Photochemical CO_2 reduction using structurally controlled g-C_3N_4

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Graphitic carbon nitride (g-C_3N_4) synthesised from a urea precursor is an excellent CO_2 reduction photocatalyst using $[Co(bpy)_n]^{2+}$ as a co-catalyst. A five-fold increase in activity for the highly polymerised urea derived g-C_3N_4 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 CO_2 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 CO_2 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 CO_2 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 CO_2 reduction in the presence of water remains an un-realised goal.

g-C_3N_4 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-C_3N_4 (typically *ca*. 2.5 eV) enables visible light activity. In addition, g-C_3N_4 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-C_3N_4 have been reported including g-C_3N_4/metal oxide heterojunctions,[13] dye-sensitised g-C_3N_4 [14] 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-C_3N_4 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-C_3N_4 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-C_3N_4.

In contrast to the substantial literature relating to hydrogen evolution there are a more limited number of studies examining the use of g-C_3N_4 for CO_2 reduction in the presence of water.[17, 18, 19 20, 21] One issue is that to overcome competitive proton reduction to H_2 in the presence of water a selective CO_2 reduction co-catalyst is required. Recently Maeda *et al*., have developed a range of $[Ru(bpy)(CO)_2Cl_2]$ derivatives (bpy = 2,2'-bipyridine) where modification of the 4,4' positions of bpy has enabled either direct or indirect binding to g-C_3N_4,[20,

[21] giving rise to a material that reduced CO_2 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-C_3N_4 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-C_3N_4 for CO_2 reduction, to date there have been relatively few systematic studies on exploring the nature of the g-C_3N_4 used with each co-catalyst. Herein we examine a range of carbon nitrides, including the previously reported highly active urea derived g-C_3N_4,[16] for CO_2 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-C_3N_4 structures derived from a range of precursors. We report both an enhancement in the activity for a g-C_3N_4/$[Co(bpy)_n]^{2+}$ mediated CO_2 reduction system and an improved overall understanding into the factors controlling the high levels of activity of urea derived g-C_3N_4 in reductive photochemistry.

g-C_3N_4 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-C_3N_4/$[Co(bpy)_n]^{2+}$ system have demonstrated successful CO_2 reduction in a solvent mixture of CH_3CN/H_2O with triethanolamine (TEOA) also being added as a sacrificial electron donor[17, 18, 19] and the same solvent system is also employed here (CH_3CN:H_2O:TEOA, 3:1:1, 5 ml total). In the presence of urea derived g-C_3N_4 (2.5 mg), $CoCl_2$ (50 μmol dm^{-3}), bpy (5 mmol dm^{-3}) under an atmosphere of CO_2 we observe photocatalytic CO production with minimal H_2 evolution (CO:H_2, 3.3:1), see Table 1. In the absence of any one of these components CO_2 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-C_3N_4 absorber. The lack of CO production in the absence of CO_2 is in-line with past isotope labelling studies which definitively confirmed CO_2 to be the carbon source for CO.[18] The lack of CO_2 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_3N_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 CO_2 reduction of the different g-C_3N_4 materials. Experiments carried out using 300 – 795 nm KG1 filter (Fig. S3), 40 mW.cm^2 illumination, 0.5 mg g-C_3N_4 per ml in CH_3CN/TEOA/H_2O (3:1:1), t = 2 h. [a:] Specific surface area, see reference 16; [b]: TON per Co^{2+} at t = 2 hours.

Under Xe lamp illumination (300 -795 nm) a turnover number (TON) per Co^{2+} of greater than 9 was achieved after 2 hours for CO production using urea derived g-C_3N_4, Table 1. At prolonged periods it was found that the rate of CO_2 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-C_3N_4 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 CO_2 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-C_3N_4, or more likely through inhibition of the co-catalyst. It is noted that CO inhibition has been previously reported during CO_2 photoreduction with other Co^{2+} catalysts.[25]

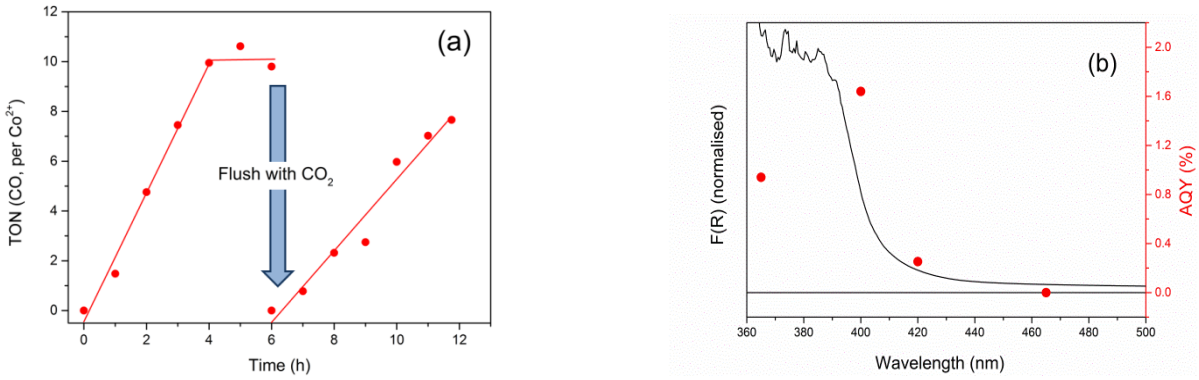

Fig. 1: Photocatalytic CO_2 reduction under (a) prolonged 400 nm LED illumination (ca. 5 mW.cm^{-2}). (b) AQY for CO production measured at wavelengths shown (red) and overlaid UV/Vis spectrum of the reaction suspension. All experiments are using g-C_3N_4 (urea, 2.5 mg) and $CoCl_2$ (50 μmol dm^{-3}), bpy (5 mmol dm^{-3}) in 5 ml CH_3CN:H_2O:TEOA, 3:1:1 purged with CO_2.

Previous hydrogen evolution studies have found that the photocatalytic activity of a platinized urea derived g-C_3N_4 is significantly greater than other precursor materials.[16] Similarly the highest efficiency material for CO_2 reduction using $[Co(bpy)_n]^{2+}$ as co-catalyst is g-C_3N_4 (urea), with relative catalytic efficiencies following the trend urea > DCDA > thiourea. The CO yield from g-C_3N_4 (urea) was 5x higher than that from DCDA-derived g-C_3N_4, and 23x higher than that from thiourea-derived g-C_3N_4, Table 1. The CO/H_2 selectivity was also 3.3x or 13.3x higher, respectively. Interestingly the relative enhancements in activity for CO_2 reduction reported here are similar to those reported for H_2 production using g-C_3N_4/Pt, where g-C_3N_4 (urea) produces H_2 at a rate of 8x relative to g-C_3N_4 (DCDA) and 13.5x relative to g-C_3N_4 (thiourea).[16] In order to benchmark the activity of the urea derived system for CO_2 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-C_3N_4 (urea) and $[Co(bpy)_n]^{2+}$ matches well to the recorded UV/Vis spectrum of g-C_3N_4. 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-C_3N_4 is at the same level of greater than current state-of-the-art g-C_3N_4 (melamine)/CoO_x/$[Co(bpy)_n]^{2+}$ systems for CO_2 reduction which utilised a ten-fold more concentrated solution of g-C_3N_4 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 CO_2 reduction photocatalysts.[20, 27, 28]

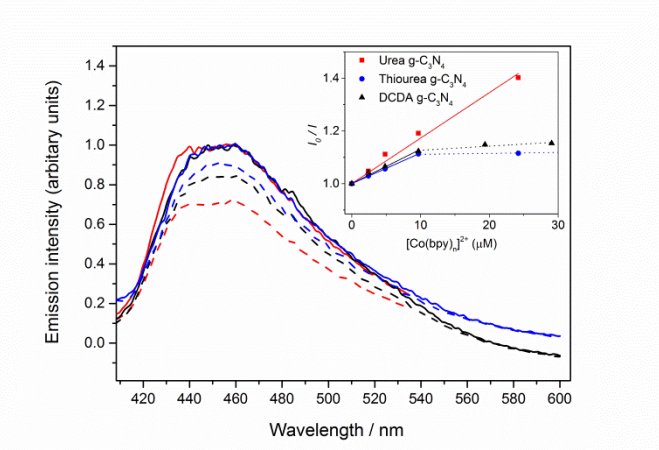

Fig. 2: Normalised emission of urea (red), DCDA (black) and thiourea (blue) derived g-C_3N_4 (0.1 mg ml^{-1} in 1:1 CH_3CN/H_2O) in the absence of a quencher (solid lines) and relative quenching in the presence of $[Co(bpy)_n]^{2+}$ (dashed lines). Inset shows the Stern-Volmer plots for g-C_3N_4 in CH_3CN/H_2O with a $[Co(bpy)_n]^{2+}$ quencher.

It is striking that the relative trends for the activity of urea, DCDA and thiourea derived g-C_3N_4 are the same for both CO_2 reduction and H_2 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 CO_2 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 sp^2 nitrogen sites (C-N-C) to sp^3 sites (H-N-$[C]_3$ and C-NH_x)).[16] DFT calculations indicated that two possible enhancement routes were occurring in materials with high sp^2:sp^3 ratios. Firstly the observed wider band gap of urea derived g-C_3N_4 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-C_3N_4 (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 CO_2 reduction system. Photoluminescence (PL) occurs in g-C_3N_4 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 (see 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-C_3N_4 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-C_3N_4 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-C_3N_4 to the $[Co(bpy)_n]^{2+}$ catalyst and the greater accessibility to the g-C_3N_4 surface are important factors behind the enhanced photocatalytic activity of this material.

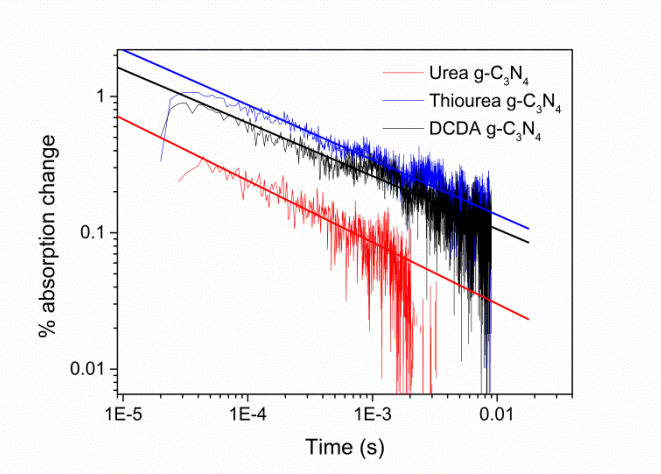

Fig. 3: DR-TA kinetic traces recorded at 850 nm for the g-C_3N_4 sample indicated under an Argon atmosphere, following UV (355 nm, 91 μJ.cm^{-2}) excitation.

Transient absorption (TA) spectroscopy is a powerful tool to probe the change in concentration of charge carriers (photogenerated electrons and holes) with time[30] and here we also examine the diffuse reflectance TA kinetics of the g-C_3N_4 samples. Recently it has been highlighted that long-lived photogenerated charges can persist in g-C_3N_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 μJ.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-C_3N_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. DR-TA data spanning the visible-NIR region are also presented in Fig. S6, which show peaks centred around 500 and 850 nm. In recent studies similar g-C_3N_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 be well fitted by a power law model (%abs $\propto t^{-\beta}$, $\beta = 0.42 \pm 0.05$) for all three g-C_3N_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-C_3N_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 N/sp^3 ratio than the untreated g-C_3N_4.[31] In contrast a recent TA study of g-C_3N_4 by Kuriki *et al*.[22] reported the presence of deeply trapped inactive charges in the visible region. 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-C_3N_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-C_3N_4 polymers, previously shown to be excellent photocatalysts for H_2 production[16] for CO_2 reduction using $[Co(bpy)_n]^{2+}$ as co-catalyst. This has led to us achieving a five-fold increase in the CO evolution rate. Given that urea derived g-C_3N_4 with a high sp^2 N: sp^3 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 $[Co(bpy)_n]^{2+}$) 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-C_3N_4.

Notes and references

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