basis for the potential theory adsorption isotherms. The Dubinin-Radushkevich and Dubinin-Astakhov equations. *Langmuir* **1994**, *10* (11), 4244-4249.

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