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Visible-light-driven photooxidation of alcohols using surface-doped graphitic carbon nitride†

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Carbon-nanodot-doped g-C_3N_4 is used as a photocatalyst to promote the aerobic oxidation of alcohols and oxyfunctionalisation of activated hydrocarbons. A critical E-factor analysis of the current reaction system reveals its limitations *en route* to environmentally acceptable oxidation procedures.

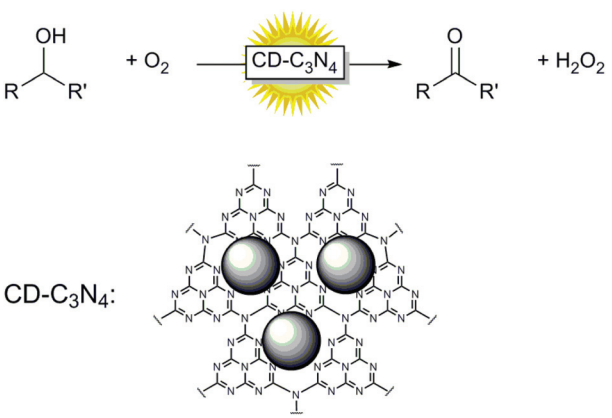
In recent years, graphitic carbon nitride (g-C_3N_4) has received substantial interest as a photocatalyst for metal-free, visible-light promoted reactions.[1] It exhibits a graphite-like, layered structure wherein tris-triazine units are connected through C–N-bonds forming a two-dimensional layer. g-C_3N_4 can be synthesized *via* various methods such as pyrolysis of urea or other nitrogen-rich precursors or layer exfoliation of bulk materials.[2]

Pure g-C_3N_4, however, is a rather poor photocatalyst, mainly due to the fast recombination of photoexcited, charge-separated states. Therefore, one focus of research lies in the improvement of its photocatalytic properties by modulating the potential of g-C_3N_4's conducting- and valence bands.[1] Particularly doping of g-C_3N_4 with other elements such as Y,[3] Fe,[4] Pt,[5] Au/Pd[6,7] K, Ag,[8,9] C[10] or carbon-nanodots[11] and many more has proven to be an efficient handle to modulate its properties. Also, doping with carbon-nanodots appears promising to increase the quantum efficiency of photocatalytic processes.

Interestingly, g-C_3N_4 is mostly considered as a photocatalyst for (sun)-light driven water splitting, remediation of organic pollutants and catalytic CO_2 reduction.[1] Applications for preparative organic synthesis are comparably few. For example, Goettmann *et al.* reported g-C_3N_4 catalysed Friedel–Crafts acylation.[12] More recently, photocatalytic acetalisation of aldehydes and ketones,[13] and hydrazine-driven reductions of alkenes and alkynes were reported using g-C_3N_4.[14,15] Selective oxidations especially of benzylic C–H-bonds have been reported using mesoporous g-C_3N_4 together with N–OH-cocatalysts,[16–19] or using transition metal doped g-C_3N_4.[14,20–22] Also the oxidative coupling of amines has been reported.[23]

However, to the best of our knowledge, carbon-nanodot doped g-C_3N_4 has so far not been evaluated as a catalyst for photocatalytic oxidation reactions. Therefore, we set out to evaluate carbon-nanodot-doped g-C_3N_4 (CD-C_3N_4) as a visible-light-driven photocatalyst for the aerobic oxidation of alcohols (Scheme 1).

For the synthesis of g-C_3N_4 we followed the procedure by Tang and coworkers[24] due to the more porous structure of the material and the resulting higher activity (due to the increased surface area). In short, calcination of urea at 600 °C for 4 h gave the desired mesoporous g-C_3N_4 as confirmed by TEM imaging and X-ray diffraction (Fig. S1 and S2†). Next, carbon nanodots were synthesized *via* thermal decomposition of sucrose.[25] The latter were deposited on the g-C_3N_4 surface *via* thermal treatment of both materials.[11] The XRD pattern of the such-obtained composite material did not change significantly compared to the starting material (g-C_3N_4) most probably due to the amorphous character of the carbon nanodots adsorbed.



Scheme 1 Photocatalytic aerobic oxidation using carbon nanodot-doped g-C_3N_4 (CD-C_3N_4) as a photocatalyst.

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The UV/Vis spectrum showed the characteristic increase in absorption at wavelengths below 600 nm (Fig. S3†), and the BET measurement revealed a surface area of 105 m^2 g^{-1} (Fig. S8†).

Having both catalysts at hand, we next compared their catalytic activity in the oxidation of benzyl alcohol to benzaldehyde as a model reaction (Fig. 1). Due to the volatility of benzaldehyde and the poor water solubility of the benzyl alcohol starting material we used a two-liquid phase approach employing benzyl alcohol as the second organic phase (phase ratio 3 : 7 organic : aqueous).

As shown in Fig. 1, CD-C_3N_4 excelled over g-C_3N_4 both in terms of activity and robustness. Not only was the initial product formation rate roughly two times higher but also the long term-stability of the reaction: the reaction rate with g-C_3N_4 levelled off significantly after several hours whereas with CD-C_3N_4 linear product accumulation was observed for at least 48 h. Overall, with CD-C_3N_4 more than 500 mM of product accumulated corresponding to a product to catalyst ratio of more than 4 : 1 (g g^{-1}), under the non-optimized conditions.

It is worth mentioning here, that in the absence of either the photocatalyst or a light source, no noticeable conversion of the starting material was observed. Also, hydrogen peroxide as a by-product was observable in trace amounts only throughout the experiments. This observation is in line with previous findings that CD-C_3N_4 is also an efficient H_2O_2 decomposition catalyst.[11]

The rate of the oxidation reaction exhibited a saturation-type dependency on both the catalyst concentration (Fig. 2) and the intensity of the light source applied (Fig. 3).

In the case of increasing catalyst concentrations, we suspect the decreasing transparency of the reaction mixture to account for this observation. The converging reaction rate at increasing light intensities may well be attributed to oxygen diffusion becoming overall rate-limiting. It should be mentioned here that for the latter experiments we utilised a specialized light-setup to control the light intensity (setup 2, Fig. S5†). Despite the much higher product formation rate attainable with this system (Fig. 3) we decided to perform the following experiment using a cheap white-light bulb in order to enable simple reproduction by others (setup 1, Fig. S4†). Nevertheless, the productivities shown in Fig. 3 (using a simple light source) of more than 0.2 $g_{product}$ $g^{-1}{}_{catalyst}$ h^{-1} demonstrate the preparative potential of the photochemical alcohol oxidation system.

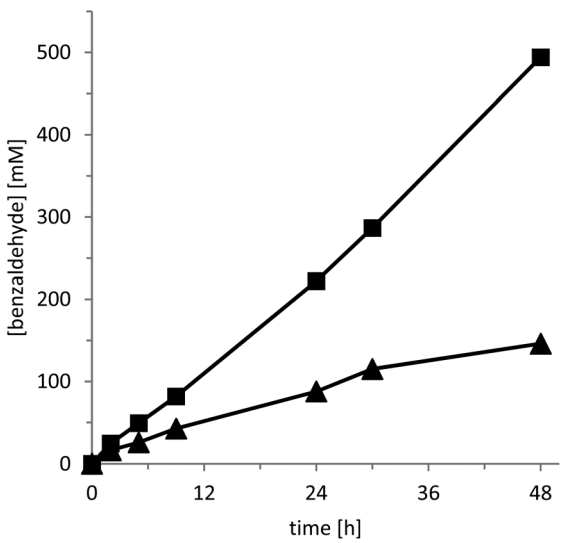


Fig. 1 Photocatalytic oxidation of benzyl alcohol to benzaldehyde using g-C_3N_4 (▲) and CD-C_3N_4 (■) as photocatalysts. Conditions: 5 g L^{-1} of photocatalyst, two phase reaction: 700 μL of water + 300 μL of benzyl alcohol, 30 °C and oxygen atmosphere under visible light illumination using setup 1 (λ > 400 nm).

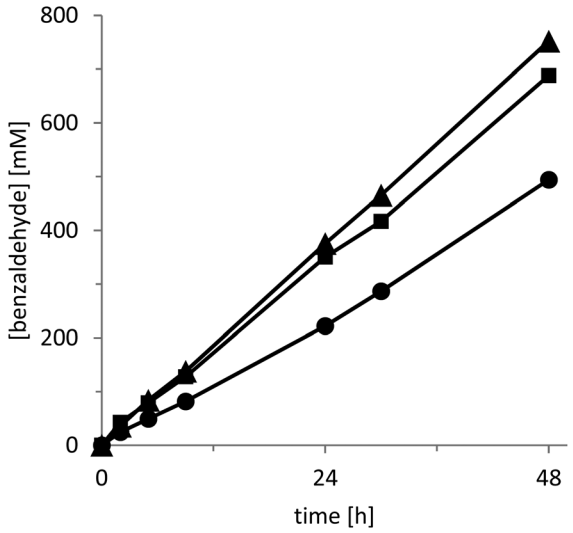


Fig. 2 Influence of the catalyst loading on the rate of the photocatalytic oxidation of benzyl alcohol. [CD-C_3N_4] = 5(●), 10 (■), 25 (▲) g L^{-1}. Conditions: Two phase reaction with 700 μL of water + 300 μL of benzyl alcohol, 30 °C and oxygen atmosphere under visible light illumination using setup 1 (λ > 400 nm).

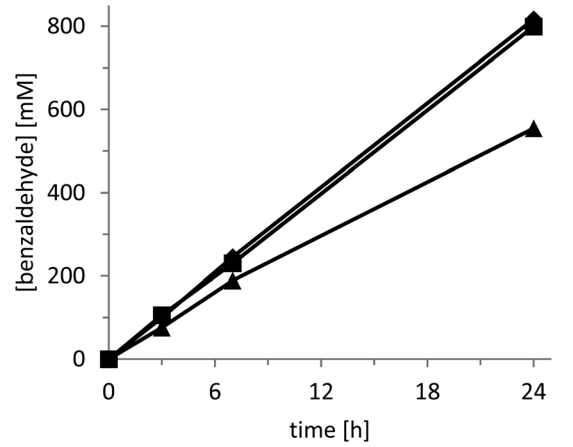


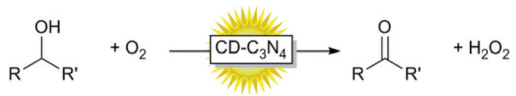
Fig. 3 Influence of the light intensity on the rate of the photocatalytic oxidation of benzyl alcohol. Light intensity of 79 (▲), 197 (■), 341 (◆) W cm^{-2}. Conditions: 5 g L^{-1} of photocatalyst, two phase reaction with 700 μL of water + 300 μL of benzyl alcohol, 30 °C and oxygen atmosphere under visible light illumination using setup 2 (λ > 400 nm).

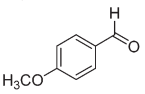
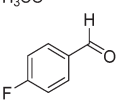
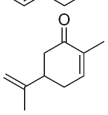
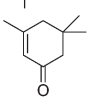
We investigated the recyclability of CD-C_3N_4 by performing benzyl alcohol oxidation reactions followed by filtration, washing and re-loading with reaction medium (Fig. S6†). As a result CD-C_3N_4 could be recycled at least 5 times. From linear regression of the initial rates, a catalyst deactivation of less than 4% per cycle was estimated.

Encouraged by these results we further explored the product scope of the reaction system (Table 1).

Especially allylic alcohols were converted at excellent rates and selectivities while benzylic alcohols were converted somewhat slower and non-activated alcohols such as cyclohexanol were rather sluggish substrates. This is roughly in-line with the general bond-dissociation energies of the C–H bonds oxidised. However, it also should be taken into account that the reactions reported in Table 1 have been obtained from two-liquid phase systems and that, depending on the partitioning coefficient of the starting material, the aqueous concentrations may vary very significantly thereby influencing the reaction kinetics.

Table 1 Examples of CD-C_3N_4-catalyzed, photocatalytic alcohol oxidations



Product	Product[a] [mM]	Rate [g g^{-1} h^{-1}]
	223	0.059
	60.1	0.020
	73.0	0.023
	40.2	0.012
	12.7/1.9[a]	0.003/0.001[a]
	228.1/41[a]	0.055/0.023[a]
	701.2	0.193
	108.4	0.040
	247.3	0.093
	252.4	0.087

Reaction conditions: 5 g L^{-1} of photocatalyst, two phase reaction with 700 μL of water + 300 μL of alcohol, 30 °C and oxygen atmosphere under visible light illumination using setup 1 (λ > 400 nm) for 24 h. [a] Product concentration in the aqueous phase.

The preparative applicability of the proposed photocatalytic oxidation was exemplarily demonstrated in the oxidation of carveol to carvone. Performing this reaction on a 6.8 mmol-scale (1.03 g) gave more than 95% conversion into the desired product (GC yield) and 0.773 g of isolated carvone (74.8% isolated yield) under non-optimised reaction- and DSP conditions.

An E-factor analysis[26] of this reaction revealed the current limitations of this reaction setup from an environmental point-of-view (Table 2). The 'classical' E-factor (including the weighable compounds only) of the overall reaction is rather moderate (144) with solvents (used both for the reaction and for the extraction of the product) contributing over 95% to the total E-factor. Obviously, dichloromethane used in this reaction is not acceptable and will be substituted by more acceptable solvents in future studies.[27] Also decreasing the contribution of water (*e.g.* by further increasing the concentration of the starting material) will be highly desirable. In fact, preliminary experiments using neat reagents (*i.e.* CD-C_3N_4 suspended in pure benzyl alcohol or cyclohexanol) showed an even faster product accumulation than in the biphasic system (Fig. S7†). Probably this is also to be attributed to a higher O_2 solubility in these media than in aqueous systems. Another advantage of using neat reagents is that extraction can be omitted as physical methods to separate the product (*e.g.* distillation) are sufficient.

However, the 'hidden' E-factor contributors demand more attention *en route* to an environmentally acceptable reaction system. Using setup 2 enabled us to quantify the power input (197 W for 90 h) and energy used for the illumination reaction (17.7 kWh). According to the European Energy Agency this corresponds to CO_2 emission of approximately 9.9 kg CO_2 [28] and an E-factor contribution of 12.800 obviously 'outshining' the values discussed above. Of course the current setup has not been optimised for efficient utilisation of light and further geometric optimisation together with the increase of the reagent payload will certainly reduce this number to acceptable values. Also, provided the aspirational trend towards renewable energies continues, less CO_2 emissions and thereby a reduced 'CO_2'-E-factor may be assumed. Furthermore, using sunlight will almost entirely eliminate this contribution.

Also, it should not be forgotten that the preparation of the photocatalyst (though exhibiting very low classical E-factors) is based on high-temperature calcination processes.

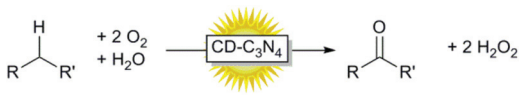
Table 2 Estimation of the waste generated in the photobiocatalytic oxidation of carveol to carvone

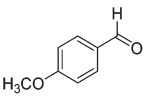
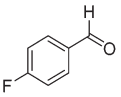
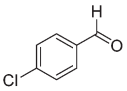
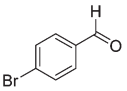
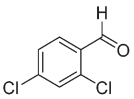
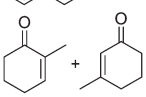
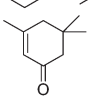
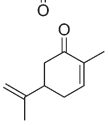
Contributor	E-factor contribution [kg kg^{-1}]
Reaction	
Water	38.8
CD-C_3N_4	0.26
CO_2 from a light source	12.800
DSP	
CH_2Cl_2	102.8
$MgSO_4$	1.9

Overall, despite the potential of photochemical, aerobic oxidation we prefer to refrain from calling the current procedure green or environmentally benign.

Finally, we evaluated oxidation/oxyfunctionalisation of non-functionalized C–H bonds (Table 3). In general, the same trend in the reaction rate was observed here as well whereas the reaction rates were significantly lower than observed for the corresponding alcohols. This is in line with the higher C–H-bond dissociation energy of these non-functionalized C–H bonds. Furthermore, accumulation of the intermediate alcohol product did not occur (generally the alcohol product accounted for less than 25% of the final product) indicating that the initial C–H-bond oxidation is overall rate-limiting.

Table 3 Examples of CD-C_3N_4-catalyzed, photocatalytic oxyfunctionalisations



Product	Product [mM]	Selectivity[a] (%)	Rate [g g^{-1} h^{-1}]
	16.3	77	0.004
	19.0	83.3	0.0065
	3.0	86.2	0.001
	12.6	—	0.0044
	3.9	—	0.002
	4.1	—	0.0018
	7.6	76.9	10.0023
	18.1	87.4	0.0067
	30.3 + 37.7	—	0.008 + 0.010
	28.14		0.011
	21.25		0.008
	10.3/9.1[b]		0.002/0.005[b]
	3.0		0.0007

Reaction conditions: 5 g L^{-1} of photocatalyst, two phase reaction with 700 μL of water + 300 μL of alkane, 30 °C and oxygen atmosphere under visible light illumination using setup 2 (λ > 400 nm) for 24 h. [a] Selectivity = [aldehyde/ketone]/([alcohol] + [aldehyde/ketone])%. [b] Product concentration in the aqueous phase.

Conclusions

With the current contribution we demonstrate that simple metal-free CD-C_3N_4 is a very suitable and recyclable photocatalyst for the oxidation of primary and secondary alcohols to the corresponding aldehydes and ketones. Furthermore, also extension of this concept to the corresponding alkanes appears feasible, albeit at reduced efficiencies.

Ongoing mechanistic studies will reveal a more detailed understanding of the reaction and put the basis for optimised catalysts and reaction setups *en route* to truly practical catalysts.

The critical E-factor analysis of the current reaction setup will guide our further studies *en route* to truly environmentally acceptable oxidation processes.

Acknowledgements

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