Visible-Light-Driven Photooxidation of alcohols using surface-doped graphitic carbon nitride

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Material and Methods

Materials

Unless stated otherwise all chemicals were purchased from Sigma-Aldrich, Fluka, Acros or Alfa-Aesar with the highest purity available and used without further treatment.

Synthesis of $g-C_3N_4$ and carbon nanodots doped (CD-C₃N₄)

The g-C₃N₄ was synthesized via the simple calcination (Carbolite furnace; CWF 12/5, 2400 W) of urea (10.0 g) at 600 °C for 4 h (5 °C/min), a yellowish powder was obtained after the cooling to room temperature.¹

The carbon nanodots were synthesized via the thermal decomposition of sucrose with slight modification.² Briefly, 0.75 g of sucrose was dissolved in 30 mL of MilliQ water and stirred at room temperature for 0.5 h. The solution was transferred into a 45 mL Teflon-lined stainless steel autoclave reactor, and heated at 180 °C for 5 h (10 °C/min). After cooling the reactor to room temperature, a brown mixture was obtained. The mixture was centrifuged (8000 rpm for 20 min), and the pellet was washed with water (3×) and freeze-dried.

In order to deposit carbon nanodots to the surface of g-C₃N₄, Liu et al's procedures were adopted.³ Firstly, a stock solution of carbon nanodots (1 mg in 25mL water) was prepared. 15.0 mL of this stock solution was mixed with 15.0 mL of NH₄OH (28 %) and sealed in a 45 mL Teflon-lined autoclave reactor. The mixture was heated at 150 °C for 5 h (10 °C/min). After cooling the reactor to room temperature, the mixture was transferred into a beaker and dried at 80 °C. The treated carbon nanodots were resuspended in 2.0 mL of water and mixed with 10.0 g of urea, which was calcined at 600 °C for 4 h (5 °C/min). The amount of doped carbon nanodots-C₃N₄ (CD-C₃N₄) is estimated to be 2.4×10⁻³ g/g in the final product.

Characterization of the photocatalyst

The structures of the synthesized photocatalysts were characterized by a Bruker D8 Advance X-ray diffractometer using Co-K α radiation (λ = 1.789 Å) at 35 kV and 40 mA. The data were collected from 2 θ = 5.0°-80° with a step size of 0.020° and a counting time of 0.25 s per step. The particle size and morphology were analysed by using Philips CM30T TEM. The surface area was measured on a Micromeritics Instrument (TriStar II 3020).

Photooxidation of hydrocarbons/alcohols

The photooxidation reactions were performed by using a homemade light-setup at 30 °C under the oxygen atmosphere (oxygen balloons), see Figure S4. Unless mentioned otherwise, to a 4 mL glass vial containing 5.0 mg of photocatalyst, 700 uL of MilliQ water and 300 uL of organic substrates were added. The reaction mixture was exposed to visible light bulb (**Setup 1**, Philips 7748XHP 200W, white light bulb) and continuously stirred by a magnetic bar at 300 rpm. The distance between the light bulb and reaction vial is 4 cm.

GC analytics

At intervals, the organic phase was taken, diluted by ethyl acetate (containing 5 mM of dodecane or 1-octanol as internal standards), dried over anhydrous MgSO₄ and analysed by GC (SHIMADZU, see Table S1).

Influence of light intensity on the reactivity

In order to investigate the effect of light intensity on the CD-C₃N₄, a super-quiet xenon lamp with ozone-free bulb was used (**Setup 2**, 150 W, total reflection type, code L9588-04, Hamamatsu Lightningcure LC8). The illumination was performed side-wise (1 cm distance from the transparent reaction vial) by using a 1-meter fibre optic cable to provide spot light. The light was filtered through a cut-off filter ($\lambda > 400$ nm, 95% transmittance, code A9616-09, Hamamatsu Lightningcure LC8). Based on the data from the manufacturer, the light intensity loss through the fibre optic cable is approx. 50%, resulting in 75 W being delivered to the liquid surface, provided that the shutter is fully open. Three aperture intensities 10, 25 and 50 %, were applied, corresponding to an intensity of 79, 197 and 341 W cm⁻², respectively.



Figure S1. TEM image of g-C $_3N_4$ prepared by calcination of urea at 600 °C for 4 h.



Figure S2. XRD patterns of C_3N_4 and CD- C_3N_4 . The results show the characteristic diffraction peak <002> at 2 θ = 32.3°. Note that there is shift of the <100> and <002> peaks compared to the literature data. This is due to the Co K α radiation (1.789 Å) source used in the XRD measurement.



Figure S3. UV–vis absorption spectra of pure $g-C_3N_4$ and $CD-C_3N_4$.



Figure S4. Images of the homemade light setup used in the experiments (Setup 1).



Figure S5. Images of the Hamamatsu light setup used in the experiments (Setup 2).



Figure S6. Recycling study of the photocatalyst CD-C₃N₄. Reaction condition: 5 g L⁻¹ of photocatalyst CD-C₃N₄, two phase reaction: 700 μ L of water + 300 μ L of benzyl alcohol, 30 °C and oxygen atmosphere under visible light illumination using Setup 1 (λ > 400 nm). The photocatalyst was recovered by centrifuge and washed three times with MilliQ water, then a fresh mixture of water and benzyl alcohol was added. Please note that slight higher product formation is observed here in comparison to the results shown in Figures 1 and 2 in the main text, which should be ascribed to a very recent replacement of the light bulb.



Figure S7. Photocatalytic aerobic oxidation of benzyl alcohol (a) and cyclohexanol (b) under neat conditions. Reaction condition: 5 mg of CD-C₃N₄ in 200 uL of alcohol, 30 °C and oxygen atmosphere under visible light illumination using Setup 1 (λ > 400 nm).



Figure S8. BET nitrogen adsorption/desorption isotherms of $CD-C_3N_4$. The BET surface area is 105 m²/g, the total pore volume is 0.31 cm³/g at P/P₀ = 0.98.



Figure S9. Representative GC chromatogram of the $CD-C_3N_4$ -catalysed oxidation of benzyl alcohol. Samples were diluted by 40 times with ethyl acetate.



Figure S10. Representative GC chromatogram of the $CD-C_3N_4$ -catalysed oxidation of 1-phenyl ethanol. Samples were diluted by 40 times with ethyl acetate.



Figure S11. Representative GC chromatogram of the $CD-C_3N_4$ -catalysed oxidation of 3-methyl-2-cyclohexen-1ol. Samples were diluted by 40 times with ethyl acetate.



Figure S12. Representative GC chromatogram of the $CD-C_3N_4$ -catalysed oxidation of 1,2,3,4-tetrahydro-1-naphthol. Samples were diluted by 40 times with ethyl acetate.

Preparative-scale synthesis

Reaction conditions: 200 mg of CD-C₃N₄ were suspended in 30 mL of water via ultra-sonication, 1.035g of carverol (6.8 mmol) was added. The illumination was performed top-wise at room temperature by the Hamamatsu fibre spot light (1 cm distance from the liquid phase, 25 % intensity). After 90 hours, full conversion (97.6%) was nearly achieved as revealed by GC. The reaction mixture was firstly filtered to remove the suspended photocatalyst. The filtrate was extracted with DCM (20mL × 3). The organic phase was separated, dried over MgSO₄ and DCM was evaporated in the last step. 0.773 g of carvone was obtained, with 74.8 % isolated yield. The reaction rate is 0.057 g_{product} g⁻¹_{catalyst} h⁻¹.



Figure S13. The obtained carvone from the $CD-C_3N_4$ -catalysed oxidation of carverol.



Figure S14. ¹H NMR of the obtained carvone in CDCl₃. Proton signals between 2.4-2.2 ppm belong to the slightly remaining carverol. The Agilent 400 MHz NMR was used.

GC analytics

Table S1. Details for GC analysis

Product	Analysis, column ^[a]	T_R [min] ^[b]	Temperature profile
H O	Column A	Benzyl alcohol 22.04 Benzaldehyde 17.2 Dodecane 10.85	55 °C hold 7 min, 10 °C /min to 80 °C hold 2 min, 15 °C /min to 145 °C hold 3 min, 20 °C /min to 185 °C hold 2 min. 30 °C /min to 250 °C hold 3 min.
H ₃ CO	Column B	<i>p</i> -Anisaldehyde 5.76 <i>p</i> -Anisyl alcohol 6.84 1-Octanol 2.69	100 °C hold 7 min, 30 °C /min to 290 °C hold 1.5 min.
F O	Column A	4- Fluoro benzyl alcohol 10.714- Fluoro benzaldehyde 7.43Dodecane 3.66	90 °C hold 2 min, 15 °C /min to 105 °C hold 1.5 min, 30 °C /min to 160 °C hold 1.5 min, 20 °C /min to 205 °C hold 2.5 min, 30 °C /min to 250 °C hold 1 min.
O C	Column A	1-Phenylethanol 11.62 Acetophenone 10.07 1-Octanol 8.75	80 °C hold 3 min, 20 °C /min to 90 °C hold 1 min, 20 °C /min to 160 °C hold 1 min, 20 °C /min to 168 °C hold 1 min, 20 °C /min to 180 °C hold 1 min, 30 °C /min to 250 °C hold 1 min.
⊖_o	Column A	Cyclohexanone 6.41 Cyclohexanol 8.92 Dodecane 3.98	90 °C hold 3 min, 20 °C /min to 100 °C hold 4.5 min, 30 °C /min to 200 °C hold 3 min, 30 °C /min to 230 °C hold 1 min.
	Column A	Cyclohexen-1-one 11.52 Cyclohexen-1-ol 12.82 Dodecane 3.98	90 °C hold 3 min, 20 °C /min to 100 °C hold 10 min, 30 °C /min to 240 °C hold 2 min.
○	Column C	3-Methyl-2-cyclohexen-1-ol 7.81 3-Methyl-2-cyclohexenone 12.65 Dodecane 8.53	100 °C hold 3.5 min, 5 °C /min to 135 °C hold 0 min, 25 °C /min to 210 °C hold 2 min.
	Column D	1,2,3,4-Tetranaphthalene 7.14 (S)-1,2,3,4-Tetrahydro-1-naphthol 10.98 (R)-1,2,3,4-Tetrahydro-1-naphthol 11.11 α -Tetralone 9.36 Dodecane 4.46	130 °C hold 2 min, 10 °C /min to 150 °C hold 4 min, 10 °C /min to 165°C hold 3.5 min, 25 °C /min to 2255°C hold 1.5 min.
	Column E	<i>p</i> -Mentha-6,8-dien-2-ol, 10.86 <i>p</i> -Mentha-6,8-dien-2-one, 10.12 &11.32, two enantiomers Dodecane 3.78	130 °C hold 3.5 min, 20 °C /min to 210 °C hold 4.1 min, 25 °C /min to 240 °C hold 2 min.
$\bigvee_{\mathcal{O}}$	Column C	3,5,5-Trimethyl-2-cyclohexen-1-ol, 10.50 3,5,5-Trimethyl-2-cyclohexen-1-one, 17.1 Dodecane 8.72	100 °C hold 3.5 min, 5 °C /min to 125 °C hold 12.2 min, 25 °C /min to 210 °C hold 2 min.

^[a] Column A: cp wax 52 CB, (50 m × 0.53 mm × 2.0 μ m), FID, N₂ is the carrier gas; Column B: cp sil 5 CB, (50 m × 0.53 mm × 1.0 μ m), FID, N₂ is the carrier gas; Column C: LIPODEX E (50 m × 0.25 mm × 0.25 μ m);), FID, He is the

carrier gas; Column D: Chiralsil Dex CB column (25 m × 0.32 mm × 0.25 μ m), FID, He is the carrier gas. Column E: CP Wax 52CB column (25 m × 0.25 mm × 1.2 μ m), FID, N₂ is the carrier gas.

References

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