Hypercrosslinked polymers as a photocatalytic platform for visible-light-driven CO$_2$ photoreduction using H$_2$O

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Abstract: The design of robust, high-performance photocatalysts is key for the success of solar fuel production via CO$_2$ conversion. Herein, we present hypercrosslinked polymer (HCP) photocatalysts for the selective reduction of CO$_2$ to CO, combining excellent CO$_2$ sorption capacities, good general stabilities, and low production costs. HCPs are active photocatalysts in the visible light range, significantly outperforming the benchmark material, TiO$_2$ P25, using only sacrificial H$_2$O. We hypothesise that superior H$_2$O adsorption capacities led to concentration at photoactive sites, improving photocatalytic conversion rates when compared to sacrificial H$_2$. 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. 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$_2$O, 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.

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. 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 $\sim$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. 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 CO$_2$ 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 CO$_2$ to CO with 92% selectivity, using visible light and sacrificial H$_2$O.$^{[14]}$ More recently, Fu et al. reported rhenium-doped covalent-organic frameworks (COFs), with high CO$_2$ 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 CO$_2$ photoreduction in the presence of water.$^{[12, 15]}$ While demonstrating the potential of porous organic polymers for CO$_2$ 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-TiO$_2$-graphene composite for the photoreduction of CO$_2$, with the HCP component aiding CO$_2$ 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 CO$_2$ to CO. Photocatalytic conversion was achieved using only visible light in the presence of sacrificial H$_2$O, without additional sacrificial agents or co-catalysts, significantly out-performing TiO$_2$ P25 (x7.5 times). The influence of the reducing agent was investigated (i.e. H$_2$ vs. H$_2$O). Surprisingly, employing sacrificial H$_2$O led to significant improvements in photoconversion rates. We hypothesise that the
preferential adsorption of $\text{H}_2\text{O}$ 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.
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 °C in both N\textsubscript{2} and air atmospheres (Figure S5-6). Char yields in N\textsubscript{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, 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, increased uptake density per unit of surface area due to more attractive interactions with the adsorbate CO₂.

The presence of adsorbed water was shown to impede CO₂ uptake in polar HCPs, due to competitive adsorption. 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 CO$_2$ by the polymers, particularly HCP-2 and HCP-3. During photoreduction experiments, we did not expose HCPs to water vapour prior to CO$_2$ reduction, but rather a stream of CO$_2$ containing water vapour. As such, the effect of co-adsorption is likely to be less significant in-situ.

**CO$_2$ photoreduction activity of hypercrosslinked polymers**

To evaluate the potential of HCPs for CO$_2$ 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 CO$_2$/CO and the VB below the oxidation potential of both H$_2$/H$_2$O and O$_2$/H$_2$O. Hence, the band diagrams point towards a sufficient thermodynamic driving force to enable the reduction of CO$_2$ to CO using either gaseous H$_2$ or H$_2$O 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 CO$_2$ photoreduction. Overall, the narrow band gaps and visible light absorption properties of HCPs, as well as their CO$_2$ adsorption capacities, make them a priori attractive candidates for CO$_2$ 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 representation 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.
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 CO₂ 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.⁴⁵ Other materials such as ZrO and coal also exhibit increased CO₂ adsorption and/or activation in the presence of co-adsorbed H₂O.⁴⁶-⁴⁸ 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.⁴⁹-⁵⁰ 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
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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