

Photochemical CO₂ reduction using structurally controlled g-C₃N₄

James J. Walsh,^a Chaoran Jiang,^b Junwang Tang^{b*} and Alexander J. Cowan^{a*}

The published form of the article can be found in Physical Chemistry Chemical Physics, 2016, DOI: 10.1039/C6CP04525A

Graphitic carbon nitride (g-C₃N₄) synthesised from a urea precursor is an excellent CO₂ reduction photocatalyst using [Co(bpy)_n]²⁺ as a co-catalyst. A five-fold increase in activity for the highly polymerised urea derived g-C₃N₄ is achieved compared to alternative precursors. Transient absorption, time-resolved and steady-state emission studies indicate that the enhanced activity is related to both an increased driving force for photoelectron transfer and a greater availability of photogenerated charges.

Increasing atmospheric CO₂ levels due to anthropogenic activity has brought carbon capture and carbon utilisation into the public consciousness and to the forefront of chemical research. The reduction of CO₂ to useful feedstocks or fuels such as CO, formic acid and methanol can be achieved through photochemical, electrochemical and thermal methods. The photochemical reduction of CO₂ is particularly attractive as when coupled to light driven water oxidation it offers a route to carbon based solar fuels. Whilst significant progress has been made in recent years towards the delivery of efficient semiconductor photocatalysts for water oxidation,¹ the development of a visible light active, scalable, stable, photocatalytic system for CO₂ reduction in the presence of water remains an un-realised goal.

g-C₃N₄ is an organic polymeric photocatalyst that has been intensely studied for photocatalytic hydrogen evolution^{2, 3, 4, 5, 6, 7, 8, 9} and to a lesser extent water oxidation,^{3, 10} since a landmark study in 2009.² The band gap of g-C₃N₄ (typically *ca.* 2.5 eV) enables visible light activity. In addition, g-C₃N₄ has been shown to be photochemically and mechanically stable and relatively facile to synthesise.^{11, 12} In addition a diverse range of approaches towards enhancing the visible light activity of g-C₃N₄ have been reported including g-C₃N₄/metal oxide heterojunctions,¹³ dye-sensitised g-C₃N₄¹⁴ and full photocatalytic water splitting z-schemes.¹⁵ Of particular significance to this study is that some of us have recently shown that platinized g-C₃N₄ prepared from different precursors can have markedly different levels of photocatalytic activity, with a urea-derived material achieving an internal quantum efficiency (IQE) of 26.5 % for hydrogen production, greatly exceeding previously reported g-C₃N₄ photocatalysts.¹⁶ This very high level of photocatalytic activity, an order of magnitude greater than comparable materials prepared from different precursors, was found to correlate to an increased degree of polymerization and decreased proton concentration within the urea based g-C₃N₄.

In contrast to the substantial literature relating to hydrogen evolution there are a more limited number of studies examining the use of g-C₃N₄ for CO₂ reduction in the presence of water.^{17, 18, 19, 20, 21} One issue is that to overcome competitive proton reduction to H₂ in the presence of water a selective CO₂ reduction co-catalyst is required. Recently Maeda *et al.*, have developed a range of [Ru(bpy)(CO)₂Cl₂] derivatives (bpy = 2,2'-bipyridine) where modification of the 4,4' positions of bpy has enabled either direct or indirect binding to g-C₃N₄,^{20, 21} giving rise to a material that reduced CO₂ to formate with an apparent quantum yield (AQY) of 5.7% at 400 nm.²² Alternative approaches have explored the use of scalable co-catalysts on g-C₃N₄ including [Co(bpy)_n]²⁺.^{17, 18, 19} In these studies the co-catalyst, which is assembled *in-situ*, has been shown to be effective for CO production with an AQY of 0.25% at 420 nm and excellent selectivity.¹⁸ Whilst these reports clearly demonstrate the potential application of g-C₃N₄ for CO₂ reduction, to date there have been relatively few systematic studies on exploring the nature of the g-C₃N₄ used with each co-catalyst. Herein we examine a range of carbon nitrides, including the previously reported highly active urea derived g-C₃N₄,¹⁶ for CO₂ reduction. The simple *in-situ* prepared [Co(bpy)_n]²⁺ co-catalyst is chosen as it has been reported to be highly effective with a wide range of different light absorbers,¹⁹ making it an ideal test platform to explore the role of different g-C₃N₄ structures derived from a range of precursors. We report both an enhancement in the activity for a g-C₃N₄/[Co(bpy)_n]²⁺ mediated CO₂ reduction system and an improved overall understanding into the factors controlling the high levels of activity of urea derived g-C₃N₄ in reductive photochemistry.

g-C₃N₄ was prepared from three different precursors (urea, thiourea and dicyandiamide (DCDA)) in the manner previously described, see ESI for full details.¹⁶ Previous reports on the g-C₃N₄/[Co(bpy)_n]²⁺ system have demonstrated successful CO₂ reduction in a solvent mixture of CH₃CN/H₂O with triethanolamine (TEOA) also being added as a sacrificial electron donor^{17, 18, 19} and the same solvent system is also employed here (CH₃CN:H₂O:TEOA, 3:1:1, 5 ml total). In the presence of urea derived g-C₃N₄ (2.5 mg), CoCl₂ (50 μmol dm⁻³), bpy (5 mmol dm⁻³) under an atmosphere of CO₂ we observe photocatalytic CO production with minimal H₂ evolution (CO:H₂, 3.3:1), see Table 1. In the absence of any one of these components CO₂ reduction does not occur (Table S1). A brief optimization of the concentrations of the catalyst components is presented in the ESI (Figs. S1, S2); however we highlight that the focus of this study is the optimization and mechanistic study of the g-C₃N₄ absorber. The lack of CO production in the absence of CO₂ and isotopic labelling studies (Fig. S7) definitively confirmed CO₂ to be the carbon source for CO.¹⁸ The lack of CO₂ reduction in the absence of the bipyridine ligand is also in agreement with past electrochemical and photochemical studies of this co-catalyst, which has previously supported an assignment of the active catalyst precursor to a molecular species, proposed to be [Co(bpy)_n]²⁺.^{23, 24}

g-C ₃ N ₄ precursor	SSA (m ² .g ⁻¹) ^a	Band gap (eV)	CO rate μmol.g ⁻¹ .h ⁻¹ /TON ^b	H ₂ rate μmol.g ⁻¹ .h ⁻¹ /TON ^b	Selectivity (CO:H ₂)
Urea	43.8	2.9	460/9.2	138/2.8	3.3:1
Thiourea	18.5	2.5	22/0.4	86/1.7	0.25:1
DCDA	12.8	2.6	92/1.8	94/1.9	~ 1:1

Table 1: Photocatalytic activity for CO₂ reduction of the different g-C₃N₄ materials. Experiments carried out using 300 – 795 nm KG1 filter (Fig. S3), 40 mW.cm⁻² illumination, 0.5 mg g-C₃N₄ per ml in CH₃CN/TEOA/H₂O (3:1:1), t = 2 h. a: Specific surface area, see reference 16; b: TON per Co²⁺ at t = 2 hours.

Under Xe lamp illumination (300 -795 nm) a turnover number (TON) per Co²⁺ of greater than 9 was achieved after 2 hours for CO production using urea derived g-C₃N₄, Table 1. At prolonged periods it was found that the rate of CO₂ production began to decrease. To explore the factors limiting the TON experiments using a 400 nm LED were carried out, Fig. 1 (a). The use of a blue LED with a small spectral distribution allows for excitation of the g-C₃N₄ whilst avoiding the potential photochemical degradation of the reduced [Co(bpy)_n]⁺ (λ_{max} ~ 600 nm).²⁴ After 6 hours of illumination at 400 nm the CO yield plateaued with a TON corresponding to ca. 10.6. Flushing the flask with fresh CO₂ leads to a recovery of activity and the system was able to achieve a TON > 18 before the experiment was terminated. This recovery in activity may indicate that a build-up of CO inhibits catalysis, either through CO interacting with the g-C₃N₄, or more likely through inhibition of the co-catalyst. It is noted that CO inhibition has been previously reported during CO₂ photoreduction with other Co²⁺ catalysts.²⁵

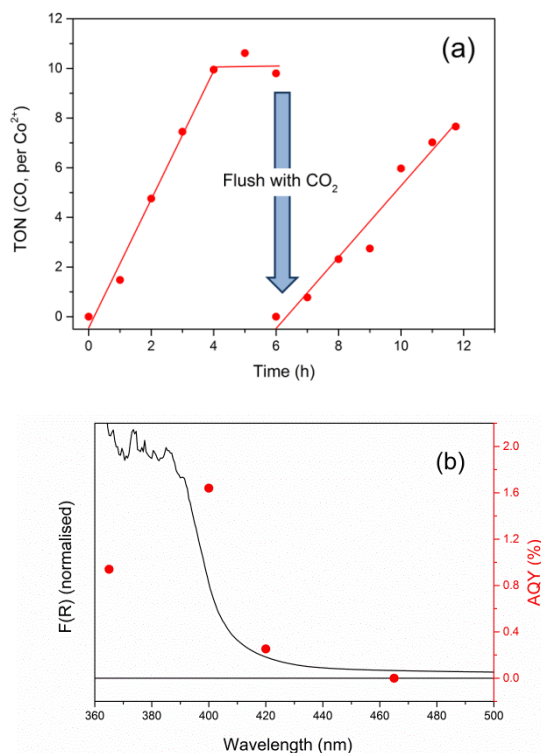


Fig. 1: Photocatalytic CO₂ reduction under (a) prolonged 400 nm LED illumination (ca. 5 mW.cm⁻²). (b) AQY for CO production measured at wavelengths shown (red) and overlaid UV/Vis spectrum of the reaction suspension. Conditions: g-C₃N₄ (urea, 2.5 mg), CoCl₂ (50 μmol dm⁻³) and bpy (5 mmol dm⁻³) in 5 ml CH₃CN:H₂O:TEOA, 3:1:1 purged with CO₂.

Previous hydrogen evolution studies have found that the photocatalytic activity of platinumized urea derived g-C₃N₄ is significantly greater than other precursor materials.¹⁶ Similarly the highest efficiency material for CO₂ reduction using [Co(bpy)_n]²⁺ as a co-catalyst is g-C₃N₄ (urea), with relative catalytic efficiencies following the trend urea > DCDA > thiourea. The CO yield from g-C₃N₄ (urea) was 5x higher than that from DCDA-derived g-C₃N₄, and 23x higher than that from thiourea-derived g-C₃N₄, Table 1. The CO/H₂ selectivity was also 3.3x or 13.3x higher, respectively. Interestingly the relative enhancements in activity for CO₂ reduction reported here are similar to those reported for H₂ production using g-C₃N₄/Pt, where g-C₃N₄ (urea) produces H₂ at a rate of 8x relative to g-C₃N₄ (DCDA) and 13.5x relative to g-C₃N₄ (thiourea).¹⁶ In order to benchmark the activity of the urea derived system for CO₂ reduction we have recorded the AQY, also known as the

photonic efficiency,²⁶ at a range of wavelengths (Fig. 1 (b)). The AQY response of g-C₃N₄ (urea) and [Co(bpy)_n]²⁺ matches well to the recorded UV/Vis spectrum of g-C₃N₄. Direct comparison of efficiencies between this study and others by AQY is complicated as the AQY does not take into account the number of photons absorbed, only those incident on the sample (see ESI for the calculations). However it is apparent that the activity of the urea g-C₃N₄ is at the same level of greater than current state-of-the-art g-C₃N₄ (melamine)/CoO_x/[Co(bpy)_n]²⁺ systems for CO₂ reduction which utilised a ten-fold more concentrated suspension of g-C₃N₄ to achieve a maximum AQY of 0.25 % at 420 nm and noted only a small increase in activity at 400 nm.¹⁸ In contrast here we reach a maximum AQY of 1.6 % at 400 nm and at 420 nm, a wavelength where incomplete light harvesting occurs in our reactor (Fig. 1 (b)), an AQY 0.25 % is also achieved. The maximum AQY of 1.6 % is indeed comparable to other state of the art CO₂ reduction photocatalysts.^{20, 27, 28}

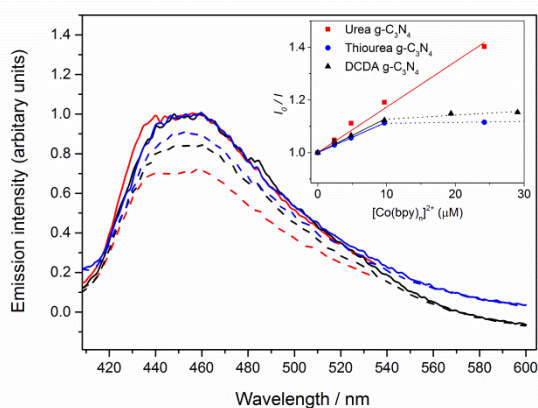


Fig. 2: Normalised emission of urea (red), DCDA (black) and thiourea (blue) derived g-C₃N₄ (0.1 mg ml⁻¹ in 1:1 CH₃CN/H₂O) in the absence of a quencher (solid lines) and relative quenching in the presence of [Co(bpy)_n]²⁺ (dashed lines). Inset shows the Stern-Volmer plots for g-C₃N₄ in CH₃CN/H₂O with a [Co(bpy)_n]²⁺ quencher.

It is striking that the relative trends for the activity of urea, DCDA and thiourea derived g-C₃N₄ are the same for both CO₂ reduction and H₂ evolution.¹⁶ This change in activity cannot be attributed to improved light harvesting of the urea derived material as it displays a wider band gap than both the DCDA and thiourea samples (Table 1, Fig. S4). The photocatalytic CO₂ activity also does not scale linearly with the relative BET surface areas of the materials, Table 1. It has been previously noted that the activity for the different materials for hydrogen evolution correlates with the degree of material hydrogenation (i.e.: the ratio of surface sp² nitrogen sites (C-N-C) to sp³ sites (H-N-[C]₃ and C-NH_x)).¹⁶ DFT calculations indicated that two possible enhancement routes were occurring in materials with high sp²:sp³ ratios. Firstly the observed wider band gap of urea derived g-C₃N₄ leads to a raising of the conduction band edge (Fig. S4), which will increase the driving force for electron transfer to any co-catalyst. Secondly a greater level of exciton delocalization was proposed to occur in g-C₃N₄ (urea), minimizing fast exciton recombination and increasing the yield of separated charges which are required for photocatalysis to occur.¹⁶ Here we have explored the potential role of both effects in the photocatalytic CO₂ reduction system. Photoluminescence (PL) occurs in g-C₃N₄ after bandgap excitation due to electron-hole recombination, displaying maxima ranging from 440 – 460 nm. In the presence of an electron acceptor it is known that this emission can be quenched by electron transfer to [Co(bpy)_n]²⁺.¹⁸ Quenching studies in the absence and presence of [Co(bpy)_n]²⁺ were performed (Fig. 2). A Stern-Volmer (SV) plot shows a good linear response for concentrations of co-catalyst up to 10 μmol dm⁻³. Notably the slopes of the SV plots yielded K_{SV} constants (Table S2) with values following the sequence urea > DCDA > thiourea, which mirrors the sequence of photocatalytic activity (transient emission studies indicate a similar lifetime for the emissive states in all three materials, Fig. S5), and the driving force for electron transfer calculated by DFT and TD-DFT previously.¹⁶ We also note that for thiourea and DCDA derived g-C₃N₄ no additional quenching occurs at [Co(bpy)_n]²⁺ concentrations above 10 μmol dm⁻³. The lack of linearity at higher quenching concentrations may indicate a population of inaccessible emissive states.²⁹ In DCDA and thiourea derived materials it is proposed that a significant population of photogenerated charges are trapped at sites inaccessible to the solution, hence making them photochemically less active. In contrast the urea derived g-C₃N₄ displays reasonable linearity at quencher concentrations up to 24 μmol dm⁻³, it is apparent therefore that both the increased driving force for electron transfer from the conduction band of urea derived g-C₃N₄ to the [Co(bpy)_n]²⁺ catalyst and the greater accessibility to the g-C₃N₄ surface are important factors behind the enhanced photocatalytic activity of this material.

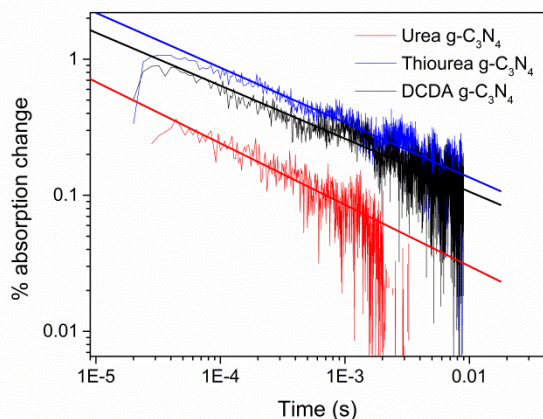


Fig. 3: DR-TA kinetic traces recorded at 850 nm for the $g\text{-C}_3\text{N}_4$ sample indicated under an Argon atmosphere, following UV (355 nm, 91 $\mu\text{J}\cdot\text{cm}^{-2}$) excitation.

Transient absorption (TA) spectroscopy is a powerful tool to probe the change in concentration of charge carriers (photogenerated electrons and holes) with time³⁰ and here we also examine the diffuse reflectance TA kinetics of the $g\text{-C}_3\text{N}_4$ samples. Recently it has been highlighted that long-lived photogenerated charges can persist in $g\text{-C}_3\text{N}_4$ into the milliseconds timescales and it has been proposed that these are important in controlling photocatalytic efficiency.^{22, 31} Following UV (355 nm, 6 ns pulse, 91 $\mu\text{J}\cdot\text{cm}^{-2}$) excitation we observe a broad long-lived feature in the visible/NIR region that persists for significantly longer timescales (signals remain at > 10 ms after excitation at 850 nm) than the strong emission that is observed between 400 – 600 nm (lifetime *ca.* 8 ns, Fig. S5). Again a clear trend between the different $g\text{-C}_3\text{N}_4$ samples is noted with the urea derived sample having a far lower yield of long-lived TA features when compared to the DCDA and thiourea samples. Full DR-TA spectra of all samples are shown in Fig. S6. In recent studies similar $g\text{-C}_3\text{N}_4$ TA features in the visible region have been assigned to trapped electrons or potentially electron-hole pairs and the same assignment is proposed here.^{22, 32, 33} The decay kinetics of the TA features at 850 nm are found to fit well to a power law model ($\%abs \propto t^\beta$, $\beta = 0.42 \pm 0.05$) for all three $g\text{-C}_3\text{N}_4$ samples studied which is likely to indicate that charge recombination is occurring *via* a trap-detrap mechanism, Fig. 3.³⁴ The weaker long-lived TA signals in our most active photocatalyst is perhaps surprising as it is often suggested that the ability to generate higher yields of long-lived charges is a characteristic of the most active semiconductor photocatalysts.³⁵ Indeed in a recent study on photoelectrochemical water splitting using a protonated $g\text{-C}_3\text{N}_4$ embedded in Nafion such a trend was noted; however it is important to highlight in this case water oxidation was studied and the protonated sample actually had a lower $sp^2\text{N}/sp^3$ ratio than the untreated $g\text{-C}_3\text{N}_4$.³¹ In contrast a recent TA study of $g\text{-C}_3\text{N}_4$ by Kuriki *et al.*²² reported the presence of deeply trapped inactive charges in the visible region. Furthermore in the TA experiments presented here, which are carried out under an argon atmosphere in the absence of the water/ $g\text{-C}_3\text{N}_4$ interface, defect sites may be critical in overcoming the large exciton binding energy³⁶ of $g\text{-C}_3\text{N}_4$ leading to the presence of deeply trapped charges. Therefore, in light of the (i) observed trap-mediated recombination kinetics (ii) the inverse correlation between photocatalytic activity and long-lived charge TA signal and (iii) the previous observation in the emission quenching study of inaccessible sites on DCDA/thiourea $g\text{-C}_3\text{N}_4$ we propose that the transient absorption observed here at 850 nm also correlates to deep lying, kinetically less reactive, photogenerated charges. The DCDA and thiourea samples appear to have a higher density of deep lying less photochemically active trap states than the urea derived material which is leading to decreased photocatalytic activity for both CO_2 reduction and hydrogen evolution.

Conclusions

We have tested a family of $g\text{-C}_3\text{N}_4$ polymers, previously shown to be excellent photocatalysts for H_2 production¹⁶ for CO_2 reduction using $[\text{Co}(\text{bpy})_n]^{2+}$ as co-catalyst. This has led to us achieving a five-fold increase in the CO evolution rate. Given that urea derived $g\text{-C}_3\text{N}_4$ with a high $sp^2:sp^3$ N ratio appears to be generally extremely active for photochemical reductions it is important that the factors controlling activity are resolved. Our TA and emission studies show that an increased driving force for charge transfer to a co-catalyst (in this case $[\text{Co}(\text{bpy})_n]^{2+}$) or to a sacrificial electron donor is a significant factor. Perhaps surprisingly we also find that the high activity of the urea derived materials correlates with a lower yield of long-lived deeply trapped photogenerated charges, highlighting the importance of defect and other potential charge trap sites in controlling the photochemistry of $g\text{-C}_3\text{N}_4$.

Notes and references

JJW and AJC acknowledge the EPSRC (EP/K006851/1) for a funding and a fellowship respectively and for equipment funding (EP/K031511/1). Thanks to Prof. Dave J. Adams and Prof. Dmitry Shchukin (UoL) for providing access to the fluorimeter and FTIR spectrometer, respectively. Thanks to Mr. Mark Forster (UoL) for his help with DR-TA experiments.

- 1 S. J. A. Moniz, S. A. Shevlin, D. J. Martin, Z.-X. Guo and J. Tang, *Energy Environ. Sci.*, 2015, **8**, 731–759
- 2 X. Wang, K. Maeda, A. Thomas, K. Takanaabe, G. Xin, J. M. Carlsson, K. Domen and M. Antonietti, *Nat. Mater.*, 2009, **8**, 76–80.
- 3 J. Liu, Y. Liu, N. Liu, Y. Han, X. Zhang, H. Huang, Y. Lifshitz, S. Lee, J. Zhong and Z. Kang, *Science*, 2015, **347**, 970–974.
- 4 J. Hong, S. Yin, Y. Pan, J. Han, T. Zhou and R. Xu, *Nanoscale*, 2014, **6**, 14984–14990.
- 5 L. Shi, L. Liang, F. Wang, M. Liu, K. Chen, K. Sun, N. Zhang and J. Sun, *ACS Sustain. Chem. Eng.*, 2015, **3**, 3412–3419.
- 6 S. Min and G. Lu, *J. Phys. Chem. C*, 2012, **116**, 19644–19652.
- 7 X. Zhang, L. Yu, C. Zhuang, T. Peng, R. Li and X. Li, *ACS Catal.*, 2014, **4**, 162–170.
- 8 Y. Shiraishi, Y. Kofuji, S. Kanazawa, H. Sakamoto, S. Ichikawa, S. Tanaka and T. Hirai, *Chem. Commun.*, 2014, **50**, 15255–15258.
- 9 C. A. Caputo, M. A. Gross, V. W. Lau, C. Cavazza, B. V. Lotsch and E. Reisner, *Angew. Chem. Int. Ed.*, 2014, **53**, 11538–11542.
- 10 X. Wang, G. Zhang, S. Zang, Z. Lan, C. Huang and G. Li, *J. Mater. Chem. A*, 2015, **3**, 17946–17950.
- 11 G. Dong, Y. Zhang, Q. Pan and J. Qiu, *J. Photochem. Photobiol. C Photochem. Rev.*, 2014, **20**, 33–50.
- 12 A. Thomas, A. Fischer, F. Goettmann, M. Antonietti, J.-O. Müller, R. Schlögl and J. M. Carlsson, *J. Mater. Chem.*, 2008, **18**, 4893–4908.
- 13 S. W. Hu, L. W. Yang, Y. Tian, X. L. Wei, J. W. Ding, J. X. Zhong and P. K. Chu, *Appl. Catal. B Environ.*, 2015, **163**, 611–622.
- 14 K. Takanaabe, K. Kamata, X. Wang, M. Antonietti, J. Kubota and K. Domen, *Phys. Chem. Chem. Phys.*, 2010, **12**, 13020–13025.
- 15 D. J. Martin, P. J. T. Reardon, S. J. a Moniz and J. Tang, *J. Am. Chem. Soc.*, 2014, **136**, 12568–12571.
- 16 D. J. Martin, K. Qiu, S. A. Shevlin, A. D. Handoko, X. Chen, Z. Guo and J. Tang, *Angew. Chem. Int. Ed.*, 2014, **53**, 9240–9245.
- 17 Y. Zheng, L. Lin, X. Ye, F. Guo and X. Wang, *Angew. Chem. Int. Ed.*, 2014, **53**, 11926–11930.
- 18 J. Lin, Z. Pan and X. Wang, *ACS Sustain. Chem. Eng.*, 2014, **2**, 353–358.
- 19 J. Lin, Y. Hou, Y. Zheng and X. Wang, *Chem. Asian J.*, 2014, **9**, 2468–2474.
- 20 K. Maeda, K. Sekizawa and O. Ishitani, *Chem. Commun.*, 2013, **49**, 10127–10129.
- 21 R. Kuriki, K. Sekizawa, O. Ishitani and K. Maeda, *Angew. Chem. Int. Ed.*, 2015, **54**, 2406–2409.
- 22 R. Kuriki, H. Matsunaga, T. Nakashima, K. Wada, A. Yamakata, O. Ishitani and K. Maeda, *J. Am. Chem. Soc.*, 2016, **138**, 5159–5170.
- 23 J.-M. Lehn and R. Ziessel, *Proc. Natl. Acad. Sci. USA*, 1982, **79**, 701–704.
- 24 R. Ziessel, J. Hawecker and J.-M. Lehn, *Helv. Chim. Acta*, 1986, **69**, 1065–1084.
- 25 J. Grodkowski and P. Neta, *J. Phys. Chem.*, 2000, **104**, 1848–1853.
- 26 H. Kisch and D. Bahnemann, *J. Phys. Chem. Lett.*, 2015, **6**, 1907–1910.
- 27 S. Sato, T. Morikawa, S. Saeki, T. Kajino and T. Motohiro, *Angew. Chem. Int. Ed.*, 2010, **49**, 5101–5105.
- 28 E. Pastor, F. M. Pesci, A. Reynal, A. D. Handoko, M. Guo, X. An, A. J. Cowan, D. R. Klug, J. R. Durrant and J. Tang, *Phys. Chem. Chem. Phys.*, 2014, **16**, 5922–5926.
- 29 J. R. Lakowicz, *Principles of Fluorescence Spectroscopy*, 3rd ed., 2006, p. 289.
- 30 A. J. Cowan, W. Leng, P. R. F. Barnes, D. R. Klug and J. R. Durrant, *Phys. Chem. Chem. Phys.*, 2013, **15**, 8772–8778.
- 31 C. Ye, J. X. Li, Z. J. Li, X. B. Li, X. B. Fan, L. P. Zhang, B. Chen, C. H. Tung and L. Z. Wu, *ACS Catal.*, 2015, **5**, 6973–6979.
- 32 H. Zhang, Y. Chen, R. Lu, R. Li and A. Yu, *Phys. Chem. Chem. Phys.*, 2016, **18**, 14904–14910.
- 33 H. Kasap, C. A. Caputo, B. C. M. Martindale, R. Godin, V. W.-H. Lau, B. V. Lotsch, J. R. Durrant and E. Reisner, *J. Am. Chem. Soc.*, 2016, **138**, 9183–9192.
- 34 A. J. Cowan, J. Tang, W. Leng, J. R. Durrant and D. R. Klug, *J. Phys. Chem. C*, 2010, **114**, 4208–4214.
- 35 A. J. Cowan and J. R. Durrant, *Chem. Soc. Rev.*, 2013, **42**, 2281–2293.
- 36 W. Wei and T. Jacob, *Phys. Rev. B*, 2013, **87**, 085202.

Photochemical CO₂ reduction using structurally controlled g-C₃N₄

James J. Walsh,^a Chaoran Jiang,^b Junwang Tang^b and Alexander J. Cowan^{a*}

^aStephenson Institute for Renewable Energy, University of Liverpool, L69 7ZF, Liverpool, UK. Email: a.j.cowan@liv.ac.uk

^bSolar Energy Group, Department of Chemical Engineering, University College London, Torrington Place, London, WC1E 7JE, UK.

Electronic supplementary information

1 Experimental

Synthesis and materials: The three types of g-C₃N₄ were synthesised according to our previously published method.^{S1} g-C₃N₄ was synthesised by thermal condensation of different organic precursors (urea, thiourea and dicyandiamide (DCDA)). Typically, a lidded alumina crucible with half the volume occupied by the precursor was placed inside a muffle furnace and heated at 600°C with a ramp rate of 5°C/min for 4 hours. The resultant powders were washed with deionised water and dried in air at 70°C for several hours before use.

CH₃CN (spec grade, Aldrich), triethanolamine (TEOA, Aldrich), 2,2'-bipyridine (bpy, Aldrich) and CoCl₂·6H₂O (Aldrich) were used as purchased. Milli-Q water was used in all experiments. CO₂ (BOC) was CP grade.

Methods: The reaction suspension (consisting of g-C₃N₄ in 3:1:1 CH₃CN/H₂O/TEOA) was made up in a glass vial and sonicated for 10 minutes to ensure dispersion of the solid g-C₃N₄. The reactor used for photocatalysis was a 1 x 2 cm quartz cuvette (Starna) equipped with a B24 neck adaptor. The reaction suspension was added to this flask with a magnetic stirring bar neck was sealed with a rubber septum and purged with CO₂ for 20 minutes. The reaction mixture containing aqueous-soluble Co²⁺ and organic-soluble bpy phases was stirred vigorously throughout the experiment to prevent phase separation.^{S2, S3} Samples for gas chromatography were taken at time zero and at intervals of one hour thereafter.

External quantum yield (EQE) measurements were conducted under LED or monochromated lamp illumination measured for each individual experiment. Optimisation of photocatalytic activity was performed using a 150 W Xe lamp equipped with a KG1 filter under constant power irradiation. Control experiments under argon, in the dark, and in the absence of either g-C₃N₄, TEOA, Co²⁺ or bpy showed minimal or no CO evolution (Table 1). Wavelength-dependent photocatalysis was conducted using a series of LEDs from LEDEngin purchased from RS Electronics: LZ1-00U600 (365 nm), LZ4-00UA00 (400 nm) LED or LZ1-00B200 (465 nm). The 420 nm LED (EPILED) were purchased from Amazon. Each LED was mounted onto a heat sink and driven using banana plugs and a power supply (TTI).

Gas product yields (dihydrogen and carbon monoxide) were quantified using an Agilent 6890N gas chromatograph employing N₆ helium as the carrier gas (5 ml.min⁻¹). A 5 Å molecular sieve column (ValcoPLOT, 30 m length, 0.53 mm ID) and a pulsed discharge detector (D-3-I-HP, Valco Vici) were employed. CO and H₂ peak areas were quantified with multiple calibrant gas injections and were re-calibrated daily. ¹H-NMR spectroscopy of the post-reaction solution, to test for liquid CO₂ reduction products such as formic acid, was not possible due to the presence of paramagnetic Co²⁺.

Inductively-coupled plasma mass spectrometry (ICP-MS) was performed using a dissolved g-C₃N₄ colloidal sol.^{S4} Three photocatalytic experiments were setup using 365 nm LED at 5 mW/cm² for 2 hours. After the reaction, the solid g-C₃N₄ was centrifuged and washed with Milli-Q water. This process was repeated a further two times using clean water. The solid g-C₃N₄ (2.5 mg) was then dissolved in 5 ml of concentrated HNO₃ and refluxed at 80°C for 3 hours. After approximately one hour the cloudy suspension turned clear. The slightly yellow colloidal solution was cooled to room temperature and was stable over a period of several months, with no obvious precipitation. The UV/Vis spectra of the colloids revealed a delaminated solution and correlated well with the literature.^{S4} Three post-reaction colloidal solutions were examined for Co content and the averaged data showed good reproducibility.

UV/Vis diffuse reflectance spectroscopy was performed using a Shimadzu 2600 spectrometer equipped with an integrating sphere using either 1 cm quartz cuvettes (suspensions) or glass microscope slides (solids).

Steady-state luminescence measurements were collected using a Perkin Elmer Fluorescence Spectrometer LS55 with slit widths of 10 nm and 2.5 nm at a scan rate of 500 nm/min. Spectra were recorded using suspensions of g-C₃N₄ in 1 x 1 cm

quartz cuvettes fitted with a B24 neck (Starna) and rubber septa. Samples were made by weighing out 1.0 mg $g\text{-C}_3\text{N}_4$ into 5 ml H_2O followed by 30 minutes sonication. The samples were then diluted 1:1 with CH_3CN containing bpy to give a final suspension of 0.1 mg/ml $g\text{-C}_3\text{N}_4$. Small aliquots (5-25 μl) of a concentrated (mM) Co^{2+} aqueous stock solution were titrated into the cuvette and the sample was purged with N_2 for 20 minutes before recording the spectrum. The excitation wavelength was chosen for each $g\text{-C}_3\text{N}_4$ type at a wavelength independent of absorbance changes upon addition of Co^{2+} .

Time-resolved luminescence measurements were recorded using a modified transient absorption setup employing the third harmonic of a Q-switched Nd:YAG laser (Continuum Minilite). Samples of $g\text{-C}_3\text{N}_4$ were compressed into solid discs for reflectance measurements using a die press either alone (DCDA, thiourea) or by mixing with an inert additive (urea, which did not form quality pellets without adding an additive such as NaCl). The samples were placed into a 1 x 2 cm quartz cuvette (Starna) fitted with a B24 neck, stoppered and purged with Ar for 20 minutes prior to excitation. The instrument response function (IRF) was recorded using BaSO_4 . The time response was recorded using 355 nm laser excitation at 0.4 Hz and averaged over 500 shots. The reflected signal was focused through a monochromator and a bandpass filter (455 nm) to the detector. Data were recorded using a Si photodiode and preamplifier (MCA-200Hz) coupled to an oscilloscope (Tektronix TDS 2014C 100 MHz) and a computer running LabVIEW 2011, and were analysed using the deconvolution functions in Decayfit v 1.3 (Fluortools).

Transient absorption spectra were recorded using a diffuse reflectance sampling mode. Briefly, part of the output from a 75 W Xe lamp (OBB/PTi) was focused through a ND 50 % filter and onto the powdered sample held in a 1 mm quartz cuvette. All samples were thoroughly purged with argon (20 minutes) prior to use. The size of the probe beam was *ca.* 5 mm \varnothing at the sample. Diffusely scattered light was collected using 1" plano-convex lens (Thor labs, UV grade silica) and directed through a monochromator (OBB/PTi) and a photodiode (Hamamatsu) coupled to a home-made preamplifier. The time resolution of the system (*ca.* 5 μs) was determined by the photodiode response and the amplification stages employed. Samples were excited using a Nd:YAG laser (Continuum Minilite) at 3 Hz, 355 nm, *ca.* 6 ns. The laser pulse was passed through a UV grade diffuser (Thor labs) to ensure that the entire sample is excited by the laser pulse. Experimental data were averaged for typically 100-250 laser shots. The transient data are presented in the manner previously employed in diffuse reflectance TA spectroscopy by Furube *et al.*, where % absorption = $(1 - R/R_0) \times 100$ where R and R_0 are the probe light intensities with and without excitation respectively.⁵⁵ Wavelength-dependent transient data were acquired by adjusting the monochromator settings and recording an averaged kinetic trace every 50 nm.

FTIR spectra were collected using a Bruker Vertex spectrometer operating in transmittance mode. FTIR analysis of isotopically labelled products was performed using a custom built FTIR gas cell. The cell was comprised of plastic tube sealed at each end with 2 mm thick CaF_2 windows (Crystran) and Loctite Hysol epoxy resin (3422 A + B). A 1 cm diameter hole was drilled into the top of the cell and sealed with a fresh septum for each experiment, and the edge of the septum was sealed with silicone gel. The cell, which was *ca.* 2 cm in diameter and *ca.* 10 cm in length, was clamped horizontally in the beam path. Spectra were recorded using air as the background, for 128 scans, at a resolution of 0.5 cm^{-1} . Catalysis was performed using a 365 nm LED for 2 hours using $^{13}\text{CO}_2$ as the substrate. After the reaction, 5 ml of gas from the cell headspace were injected into our custom made cell and the spectrum acquired.

2 Optimization of photocatalytic conditions

Parameter						CO ($\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$)
$g\text{-C}_3\text{N}_4$	Light ^a	CO_2 ^b	bpy	Co^{2+}	TEOA ^c	
Urea	✓	✓	✓	✓	✓	460
x	✓	✓	✓	✓	✓	< 0.01
✓	x	✓	✓	✓	✓	< 0.01
✓	✓	x	✓	✓	✓	0.01
✓	✓	✓	x	✓	✓	< 0.01
✓	✓	✓	✓	x	✓	< 0.01
✓	✓	✓	✓	✓	x	< 0.01

Table S1: Control experiments showing that photocatalysis depends on all factors being present. Conditions: 0.5 mg $g\text{-C}_3\text{N}_4$ per ml in $\text{CH}_3\text{CN}/\text{TEOA}/\text{H}_2\text{O}$ (3:1:1), $t = 2$ h. a: KG1 illumination (see Fig. S3, $\lambda = 300 - 795$ nm with % $T \geq 10$, 29 $\text{mW}\cdot\text{cm}^{-2}$), b: Purged with Ar, c: Solvent mixture was 3:1 $\text{CH}_3\text{CN}/\text{H}_2\text{O}$.

In addition to the types of $g\text{-C}_3\text{N}_4$ screened (shown in Table 1, main paper), the ratios of $\text{bpy}:\text{Co}^{2+}$ and the quantity of $g\text{-C}_3\text{N}_4$ per experiment were both tested over a range of values. An optimum ratio of 100 bpy per Co^{2+} was observed, in-line with studies using other types of $g\text{-C}_3\text{N}_4$ and *in-situ* formed $[\text{Co}(\text{bpy})_n]^{2+}$.⁵⁶

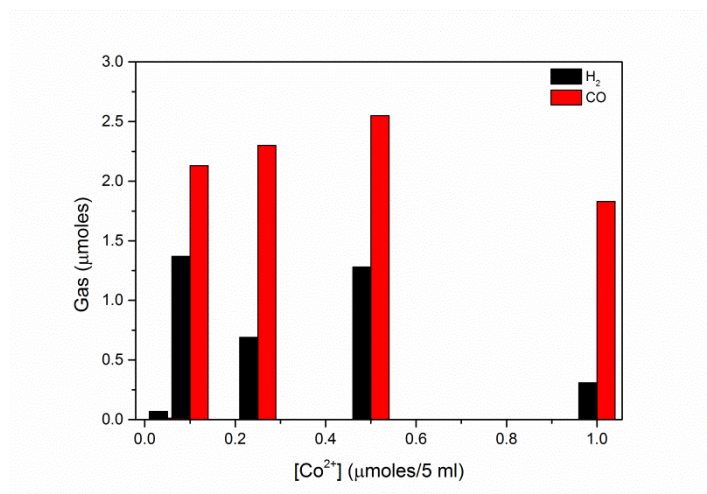


Fig. S1: Varying $[\text{Co}^{2+}]$ concentration at constant $[\text{bpy}]$ and $g\text{-C}_3\text{N}_4$ loading. Conditions: 0.5 mg $g\text{-C}_3\text{N}_4$ per ml in $\text{CH}_3\text{CN}/\text{TEOA}/\text{H}_2\text{O}$ (3:1:1), $t = 2$ h, under KG1 illumination (see Fig. S3, $\lambda = 300 - 795$ nm with % $T \geq 10$, $29 \text{ mW}\cdot\text{cm}^{-2}$).

The relative photocatalytic efficiencies were then tested using the most efficient type of $g\text{-C}_3\text{N}_4$ (urea, data in Table 1) at optimised co-catalyst loading (100:1 $\text{bpy}/\text{Co}^{2+}$, data in Fig. S1). This was achieved by changing the loading of suspended $g\text{-C}_3\text{N}_4$. These data, shown in Fig. S2, revealed that a $g\text{-C}_3\text{N}_4$ concentration 2.5 mg/5 ml yielded the best photocatalytic response. This is likely the $g\text{-C}_3\text{N}_4$ loading with an optimum light absorption profile, neither too dilute nor too scattering.

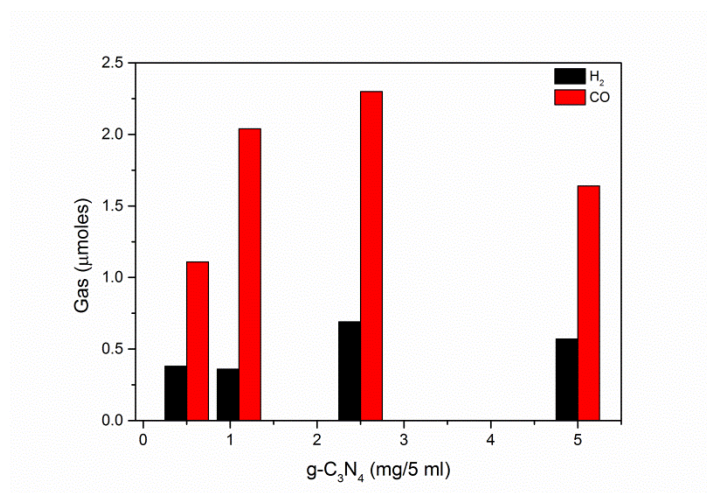


Fig. S2: Comparison of product yields using different quantities of $g\text{-C}_3\text{N}_4$ (urea) and constant concentrations of $[\text{Co}(\text{bpy})_n]^{2+}$. Conditions: 0.5 mg $g\text{-C}_3\text{N}_4$ per ml in $\text{CH}_3\text{CN}/\text{TEOA}/\text{H}_2\text{O}$ (3:1:1), $t = 2$ h, under KG1 illumination (see Fig. S3, $\lambda = 300 - 795$ nm with % $T \geq 10$, $29 \text{ mW}\cdot\text{cm}^{-2}$).

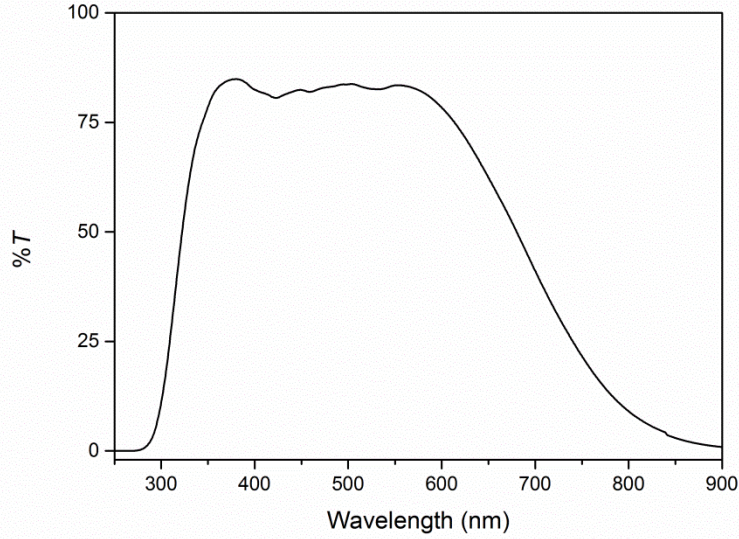


Fig. S3: Transmittance of KG1 filter used in Table 1, Fig. S1 and Fig. S2.

3 LED profiles and AQY measurements

The data in Fig. 1 (b), plotted overlaid with the diffuse-reflectance (DR) UV/Vis spectrum of g-C₃N₄ (urea), show that the photocatalytic activity drops off at 420 nm, in line with the reduced absorptivity of g-C₃N₄ (urea) at this wavelength, and by 465 nm the activity had dropped to zero. The photocatalytic activity is given as apparent quantum yield (% AQY) as calculated using Eq. S1.⁵⁷

$$\% AQY = \left[\frac{(2n_{CO} N_A h c)}{(t_{irr} I \lambda A)} \right] 100 \quad (S1)$$

Where n_{CO} is moles of CO photogenerated; N_A is Avogadro's constant ($6.022 \times 10^{23} \text{ mol}^{-1}$); h is Planck's constant ($6.626 \times 10^{-34} \text{ J.s}$); c is the speed of light ($3 \times 10^8 \text{ m.s}^{-1}$); t_{irr} is the irradiation time; I and λ are the incident intensity (W.cm^{-2}) and wavelength of light (nm), respectively; and A is the irradiated area of the cell (cm^2).

4 Spectroscopy

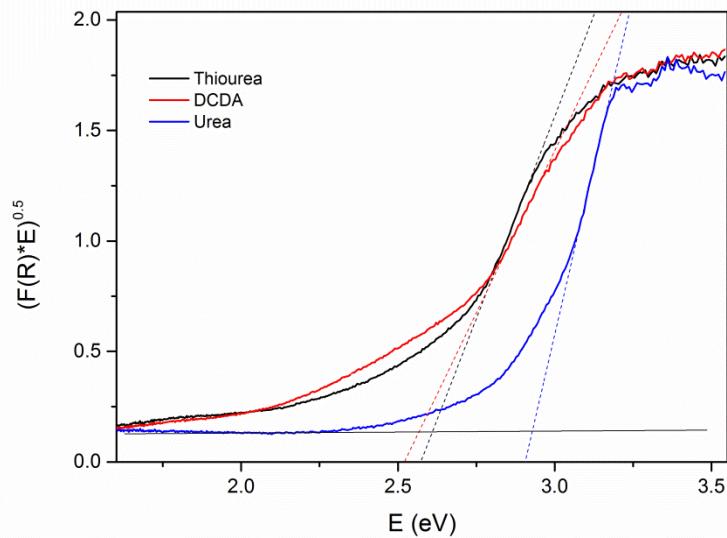


Fig. S4: Tauc plot of g-C₃N₄ derived from the precursors indicated.

Equation	$y = a + b \cdot x$	
	Value	Standard Error
DCDA	Intercept	1 --
	Slope	17009.58162 63.80002
Urea	Intercept	1 --
	Slope	26252.12814 1275.53042
Thiourea	Intercept	1 --
	Slope	9262.82082 115.37089

Table S2: Fitting data for Stern-Volmer plots in Fig. 2. Data points and error bars are the mean and standard deviation of data from two independent datasets.

The data in Fig. 2 were plotted using the Stern-Volmer equation (Eq. S2):

$$\frac{I_0}{I} = 1 + K_{SV}[Q] \quad (S2)$$

Where I and I_0 are the emission intensities of the quenched and unquenched fluorophores, respectively; $[Q]$ is the concentration of Co^{2+} quencher and K_{SV} is the Stern-Volmer constant (Eq. S3):

$$K_{SV} = k_q \cdot \tau_0 \quad (S3)$$

From the SV plots it is possible to obtain a quenching rate constant; however care should be taken as the lack of linearity at higher concentrations may indicate the presence of inaccessible emissive sites^{S8} and the emission decay kinetics of $g\text{-C}_3\text{N}_4$ are also shown to be multi-exponential complicating such analyses. Measurements of the photoluminescent lifetimes using a 355 nm Nd:YAG laser (5-6 ns FWHM) show that the three types of $g\text{-C}_3\text{N}_4$ all display lifetimes of similar length and all considerably longer than the IRF (Fig. S5). While the true lifetime values of each $g\text{-C}_3\text{N}_4$ type are difficult to measure accurately with our apparatus, we can draw two firm conclusions. Firstly the lifetimes of all three $g\text{-C}_3\text{N}_4$ agree very closely, and secondly the lifetimes do not exceed 10 ns. The similarities in τ_0 permit us to estimate relative k_q values for each $g\text{-C}_3\text{N}_4$ type, with $g\text{-C}_3\text{N}_4$ showing the highest relative k_q . Values for k_q are on the order of 10^{12} s^{-1} , which exceeds the diffusion controlled limit, implying a static quenching mechanism. Indeed, ICP-MS analysis of post-reaction $g\text{-C}_3\text{N}_4$ (urea) colloids^{S4} revealed the presence of 44 ± 6 ppb Co, in contrast to < 1 ppb for $g\text{-C}_3\text{N}_4$ not used in photocatalysis. This corresponds to approximately 3.7 nmol of deposited Co^{2+} , meaning that *ca.* 1.5 molar % of Co^{2+} is deposited throughout a typical reaction (2 hours photocatalysis with 365 nm LED at 5 mW/cm²). Photodeposition of Co^{2+} onto $g\text{-C}_3\text{N}_4$ has been observed previously.^{S9, S10} While the photoluminescence experiments were performed under non-catalytic conditions (*i.e.*: in the absence of both CO_2 and TEOA), the ability of Co^{2+} to deposit on $g\text{-C}_3\text{N}_4$ can potentially provide a pathway for static quenching and explain the high k_q values obtained. Static quenching has been observed previously for $g\text{-C}_3\text{N}_4$ used as a photoluminescent sensor for metallic dications in solution, such as Hg^{2+} ,^{S11} while mixed static/dynamic quenching has been observed for $g\text{-C}_3\text{N}_4$ quenching by Cu^{2+} .^{S12}

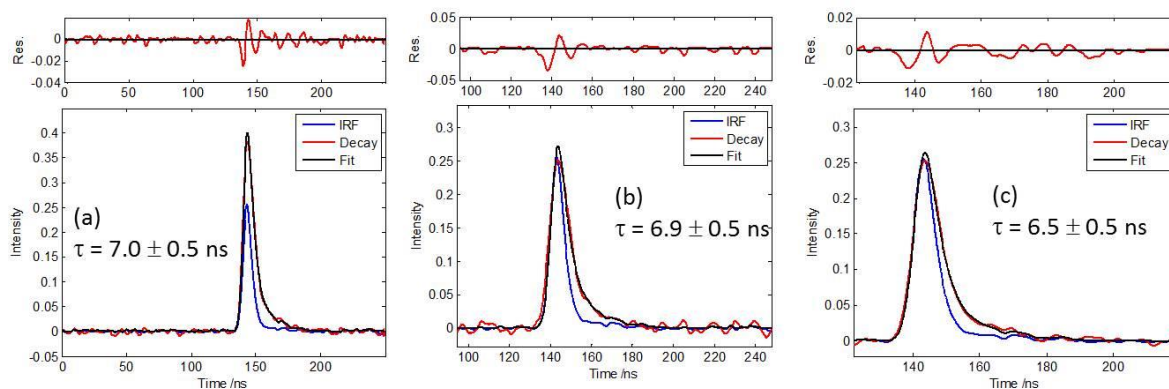


Fig. S5: Time-resolved emission decays monitored at 455 nm following 355 nm excitation of urea (a) thiourea (b) and DCDA (c) derived $g\text{-C}_3\text{N}_4$. The IRF is measured using a BaSO_4 standard. The lifetimes should be viewed as an approximate value given the similarity between the IRF and the decay functions. Data was fitted using the DecayFit v1.3 software by Fluortools (www.fluortools.com).

Wavelength dependent DR-TA spectra have been normalised for OD response over the range studied.

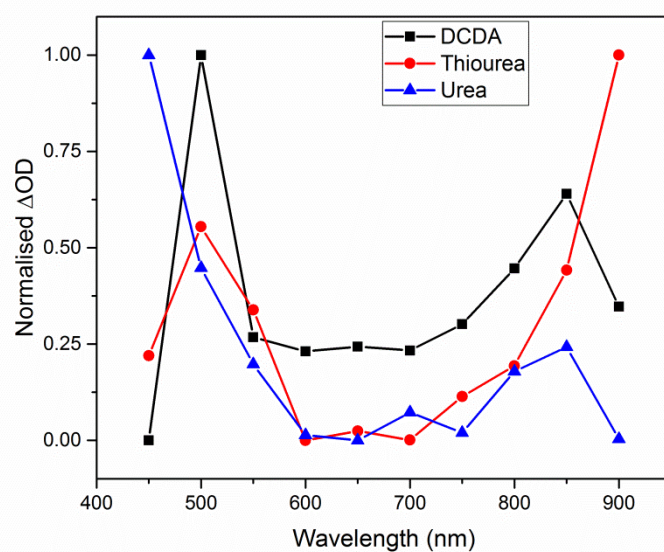


Fig. S6: Diffuse reflectance transient absorption spectra (normalised) 100 μs after laser pulse excitation.

The FTIR spectrum of the products formed from an experiment using $^{13}\text{CO}_2$ is shown in Fig. S7. The spectrum shows the presence of the ^{13}CO product with branches centred at 2075 and 2130 cm^{-1} , in line with the literature spectrum for ^{13}CO .⁵¹³ The rising baseline at longer wavelengths is due to the presence of a very large $^{13}\text{CO}_2$ absorption. There is no detectable trace of ^{12}CO . The feature centred at 2017 cm^{-1} is due to the $^{13}\text{CO}_2$ substrate.

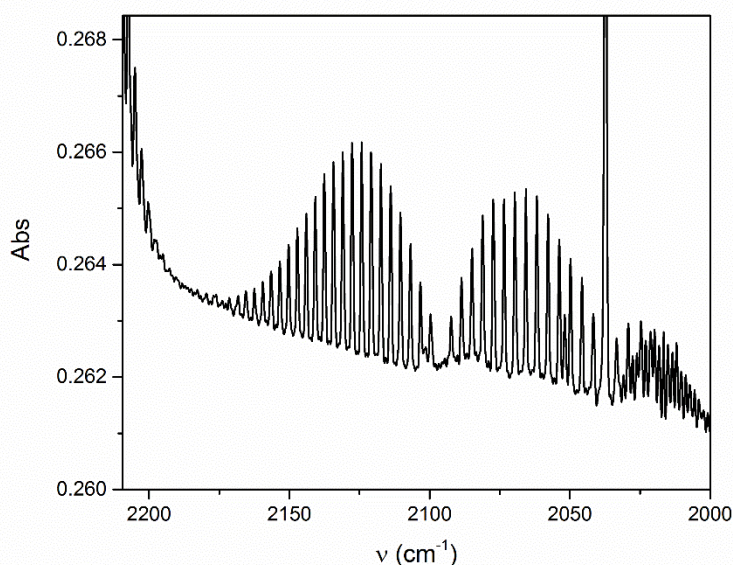


Fig. S7: FTIR spectrum of cell headspace of a $^{13}\text{CO}_2$ purged sample post-photocatalysis at 365 nm. The presence of ^{13}CO confirms that CO_2 is the carbon source for the CO production.

5 References

- S1 D. J. Martin, K. Qiu, S. A. Shevlin, A. D. Handoko, X. Chen, Z. Guo and J. Tang, *Angew. Chem. Int. Ed.*, 2014, **53**, 9240–9245.
- S2 J.-M. Lehn and R. Ziessel, *Proc. Natl. Acad. Sci. USA*, 1982, **79**, 701–704.
- S3 R. Ziessel, J. Hawecker and J.-M. Lehn, *Helv. Chim. Acta*, 1986, **69**, 1065–1084.
- S4 J. Zhang, M. Zhang, L. Lin and X. Wang, *Angew. Chem. Int. Ed.*, 2015, **54**, 6297–6301.
- S5 A. Furube, Z.-S. Wang, K. Sunahara, K. Hara, R. Katoh and M. Tachiya, *J. Am. Chem. Soc.*, 2010, **132**, 6614–6615.
- S6 J. Lin, Z. Pan and X. Wang, *ACS Sustain. Chem. Eng.*, 2014, **2**, 353–358.
- S7 C. A. Caputo, M. A. Gross, V. W. Lau, C. Cavazza, B. V. Lotsch and E. Reisner, *Angew. Chem. Int. Ed.*, 2014, **53**, 11538–11542.
- S8 J. R. Lakowicz, *Principles of Fluorescence Spectroscopy Principles of Fluorescence Spectroscopy*, 3rd ed., 2006, p 289.
- S9 R.-L. Lee, P. D. Tran, S. S. Pramana, S. Y. Chiam, Y. Ren, S. Meng, L. H. Wong and J. Barber, *Catal. Sci. Technol.*, 2013, **3**, 1694–1698.
- S10 L. Ge, C. Han, X. Xiao and L. Guo, *Appl. Catal. B Environ.*, 2013, **142-143**, 414–422.
- S11 S. Barman and M. Sadhukhan, *J. Mater. Chem.*, 2012, **22**, 21832–21837.
- S12 N. Cheng, P. Jiang, Q. Liu, J. Tian, A. M. Asiri and X. Sun, *Analyst*, 2014, **139**, 5065–5068.
- S13 J. Agarwal, T. W. Shaw, C. J. Stanton, G. F. Majetich, A. B. Bocarsly and H. F. Schaefer, *Angew. Chem. Int. Ed.*, 2014, **53**, 5152–5155.