Unique hole-accepting carbon-dots promoting selective carbon dioxide reduction nearly 100% to methanol by pure water

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Solar-driven CO2 reduction by abundant water to alcohols can supply sustainable liquid fuels and alleviate global warming. However, the sluggish water oxidation reaction has been hardly reported to be efficient and selective in CO2 conversion due to fast charge recombination. Here, using transient absorption spectroscopy, we demonstrate that microwave-synthesised carbon-dots (mCD) possess unique hole-accepting nature, prolonging the electron lifetime (τ50%) of carbon nitride (CN) by six folds, favouring a six-electron product. mCD-decorated CN stably produces stoichiometric oxygen and methanol from water and CO2 with nearly 100% selectivity to methanol and internal quantum efficiency of 2.1% in the visible region, further confirmed by isotopic labelling. Such mCD rapidly extracts holes from CN and prevents the surface adsorption of methanol, favourably oxidising water over methanol and enhancing the selective CO2 reduction to alcohols. This work provides a unique strategy for efficient and highly selective CO2 reduction by water to high-value chemicals.
The consumption of fossil fuels has been increasing the level of atmospheric CO$_2$ and consequently causing imminent climate change$^{2-3}$. To mitigate energy and environmental issues as well as generate sustainable fuels, people have devoted continuous efforts to reproducing natural photosynthesis to fix CO$_2$ to sugar since the 1970s$^{13,15}$. In an ideal photocatalytic CO$_2$ conversion system, a semiconductor is excited by photons of appropriate energy and generates pairs of electrons and holes. These then transfer to the surface to reduce CO$_2$ and oxidise water, competing with the undesired electron-hole recombination. Such recombination occurs at $< \mu$s timescale, much faster than the water oxidation by holes, which proceeds at $\sim 1$ s timescale$^{6}$. Therefore, it remains challenging to reduce CO$_2$ by pure water and benchmark systems mostly use sacrificial hole acceptors, instead of water, to rapidly scavenge holes and prolong the lifetime of photoelectrons$^{7,8}$. Although the efficiencies of CO$_2$ reduction have been increased by a few orders of magnitude in recent years, the majority of these systems are uneconomical and unsustainable$^{7,8}$. In order to replace those sacrificial regents by abundant water to achieve sustainable CO$_2$ conversion, one has to develop satisfactory semiconductors with long-lived charge carriers as well as co-catalysts to extract the photoholes, thus favouring the water oxidation reaction instead of charge recombination.

Carbon nitrides, which always comprise carbon, nitrogen and hydrogen instead of ideal structure C$_3$N$_4$ when prepared in the laboratory$^{9}$ (denoted CN herein), is an emerging group of easy-to-tune organic semiconductors$^{10-12}$ and has demonstrated uncommonly-observed long-lived charge carriers owing to its unique defective structure$^{13,14}$. In the presence of reduction co-catalysts and visible-light illumination, CN has shown promising activities in hydrogen production and CO$_2$ reduction due to its negatively-positioned conduction band (CB)$^{15-19}$. However, there are only a few reports on water oxidation using CN, because its valence band (VB) is too close to the water oxidation potential as well as the inherent kinetic challenge of water oxidation$^{17,20}$. Hence, an active co-catalyst for water oxidation is crucial to take advantage of long-lived charge carriers in CN. Carbon-dots (CD, $< 10$ nm in diameter), another emerging class of carbon nanomaterials with unique electronic structures, have recently been used as co-catalysts to enhance light absorption, decompose peroxide and more importantly store electrons for reduction reactions$^{17,21-24}$. Although an electron-accepting CD co-catalyst prolongs the lifetime of electrons, it is associated with a loss of electrochemical potential of photogenerated electrons without accelerating the sluggish water oxidation. A better solution is to apply a hole-accepting CD to tackle the difficult water oxidation since electron-accepting co-catalysts with a less negative CB waste a portion of the reductive potential of electrons photogenerated in CN and do not thermodynamically favour proton reduction. However, limited evidence has been reported on CD for its function of selective charge carriers acceptance. On the other hand, such hole-accepting CD co-catalyst, albeit decisive for improved water oxidation, has been rarely observed in experiments until now$^{25-30}$.

Methanol, a useful liquid hydrogen source with the convenience of storage and transport for fuel cells$^{31}$, is a more desirable reduction product from CO$_2$ compared to CO, methane and formic acid. However, the generation of methanol is a 6-electron process, hence requiring an exceptionally prolonged lifetime of charge carriers to allow for electrons accumulation. Moreover, methanol traps holes in $\sim 10$ ns on TiO$_2$, and its oxidation is thus kinetically much favoured over water oxidation ($\sim 1$ s)$^{9}$, making the continuous production of methanol a significant challenge. So far, stoichiometric production of methanol and oxygen from CO$_2$ and water has hardly been reported with high selectivity (confirmed by isotopic labelling), long-term stability and satisfactory internal quantum yield (IQY) which is more reliable than product evolution rates (Supplementary Table 1)$^{32}$, again due to the lack of suitable co-catalysts to selectively transfer holes towards water instead of methanol. Accordingly, in order to utilise water as a sustainable hole scavenger and selectively produce methanol from CO$_2$, we need to design an ideal hole-accepting CD, which is mainly dependent upon our fundamental knowledge of photophysical processes$^{13}$. Although transient absorption spectroscopy (TAS) plays an essential role in understanding the charge carrier dynamics of semiconductors for water splitting$^{13}$, the spectroscopic characteristics in CO$_2$ conversion processes are still unknown at ultrafast timescale, potentially hindering the rational development of target photocatalysts$^{33}$.

Herein, using TAS investigation, we distinguish a unique species of CD as a hole acceptor in the mCD/CN composite when fabricated by a scalable microwave method (mCD, graphite phase). CDs could also behave as an electron acceptor in the CD/CN composite where they are fabricated by a sonication-based method (CD, amorphous). mCD prolongs the lifetime of electrons in CN by a factor of four compared to CD, favouring the multi-electron reduction process. Remarkably, the mCD/CN nanocomposite stably produces stoichiometric oxygen and methanol with near-unity selectivity, confirmed by $^{13}$C labelling, with an IQY of 2.1% at 420 nm. On the other hand, the sCD/CN composite only generates CO$_2$, a two-electron product. Furthermore, the unique mCD captures holes from electrons and prevents the adsorption of the reduction product methanol, hence favourably oxidising water instead of methanol and enhancing the selectivity of CO$_2$ reduction to alcohols.

**Results**

**Synthesis and characterisation of all photocatalysts.** As discussed above, the widely reported electron-accepting co-catalysts with a less negative CB waste a portion of the reductive potential of electrons photogenerated in CN and do not promote the sluggish reaction between holes and water molecules. Hole-accepting co-catalysts can prolong the lifetime of photogenerated charges, preserve the reduction potential of photoelectrons on the CB and also turn water molecules to preferable products, e.g., O$_2$, thus meeting our targeted ideal system for CO$_2$ conversion. Therefore, an efficient hole-accepting co-catalyst is highly sought after for photon-driven CO$_2$ reduction. We explored CD co-catalysts by synthesising two CD samples according to different recipes, and their properties were then investigated via extensive and thorough characterisations. Both carbon-dots were loaded to CN at their optimal concentrations: 3.5% for mCD/CN and 3% for sCD/CN, respectively.

The novel mCD were synthesised via a modified 10-minute microwave method from urea and citric acid precursors, much faster than other reported methods for high-quality CD$^{17,24,28}$. Then the purified mCD were dissolved with dicyandiamide (DCDA, a precursor for CN) in DMF and stirred for ten hours at 60 °C before transferring into a ceramic crucible, followed by thermal polymerisation at 500 °C and exfoliation processes to obtain sCD/CN. For comparison, the other carbon-dots reported as reduction co-catalysts were fabricated via an alkali-assisted sonication treatment of glucose precursor (CD) and loaded to carbon nitride to form sCD/CN$^{30}$. Pristine CN was synthesised from a DCDA precursor followed by identical thermal oxidation etching$^{34}$. Detailed nanocomposite photocatalyst preparation procedures and other characterisation methods are listed in the Method.

Powder X-ray diffraction (PXRD) patterns were measured (Fig. 1a) to obtain the crystallinity information of CN, mCD/CN
and sCD/CN. At first glance, both carbon-dots exhibit poor crystalline patterns. However, mCD shows a broadened (002) peak around 26.5° (3.36 Å), close to the graphite structure reported in the literature. The weak and widened band of 1° (110) planes of CN (characteristic d-spacing of 0.63 nm), which matches well with the images of CN (Fig. 1b) show hexagonal lattice fringes with a crystalline pattern. However, mCD shows a broadened (002) peak around 26.5° (3.36 Å), close to the graphite structure reported in the literature. The weak and widened band of (110) planes of a 2 × 2 × 1 hexagonal super unit cell of graphite (a = 0.46 and c = 0.67 nm) is (110) crystal fringes of CN. a PXRD pattern of mCD, sCD and CN. b HRTEM images of CN. Scale bar: 10 nm. Inset: an enlarged image showing (110) crystal fringes of CN. c HRTEM images of mCD/CN nanocomposite. Scale bar: 5 nm. mCD are marked by circles. Inset: an enlarged image showing graphite superstructure of mCD. d Raman, e Fourier transform infrared (FTIR) and f UV–vis spectra of mCD, sCD and CN. Source data are provided as a Source Data file.

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stronger absorption than CN in the visible region to 600 nm (Fig. 2a, dashed line). In order to determine the nature of the excited states, we first measured the TAS spectra of CN with and without Ag⁺ ions, a well-known efficient electron scavenger which can yield long-lived holes. Kinetic traces probed at 510 and 700 nm (Supplementary Fig. 3a, b) show that in the presence of Ag⁺ ion scavenger the amplitude at 700 nm decreases but the 510 nm signal enhances and features a longer-lived species. Therefore, the signal observed at 510 nm is mainly assigned to the 510 nm signal of holes residing in CN. A slight increase in t50% (from 25 to 40 µs) compared to bare CN (Fig. 2g) was attributed to the separation of charges by ⁴CD. These observations are consistent with the hypothesis of the extraction of electrons from CN by ⁴CD. The µs-TAS decay at 700 nm is well represented by a power law of the form I ∝ t⁻α, as evidenced by the linear decay on a log-log plot, indicating a trapping-detrappping dynamics (Fig. 2h)³⁻. Briefly, we have identified the desired hole-accepting ⁴CD co-catalyst in the ⁴CD/CN composite. Different functions of two CDs could be seen for charge separation, and the specific CD/CN interaction can influence the direction of charge transfer.

**Charge carrier dynamics of all samples.** As discussed above, two major obstacles hindering sustainable light-driven CO₂ reduction by water are (i) the intrinsic weak reduction potential of water and (ii) the lack of fundamental understandings of charge carrier dynamics of co-catalysts. Most of the reported CDs promote reduction process as an electron acceptor while very few are distinguished as an advantageous hole acceptor for efficient water oxidation. Therefore, to understand the role of different carbon-dots, we investigated the charge transfer kinetics of CN, ⁴CD/CN and ⁴CD/CN samples after synthesis and characterisation. TAS, a powerful technique to elucidate the charge carrier dynamics of photocatalysts, was used to experimentally determine the electron-hole dynamics of ⁴CD/CN and ⁴CD/CN nanocomposite at µs-s timescales. Photoexcitation of CN alone yields a broad absorption spanning from 450 to 1000 nm, which peaks near 700 nm (Fig. 2a, dashed line). In order to determine the nature of the excited states, we first measured the TAS spectra of CN with and without Ag⁺ ions, a well-known efficient electron scavenger which can yield long-lived holes. Kinetic traces probed at 510 and 700 nm (Supplementary Fig. 3a, b) show that in the presence of Ag⁺ ion scavenger the amplitude at 700 nm decreases but the 510 nm signal enhances and features a longer-lived species. Therefore, the signal observed at 510 nm is mainly assigned to the photogenerated holes in CN and the broad photoinduced signal observed at 700 nm is assigned to photogenerated electrons in CN, similar to previous observations on CN¹³.

Turning to the CD/CN nanocomposites, the TAS spectra of ⁴CD/CN (Fig. 2b) resemble that of the CN rather than the isolated ⁴CD (Supplementary Fig. 3c). Moreover, the change in collected probe light is on the order of 1% for both the ⁴CD/CN and CN, while it is on the order of 0.005% for ⁴CD. These considerations indicate that TAS predominantly probes CN, and the main feature observed for the ⁴CD/CN nanocomposite remains that of electrons localised in CN. Compared to the results with CN, the amplitude of the 700 nm feature (electron signals in CN) is higher (increasing from 1.25 to 1.5%) in the case of ⁴CD/CN (Fig. 2b), suggesting that more efficient charge separation increases the number of long-lived electrons localised on CN at these timescales. The increased electron signal in CN indicates that holes were efficiently extracted from CN to ⁴CD. In contrast, ⁴CD/CN shows a smaller signal amplitude than pure CN (decreasing from 1.25 to 0.95% at 700 nm) throughout the probed window, inferring electron transfer from CN to ⁴CD. The addition of AgNO₃ does not affect the signal (Fig. 2c,f), suggesting that electrons were already effectively extracted from CN by ⁴CD.

The half-life time (for an initial time t₀ = 2 µs) of the signal observed at 700 nm increases over 6-fold from 25 µs (CN) to 160 µs (⁴CD/CN) (Fig. 2g), indicating suppressed electron-hole recombination due to charge separation across the ⁴CD/CN junction. A long-lived shoulder near 550 nm for ⁴CD/CN was also noted, in line with the 510 nm feature of holes residing in CN. A slight increase in t50% (from 25 to 40 µs) compared to bare CN (Fig. 2g) was attributed to the separation of charges by ⁴CD. These observations are consistent with the hypothesis of the extraction of electrons from CN by ⁴CD. The µs-TAS decay at 700 nm is well represented by a power law of the form I ∝ t⁻α, as evidenced by the linear decay on a log-log plot, indicating a trapping-detrappping dynamics (Fig. 2h)³⁻. Briefly, we have identified the desired hole-accepting ⁴CD co-catalyst in the ⁴CD/CN composite. Different functions of two CDs could be seen for charge separation, and the specific CD/CN interaction can influence the direction of charge transfer.

**Photocatalytic CO₂ conversion to methanol.** After identification of the different structures and physical functions of these junctions, the activity of the photocatalysts for reduction of CO₂ in pure water was evaluated under 1 bar of CO₂ at room temperature under visible-light irradiation (λ > 420 nm; see Supplementary Figs. 6–8 for raw data and calibration curve).

The ⁴CD/CN nanocomposite, which contained hole-accepting ⁴CD, exhibits a remarkably enhanced activity towards the production of methanol and oxygen from CO₂ photoreduction with water as the only electron donor (Fig. 3a). The concentration of ⁴CD was optimised to 3.5% wt (Supplementary Fig. 5a), presumably, to balance light absorption and reaction sites for water oxidation since further increases in the ⁴CD concentration lowers the photocatalytic activity. The yields of both methanol and CO on ⁴CD (3.5)/CN increase nearly linearly over time (Supplementary Fig. 5b) and the average production rates are 13.9 and 0.05 mmol/h, showing a ~99.6 ± 0.2% (calculated from three consecutive runs) selectivity towards methanol. Moreover, O₂ is evolved as the only oxidation product, and the evolved amount increases linearly with the reaction time, similar to the production profile of CO and methanol (Supplementary Fig. 5b). The ratio of O₂ to methanol is about 1:4.5:1, very close to the expected stoichiometric ratio of 1:1 when assuming all generated electrons reduce CO₂ to methanol and all holes oxidise water to O₂. Neither H₂ nor oxidation products other than O₂ were detected. The evolution of stoichiometric O₂ again confirms the significance of the unique function of hole-accepting ⁴CD.

On the contrary, ⁴CD as a reduction co-catalyst was also optimised to a 3% loading on CN to form ⁴CD/CN, which only produces the two-electron product CO instead of the six-electron product methanol, together with negligible O₂ gas (Fig. 3b). This is not surprising because CN itself can hardly produce oxygen in the absence of hole-accepting co-catalysts and ⁴CD here is an electron acceptor as proved by our TAS results, which facilitate charge separation across the ⁴CD/CN junction. A similar CD/g-C₃N₄ junction was previously reported for CO₂ reduction to CO and others⁴⁰. A tiny amount of generated O₂ might also be dissolved in water, consumed via back reactions or below the detection limit of GC. In total, the photocatalytic activity of ⁴CD/CN is ca. 12 times higher than ⁴CD/CN for CO₂ reduction under identical experimental conditions.

Several control experiments were also performed (Fig. 3c): (i) without a CO₂ feed (for ⁴CD/CN nanocomposite), (ii) in the absence of a photocatalyst and (iii) with a lack of light. Under
these conditions, the production of both CO and methanol were negligible, indicating that the CN and mCD could not be decomposed to the products under irradiation. Also, mCD or pure CN showed nearly zero activity. The physical mixture of mCD and CN was also tested and showed no evident activity compared to pure CN, which also supports that a strong interaction between mCD/CN was only prepared in situ by microwave heating and is crucial for CO2 photoreduction.

Isotopic measurement is crucial to avoid misleading information because inevitable organic impurities in carbon-based catalysts can possibly be oxidised to hydrocarbons (e.g., methanol or other organic products). To further confirm the conversion of CO2, the photoreduction of 13C-labeled CO2 was conducted over the mCD/CN photocatalyst. Dominant peaks of 13CO (m/z = 29) and 13CH3OH+ (m/z = 33) were observed at m/z = 29, 32 and 33, which were assigned to 13CO, 13CH3OH+ and fragments of 13CH3O+ produced during the MS measurement (Fig. 3d). The evidence indicates that the evolved products originate from the photoreduction of 13CO2.

Three consecutive runs were then carried out over the mCD/CN photocatalyst (Fig. 3c) to investigate its stability. The CO and methanol evolution rates did not show noticeable changes, indicating the excellent stability of the nanocomposite. For comparison with other reported systems, quantum yield (IQY) is the more preferable and more reliable metric to evaluate one material’s property rather than activity, since the total production rate is highly dependent on the experimental conditions9. The IQY (Fig. 3f) of the optimised mCD/CN photocatalyst was measured to be 2.1% at λ = 420 nm, 0.7% at λ = 500 nm and 0.4% at even λ = 600 nm under 1 bar conditions at room temperature, which is over an order of magnitude higher than that recently reported for CN (0.076% at 420 nm)30. The IQYs at longer wavelengths might be due to the light absorption of mCD or mCD/CN interfacial states as CN could not harvest 500–600 nm photons by itself. Long-lived TAS signal attributed to charges is observed in the mCD/CN composite but not with CN alone under 600 nm excitation (Supplementary Fig. 4). Therefore, water has been successfully used as the sole electron source in the photoreduction of CO2, and for the first time, methanol was produced with nearly unity selectivity in one step under visible-light.

To further demonstrate the improved properties of the mCD/CN composite, we prepared and tested photoelectrodes. The photocurrent of mCD/CN photoanode is approximately twice higher than that of the CN photoanode (Supplementary Fig. 5c), demonstrating the improved separation efficiency of photoexcited charge carriers in mCD/CN and nature of hole acceptor of mCD, which agrees with the results of CO2 photoreconversion. To better understand the photophysical characteristics of photoinduced charge carriers in photocatalysts, the ns-level time-resolved fluorescence of mCD/CN and CN were measured (Supplementary Fig. 5d). The mCD/CN presents slower decay kinetics compared with pure CN, namely, the photogenerated charge carriers in mCD/CN live longer than those generated by CN. The average lifetimes of the carriers (τavg) were determined to be ~15.3 and 13.3 ns for mCD/CN and CN according to the fitting calculation,
respectively, supporting better electron transfer and higher charge separation efficiency in mCD/CN.

It seems ideal that methanol, a highly desirable product from CO₂ conversion, has been produced with near-unity selectivity and remains intact. This is particularly remarkable because methanol is among the most commonly used holes scavengers for hydrogen production from water as it is easily and rapidly oxidised (~10 ns timescale), as mentioned above. How can methanol be conserved as an inert product in a photocatalytic system which generates holes continuously? To elucidate the high selectivity of the mCD/CN junction for H₂O oxidation and methanol production, we employed theoretical calculations of adsorption energy based on Density Functional Theory (DFT). The calculations were carried out using the Vienna ab-initio Simulation Package (VASP)⁴⁴. To mimic the structure of the mCD, the model (Supplementary Fig. 9c) consisting of a coronene (Supplementary Fig. 9a) with a pyrene (Supplementary Fig. 9b) on the top was placed in a 20 × 20 × 10 Å³ box. Two nano-flakes were symmetrically mass-centred with a relaxed interlayer distance of 3.37 Å, consistent with the XRD and HRTEM observation (Fig. 1a,c). This model has been proven effective to mimic the CD (Supplementary Fig. 9a–c)⁴⁵. For the CN, we have adopted the structures used in the previous calculations (Supplementary Fig. 9d,e)⁴⁶. Detailed computational settings are illustrated in the SI.

The adsorption energy, E_ad, was calculated according to

\[ E_{\text{ad}} = E_{\text{total}} - (E_{\text{adsorbate}} + E_{\text{adsorbent}}) \]  

where \( E_{\text{total}} \), \( E_{\text{adsorbate}} \) and \( E_{\text{adsorbent}} \) represent the energies of the absorbing system, the adsorbate and the adsorbent at equilibrium configurations, respectively. According to the calculated adsorption energy of the most stable configurations (Supplementary Tables 3 and 5), both CO₂ and more importantly CH₃OH bind more favourably to CN rather than mCD (Fig. 4a left and middle). On the contrary, H₂O molecules prefer to be absorbed on the surface of mCD instead of CN (Fig. 4a right). According to the TAS results and calculations of E_ad on mCD/CN, CN maintains electrons and adsorb CO₂, while mCD selectively accepts holes and absorbs H₂O. Hence for the mCD/CN composite, CO₂ is reduced by photoelectrons on CN and photoholes on mCD are preferably used to oxidise H₂O instead of methanol. Based on the above results, a pathway of visible-light-driven CO₂ photoconversion on mCD/CN has been proposed in Fig. 4b. Electron-hole pairs are generated in CN under visible-light excitation. Photoelectrons accumulate on the surface of CN where CO₂ reduction to CH₃OH occurs, while photoholes transfer from CN to the surface of mCD to oxidise H₂O into O₂. On the other hand, for mCD/CN, CO₂ reduction takes place on electron-accepting sCD to produce CO while the holes on CN relatively slowly oxidise H₂O molecules or oxidise methanol if produced. Thus, CO could come from both direct reduction of CO₂ and the subsequent oxidation of methanol, which is difficult to distinguish in this case.

To confirm the compatibility of methanol with mCD/CN to rationalise the high selectivity to methanol experimentally, we directly tested the oxidation of methanol by mCD/CN and CN. Figure 4c shows that under visible-light, methanol can be readily oxidised to CO by photoholes of pure CN, which might be the reason why there is no methanol produced by mCD/CN system, no CO was detected, consistent with the theoretical calculations that methanol could not be readily adsorbed on the surface of mCD where holes accumulate, and photooxidation of water occurs. Therefore, the mCD possesses the unique functions of selectively accepting

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**Fig. 3 Photocatalytic CO₂ conversion to methanol.** The photocatalytic activity of a mCD/CN and b sCD/CN measured under visible light (λ > 420 nm). c Control experiments on mCD, sCD, CN, mCD/CN and sCD/CN. Error bar: mCD/CN 13.9 ± 1.7 μmol/g/h, sCD/CN 15.5 ± 0.4 μmol/g/h. d Mass spectra of the product 13CH₃OH from 13CO₂ photoconversion by the mCD/CN photocatalyst. Inset: the mass spectra of the 13CO from 13CO₂ photoconversion over the mCD/CN photocatalyst. e Consecutive three runs of CO₂ photoconversion to methanol on mCD/CN under visible light. f IQY of mCD/CN measured at atmospheric pressure under nearly one sun irradiation condition. Source data are provided as a Source Data file.
Discussion

For $^{13}$CD, its amorphous carbon nature indicates a mixture of sp$^2$ and sp$^3$ species. Hence the charge transfer is less efficient than pure sp$^2$ hybrid of the graphite structure ($^{12}$CD), which partially explains why the $^{12}$CD shows a larger enhancement of lifetime of charges. Holes on CN could not intrinsically oxidise water in the absence of co-catalysts. The activity of O$_2$ production is thus negligible and CO$_2$ reduction is not efficient due to fast charge recombination in CN/CN and poor hole activity. On the other hand, CN/CN favours electron accumulation on the surface of CN due to efficient hole transfer to CN, which facilitates a multi-electron reduction process to produce methanol instead of CO. Therefore, this study demonstrates the superiority of the design of hole-accepting co-catalysts $^{12}$CD to the widely reported electron acceptor $^{13}$CD in promoting the reaction of CO$_2$ reduction to higher-value chemicals.

To summarise, through TAS investigations over six orders of magnitude in time on carbon-based nano architectures, we observe that $^{13}$CD work as an electron acceptor in $^{13}$CD/CN, while $^{12}$CD serves as a notable hole acceptor in $^{12}$CD/CN after excitation. Charge separation across the CD/CN interface increases the lifetime of the charge carriers from 25 µs (CN) to 160 µs ($^{12}$CD/CN) or only 40 µs ($^{13}$CD/CN) and enhances participation in subsequent CO$_2$ conversion. The differences in photophysical functions of CDs result in the differences in both conversion efficiency and more importantly, selectivity. $^{12}$CD/CN junction converts CO$_2$ into CO while the $^{12}$CD/CN junction could unprecedentedly and selectively reduce CO$_2$ to methanol, which has been further confirmed by $^{13}$C labelling with nearly unity selectivity. Furthermore, the $^{12}$CD/CN composite is ca. 12 times more active than $^{13}$CD/CN for CO$_2$ conversion observed under the same experimental conditions.

Such $^{12}$CD show more favourable water adsorption yet unfavourable methanol adsorption compared to CN, thus facilitating selective oxidation of water to O$_2$ while avoiding unproductive oxidation of the photoreduction product, methanol. Therefore, the uncommon $^{12}$CD co-catalyst is a crucial reason for such high selectivity of CO$_2$ reduction to methanol using water as the only reductant. Overall, electrons reach the surface of CN and possess enough chemical potential to reduce CO$_2$, together with protons, to produce methanol with an exceptional 99.6 ± 0.2% selectivity and high IQY of 2.1% at 420 nm and benchmark IQY at 500 and 600 nm (0.7 and 0.4%, respectively). The unique function of hole-accepting carbon-dots should not only excite broad interest in selective photocatalytic oxidation in organic synthesis and environmental purification but also be potentially useful for promoting charge transfer in photovoltaics, photoelectrochemical devices and light-emitting diodes. This work paves a metal-free avenue to the sustainable production of methanol, which is among the most promising hydrogen sources for fuel cells.

Methods

Materials preparation. All chemical reagents were analytical grade and were used without further purification. Citric acid, N,N-dimethylformamide (DMF), urea, dicyandiamide, methanol, dichloromethane were purchased from Sigma-Aldrich Company Ltd. Deionised water used in all the experiments has a resistivity of 18.1 MΩ cm.

CN Nanosheets. Dicyandiamide (2 g) in a closed crucible was heated at 500 °C for 4 h in static air with a ramp rate of 5 °C/min. The yellow solid agglomerates were milled into powders using an agate mortar. 0.5 g of this as-prepared powders were placed on a ceramic plate and heated at 500 °C for 4 h in air with a ramp rate of 10 °C/min. Then, the CN nanosheets with light yellow colour were finally obtained. This CN nanosheets sample was named CN.

Carbon-dots via microwave method ($^{13}$CD). The citric acid (3 g, 15.6 mmol) and urea (1 g, 16.7 mmol) were added into 8 ml deionised water in a beaker and vigorously stirred to form a transparent solution. This beaker containing solution was then moved into the microwave oven and heated for 10 min under the power mode.
of 600 W. During the reaction, the solution changed from a colourless liquid to a dark brown porous solid, which indicates the CD was finally produced. The solid product was then put into an oven and dried at 80 °C for 10 h to remove the small residual molecules. The suspension of the crude CD was purified in a centrifuge at 8000 rpm for 1 h to remove large or agglomerated particles. The final brown aqueous solution was eluted with a mixture of methanol and dichloromethane at ratios of 1:2 and 1:1 (v/v) to obtain 10% CD. At last, the resulting 10% CD were dried into solid powders.

mCD/CN nanocomposite. Dicyandiamide (2 g) and x mg of mCD obtained above (x = 30, 50, 70 and 90) equal to w.t. 1.5, 2.5, 3.5, and 4.5% to dicyandiamide precursor) were added to 10 mL of DMF and stirred for 1 h; then the liquid was dried at 60 °C for 10 h to completely evaporate DMF. The resulting mixture was placed into a crucible with a cover and annealed at 500 °C in the air for 4 h with a ramping rate of 5 °C/min. The brown solid was washed with DI water and dried at 80 °C, then milled into powders with an agate mortar. A concentration of 0.5 g of mCD/CN nanocomposite was obtained. The dried mixture was then put into an oven and dried at 80 °C for 10 h to remove the small residual molecules. The suspension of the crude CD was purified by deionised water and sonicated for 15 min and stirred vigorously at room temperature for 30 min. The mixture was then subjected to hydrothermal treatment in a Teflon-sealed autoclave with stirring at 120 °C for 4 h to form the mCD/CN nanocomposite.

Characterisations. The morphologies and structures of the samples were characterised by HRTEM using an FEI Titan Themis microscope, operated at 200 kV. UV/Vis spectra were carried out on a Shimadzu UV/Vis 2550 spectrophotometer with an integrating sphere device at RT and transformed to the absorption spectra according to the Kubelka-Munk relation. XPS measurements were recorded by using a Thermo Scientific XPS spectrometer. Time-resolved fluorescence emission spectra were carried out at room temperature with a Fluorescence spectrophotometer (Edinburgh Instruments, FLS-920) monitoring at 470 nm (excitation wavelength of 330 nm). The X-ray diffraction (XRD) patterns were measured by a PANalytical X′pert MPD Pro diffractometer operated at 40 kV and 40 mA using Ni-filtered Cu-Kα irradiation (Wavelength 1.5406 Å). ATR-FTIR spectroscopy was performed using a Perkin Elmer 1605 FTIR spectrometer in the wavenumber range of 500–4000 cm−1 with a resolution of 0.5 cm−1. Raman spectroscopic measurements were performed on a Renishaw InVia Raman Microscope, using a 325 nm excitation laser and a wavenumber range of 100–2000 cm−1.

Photocatalysis measurement. Before the photocatalytic reduction of CO2, 10 mg photocatalyst and 10 mL water were added into a septum-sealed borosilicate glass reactor with a volume of 140 mL. Then, the reactor was purged with CO2 for the photocatalysis experiment. A 300 W Xe lamp (Newport) was utilised as a light source, and the light output power was measured by a Newport 918-D calibrated photodetector. During the reaction, the products were analysed by GC (Varian GC-450) with a thermal conductivity detector (TCD), connected to a capillary column containing a flame ionisation detector (FID, connected to a Poropak S guard column) containing a methanizer equipment. Ar gas was used as the GC carrier gas.

For the isotope-trace experiment, the same photocatalytic process was applied except that 14CO2 (14C 99%, Sigma-Aldrich) was used as the feed gas. The products containing C-isotope were analysed by GC–MS (Shimadzu QP-2010SE) with a molecular sieve 5 Å capillary column (for CO) or a Rxi-624Sil MS capillary column (for methanol). He gas was used as a carrier gas during the measurement.

The CH3OH oxidation conditions: 10 ml H2O, 0.12 μmol MeOH, 10 mg 10% CD/CN photocatalyst, 300 W Xenon lamp irradiation with 420 nm long-pass filter in 1 bar Argon atmosphere.

Fabrication of film electrodes and electrochemical measurements. A total of 10 mg photocatalyst and 10 μL Nafion solution (5 wt%) was dispersed in a water/methanol mixture (1 mL, 1:1 v/v). After sonication treatment for at least 2 h, the mixture formed a homogeneous catalyst colloid. Before the measurements, the catalyst colloid (200 μL) was deposited on an FTO conductive glass with an area of 1 cm2 to form the working electrode. The photocurrent was measured using three electrodes at 1 V bias voltage, of which Ag/AgCl and Pt net electrodes were used as the reference and counter electrodes, respectively. The electrolyte was 1 M Na2SO4 aqueous solution degassed with Ar.

Calculation of internal quantum efficiency. The internal quantum yields for CD/CN photocatalyst was measured using the same experimental setup as the photocatalysis measurement, with a bandpass filter (λ = 420, 500, or 600 nm). The average intensity of irradiation after the 420, 500, and 600 nm bandpass filter was 221, 347, and 398 μW/cm2, respectively (calculated by five points measured in the beam).

\[
\text{Absorption} = \frac{100\% \times (T_0 - T_f)}{T_0} \times \frac{(T_i - T_f)}{T_i} \times 100\% \times \left(10^{-\frac{A}{10}} - 1\right)
\]

The absorbed light density is 110.9, 134.5, and 132.7 μW/cm2 for λ = 420, 500, or 600 nm, respectively. For the photocatalytic reaction, 10 mg CD/CN photocatalysts were dispersed into 10 mL DI water. The measurement was carried out under a 300 W Xe lamp with the bandpass filter for 4 h. The amount of CO and CH2OH is 0.00838 and 0.235, 0.00025, and 0.114 μmol, and 0.074 μmol for 420, 500, and 600 nm bandpass filters, respectively. Also, the irradiation area of the reactor is 12 cm2. Thus, the IQYS at 420, 500, and 600 nm is c.a. 1.1, 0.7, and 0.4%, respectively.

The internal quantum yields are defined by the following equation:

\[
\text{IQYS} = \frac{\text{number of reacted electron}}{\text{number of absorbed photon}} \times 100\%
\]

Two electrons are consumed per CO molecule evolved, and six electrons are consumed per CH2OH molecule evolved according to reaction (3) or (4).

\[
\text{CO}_2 + 2e^- + 2H^+ \rightarrow \text{CO} + \text{H}_2\text{O}
\]

As a result, the internal quantum efficiency can be estimated by the equation:

\[
\text{IQYS} = \frac{N_{\text{CO}} \times 2 \times N_a \times N_{6\text{H}} \times 6 \times N_a}{H_a \times 4 \times h \times \lambda}
\]

where \(N_{\text{CO}}\) is the amount of CO after 4 h reaction, \(N_a\) is the amount of CH2OH after 4 h reaction, \(N_a\) is the Avogadro’s number, \(H_a\) is the average intensity of absorbed light, obtained by the subtraction of the transmitted intensity from the incident intensity. \(A\) is the irradiation area (12 cm2), \(h\) is the Planck’s constant, \(c\) is the speed of light, \(\lambda\) is the wavelength of the incident light, \(t\) is the time.

Data Availability

The source data underlying Figs. 1a,d, 2a–h, 3a–f and 4a,c and Supplementary Figs 2a–d, 3a–c, 4 and 5a–d are provided as a Source Data file.

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Author Contributions
J.T. conceived and supervised the entire project. Y.W and X.L prepared the materials and carried out the photocatalytic activity tests and nano junctions’ characterisations. X.H., S.A.S. and Z.G. carried out the simulation and coordinated the whole version. R.G, J.F.T. and J.R.D. carried out the TAS measurements and analysis. C.J. repeated the nano junction synthesis and carried out the methanol oxidation test. K.B.M. did TEM and FTIR analysis. J.C. and W.Z. performed HRTM characterisation. Y.W., X.L., X.H, R.G wrote the manuscript. All authors contributed to discussion and revisions.

Competing interests
The authors declare no competing interests.

Additional information
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