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mpg-C_3N_4-Catalyzed Selective Oxidation of Alcohols Using O_2 and Visible Light

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Abstract: Mesoporous carbon nitride (mpg-C_3N_4) polymer can function as a metal-free photocatalyst to activate O_2 for the selective oxidation of benzyl alcohols with visible light, avoiding the cost, toxicity, and purification problems associated with corresponding transition-metal systems. By combining the surface basicity and semiconductor functions of mpg-C_3N_4, the photocatalytic system can realize a high catalytic selectivity to generate benzaldehyde. The metal-free photocatalytic system also selectively converts other alcohol substrates to their corresponding aldehydes/ketones, demonstrating a potential pathway of accessing traditional mild radical chemistry with nitroxyl radicals.

The use of solar radiant energy to drive organic reactions provides a sustainable pathway for green synthesis and has gained significant interest. However, most common organic molecules do not absorb light in the visible light region (400−800 nm) that accounts for 43% of the incoming solar spectrum. This restricts photochemical applications, and thus, it motivates the search for further approaches to enable the direct utilization of visible light in organic synthesis.[1] One approach is to activate target reactions via charge-transfer catalysis mediated by photosensitizers, such as inorganic ions/semiconductors and organometallic complexes.[2] In the past, Ru(bipy)$_3^{2+}$ and its derivatives have been widely exploited as visible-light-harvesting complexes to initiate such photochemical reactions as oxidation,[3a] reduction,[3b] cycloaddition,[1b] dehalogenation,[1c] and asymmetric alkylation[1a] of organic matter. Dye molecules have also been used to sensitize inorganic semiconductors via electron transfer to achieve longer lifetimes of the excited states, such as in the well-known case of the dye sensitized TiO_2 solar cell.[4] Recently, Zhao and co-workers coupled dye/TiO_2 photoredox catalysis with the TEMPO (2,2,6,6-tetramethylpiperidinyloxyl) oxidation scheme to activate oxygen for selective alcohol oxidation,[5] a key transformation in laboratory and industrial syntheses.[6] Their catalytic system avoids toxic metal salts as oxidation catalysts, and the use of visible light avoids the induction of the strong, nonselective hydroxyl radicals, •OH. Although the excited states of some dye molecules are stable against self-sensitized degradation in light-driven organic synthesis, they have not found significant application in synthetic transformations, partly due to the employment of precious metals such as Ru.

Recently, we have introduced a solid-state semiconductor based on polymeric melon (a slightly disordered precursor of graphitic carbon nitride, g-C_3N_4; for simplicity, we use the latter notation for the whole family of substances), as a stable visible light photocatalyst for hydrogen and oxygen evolution.[7] This easily available organocatalyst features a semiconductor band gap of 2.7 eV corresponding to an optical wavelength of 460 nm.

Electrochemical analyses were therefore performed to study the band positions of the g-C_3N_4 semiconductor. The studies revealed a high oxidation potential of the conduction band (CB) at −1.3 V at pH 7 vs the normal hydrogen electrode (NHE) ($E°$), while the reduction level of the valence band (VB) is located at 1.4 V (pH 7).[8] These band positions are in agreement with a theoretical calculation.[7] A comparison of the band positions of g-C_3N_4 with those of the current "golden" photocatalyst, TiO_2, as well as some redox potentials of reactive oxy-radicals, are illustrated in Scheme S1 (Supporting Information). As revealed from these band characteristics, light-excited electrons in the CB of melon possess a large thermodynamic driving force to reduce O_2 ($E°(O_2/•O_2^-) = -0.16$ V), but the potential of the photogenerated hole in the VB is inadequate to oxidize −OH to hydroxyl radicals ($E°(-OH/•OH) = 2.4$ V). These features provide an argument that g-C_3N_4 might act as a suitable candidate for photooxidation and related transformations in aqueous media, in which TiO_2 photocatalysis can achieve selective oxidation of aromatic alcohols to aldehydes and mineralization to CO_2 with UV light.[9]

When we extended our original work to organic functional group transformations, we discovered a remarkable selectivity (>99%) of bulk g-C_3N_4 (surface area: ca. 8 m^2/g) for the oxidation reaction of benzyl alcohol to benzaldehyde with visible light, yet with a moderate catalytic conversion under the applied standardized conditions (5%, see entry 1, Table 1). The system presented here is however metal-free, using cheap and environmentally benign molecular oxygen as a primary oxidant.

To make the carbon nitride polymer semiconductor more valuable for heterogeneous (photo)catalysis, an increase of its specific surface area is important. Porosity was introduced into the bulk g-C_3N_4 by using silica nanoparticles as templates[10] (the resultant mesoporous polymeric g-C_3N_4 is denoted as mpg-C_3N_4 in the following), rendering the materials a high mesopore surface area (ca. 200 m^2/g) and accessible surface sites for interfacial (photo)reactions. It is underlined that mpg-C_3N_4 is functionally not only a semiconductor but also a solid state organic reagent with its surface-terminating amino groups and lone-pair N heteroatoms of the poly(tri-*s*-triazine) framework.

Such N-containing graphitic-like carbon materials can in principle show the ability to reductively adsorb O_2,[11] being a potential carrier for catalytic oxidations. We were thus inspired to employ mpg-C_3N_4 to activate O_2 with visible light for liquid-phase oxidation of benzyl alcohol, a model reactant often employed to evaluate the activity of the oxidation of alcohols.[12]

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A series of experiments was conducted at 373 K using O_2 (8 bar) in a closed autoclave with a quartz window for coupling in the incident photon flux (see Experimental Section in the Supporting Information) to test the synergistic reactivity of mpg-C_3N_4, dioxygen, and photonic energy (Table 1). In the absence of the mpg-C_3N_4 photocatalyst, benzyl alcohol (BA) was not converted to the corresponding aldehyde, even with light irradiation under a high pressure of oxygen for 3 h (entry 5, Table 1). Under the same conditions, mpg-C_3N_4 catalyzes the oxidation to benzaldehyde with >99% selectivity and 57% (visible light irradiation for 3 h) and 38% (UV irradiation for 1 h) (entries 2 and 3, Table 1) conversion yield, respectively. In the absence of light, a negligible thermocatalytic conversion (<1%, entry 4, Table 1) of BA was observed for the same system. These results demonstrate that the selective oxidation is clearly due to heterogeneous organo-photocatalysis. The photocatalytic system also works when the oxygen is replaced by air, thus enabling aerobic oxidation of BA with 44% conversion and >99% selectivity to benzaldehyde (entry 6, Table 1).

Table 1. Study of Reaction Conditions[a]

	Solvent	*hv*	O_2 source	Con. [%][b]	Sel. [%]
1[c]	trifluorotoluene	+	O_2 (8 bar)	5	>99
2	trifluorotoluene	+	O_2 (8 bar)	57	>99
3[d]	trifluorotoluene	+	O_2 (8 bar)	38	>99
4	trifluorotoluene	−	O_2 (8 bar)	<1	−
5[e]	trifluorotoluene	+	O_2 (8 bar)	0	−
6	trifluorotoluene	+	Air (8 bar)	44	>99
7[f]	trifluorotoluene	+	−	11	>99
8[f]	trifluorotoluene	−	−	<1	−
9	toluene	+	O_2 (8 bar)	40	>99
10	acetonitrile	+	O_2 (8 bar)	70	68
11[g]	perfluorohexane	+	O_2 (1 bar)	46	>99
12[g]	trifluorotoluene	+	O_2 (1 bar)	21	>99

[a] In a typical reaction mpg-C_3N_4 (50 mg) was added to the solvent (10 mL) in a 100 mL stainless steel autoclave with a quartz window. The O_2 source was introduced and the closed autoclave was heated to 100 °C, followed by visible light irradiation for 3 h. [b] Conversion rates were determined by GC with an FID detector. [c] Using bulk g-C_3N_4. [d] Initiated with UV for 1 h. [e] Reference experiment without catalyst. [f] Reference experiments in the absence of O_2. [g] Performed in a closed glass reactor with 1 atm of O_2 at 25 °C.

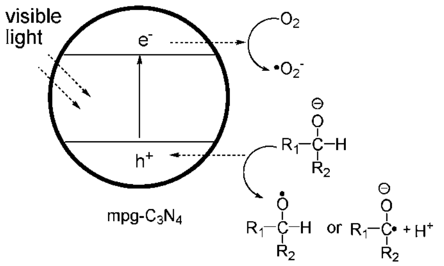
The dependence of activity on the wavelength of the incident light was also investigated. The activity of mpg-C_3N_4 corresponds well with its UV/vis diffuse reflectance spectrum (Supporting Information, Figure S1), providing an extra confirmation that the reaction is really enabled by photocatalysis.

Some organic substrates can undergo photocatalytic dehydrogenation to produce H_2, namely the formally abstracted H^+ accepts the photogenerated electrons from the CB of the photocatalyst while the formal negative organic fragment left captures the photogenerated hole from the VB. This is indeed found for BA in our system, when the reaction was carried out in the absence of oxygen. The conversion rate for the photocatalytic dehydrogenation of BA is lower with 11% under standard conditions, however, with >99% selectivity toward benzaldehyde (entry 7, Table 1). Because the interfacial transfer of the light-induced electron is considered to induce photochemical reaction in heterogeneous photocatalysis,[13] it is expected that the electron transfer can be promoted by the introduction of more electrophilic species like O_2 ($\Delta G = -110$ kJ mol^{-1} per electron transferred) as compared to a proton ($\Delta G = -85$ kJ mol^{-1}) to capture the electron. As some oxygen is presumably chemically preadsorbed on the mpg-C_3N_4 via Lewis acid−base interaction, a potential acceleration by the acid−base interaction is assumed by us. Indeed, in the presence of oxygen, the conversion rate (57%) of BA was five times higher than that (11%) in the absence of oxygen (entry 7, Table 1), while keeping the selectivity at >99%.

Fluorinated solvents which are known to dissolve a larger amount of oxygen[14] turned out to be favorable for the reaction. When perfluorohexane was used as solvent in an initial experiment under nonoptimized conditions, 46% conversion of BA was achieved already at 25 °C with 1 atm of O_2. Under the same conditions, BA conversion in a partly fluorinated solvent, trifluorotoluene, was 21% (entries 11 and 12, Table 1). The activity in toluene (entry 9, Table 1) was still lower, while in acetonitrile a significantly decreased selectivity was observed (68%, entry 10, Table 1), with benzoic acid as the only side product. This is presumably due to the solvolysis of O−O bonds in polar media,[15] making the reaction less surface controlled.

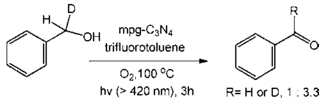
The induction of a formal, presumably still surface-mediated $\bullet O_2^-$ by mpg-C_3N_4 was confirmed by electron spin resonance (ESR) and the DMPO (5,5-dimethyl-1-pyrroline *N*-oxide) spin trap technique in methanol.[16] There is no ESR signal in the dark (Figure S2), but a gradual evolution of clear ESR signals for DMPO−$\bullet O_2^-$ adducts was observed with visible light irradiation. Note that we do not detect DMPO−•OH adducts in water (Figure S3). On the basis of the aforementioned results, the electron transfer reactions involved in the selective photooxidation of alcohols using mpg-C_3N_4 with oxygen are proposed in Scheme 1.

Scheme 1. Electron Transfer Reactions with mpg-C_3N_4



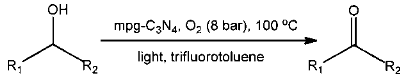
To test the reusability of the catalyst system, the used mpg-C_3N_4 was washed with ethanol, dried at 80 °C, and then re-employed with a new reactant mixture. Gradual deactivation of the catalyst was observed during four consecutive experiments while about one-third of the activity was lost, overall. However, the mpg-C_3N_4 can be completely recovered simply by washing with 0.2 M NaOH. This result not only indicates surface protonation as the deactivation mechanism but also proves the promoting role of surface basic sites in photocatalysis. The total production of benzaldehyde in this series summed up to 2.7 mmol, and the turnover number (TON) was calculated to be 100, confirming that the reaction proceeds catalytically.

Scheme 2. Kinetic Isotope Effect



The kinetic isotope effect of this reaction was studied using monodeuterated benzyl alcohol (Scheme 2) to gain more insight into the mechanistic details. The crude aldehyde obtained after the reaction was converted to the corresponding hydrazone derivative and analyzed using ESI mass spectroscopy. Results showed that the abstraction of hydrogen during the reaction is 3.3 times faster compared to that of deuterium. This clearly proves that the secondary abstraction of H/D as indicated in Scheme 1 is a rate-determining step in the oxidation of alcohol.

Table 2. Selective Oxidation of Alcohols



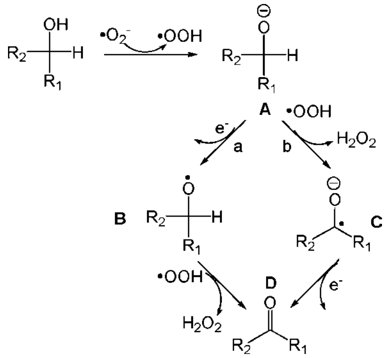
	R^1	R^2	Time [h]	Con. [%]	Sel. [%]
1	Phenyl	H	3	57	>99
2	Phenyl	CH_3	3	77	>99
3	4-Methylphenyl	H	3	86	90[a]
4	4-Chlorophenyl	H	3	79	>99
5[b]	4-Methoxyphenyl	H	1.8	100	95[c]
6	4-Methylbenzoate	H	3	80	>99
7	$PhCH{=}CH_2$	H	3	92	64[d]
8	Pentyl	CH_3	5	35	>99
9	Phenyl	Cyclopropyl	3	32	90[d]

[a] Acid (10%) was formed. [b] 4-Methoxybenzylalcohol 0.65 mmol. [c] Acid (5%) was formed. [d] Benzaldehyde (36%) was detected. [e] 1-(1,2-Dicyclopropyl-2-phenylethyl)benzene (10%) was formed.

The effect of substitution on the aromatic ring has also been studied. Both electron-withdrawing and electron-donating substituents have been found to enhance the rate of the reaction (Table 2). These results also strongly support a radical mechanism. We also examined the chemoselectiviy of the current system using some additional substrates incorporating both aliphatic and benzylic alcohols. The system showed high chemoselectivity toward the benzylic alcohol moiety (Table S1).

A radical clock experiment using the cyclopropyl-phenylcarbinol however failed. Oxidation of the substrate resulted in the formation of the corresponding ketone with an intact cyclopropyl ring. This is a strong indication that either no solution-based radicals are relevant for the reaction or the reaction runs through an alkoxide anion α to the benzyl radical which considerably decelerates the rate of ring-opening.[17] Another possibility is that the initial radical formation is on the oxygen atom which immediately forms the C═O bond through abstraction of a hydrogen radical.

Scheme 3. Proposed Potential Oxidation Mechanism



Based on the results, a mechanistic proposal for the oxidation reaction is given in Scheme 3. The superoxide radical anion ($\bullet O_2^-$) formed by the reduction of molecular oxygen (by the excited electrons from the conduction band of the mpg-C_3N_4) stays obviously surface bound to the C_3N_4, presumably as an interface bound exciton pair to compensate for the positive charge within the catalyst. The base character of the material also helps to deprotonate a benzyl alcohol toward the alkoxide anion A, which then can react with the positive hole by electron transfer to form the radical B. Recombining this radical with the superoxide radical finally results in the observed ketone and the formal liberation of H_2O_2, the two-electron reduction product of O_2.

As we never observe molecular H_2O_2, a more reactive oxidation agent than O_2, H_2O_2, is presumably quickly rebound and undergoing a second, similar two-electron cycle on the catalyst, which leads to the formation of (more stable) water. Indeed, by adding, in a reference experiment, H_2O_2 instead of O_2 to the system, an even higher turnover of benzylalcohol to benzaldehyde resulted (as described in the Supporting Information), however, with lower selectivity. We attribute this lower selectivity to the higher overall concentration of perhydrol, while only the catalyst-surface bound species are sufficiently mild to be highly selective.

In conclusion, we have shown that mpg-C_3N_4 can function as a photocatalyst to activate O_2 for the selective oxidation of benzyl alcohols under visible light irradiation. By combining the surface basicity and semiconductor functions of mpg-C_3N_4, the photocatalytic system can realize a high catalytic selectivity to generate benzaldehyde. The system also selectively converts other alcohol substrates to their corresponding aldehydes/ketones.

The whole set of experiments demonstrated a potential pathway of accessing traditional mild radical chemistry, as it is otherwise only done via nitroxyl radicals, such as TEMPO. The "mild" nature of the mpg-C_3N_4 photocatalyst, together with its unique electronic and surface properties, had already found some interesting applications in metal-free coordination chemistry and metal-free heterogeneous catalysis[18] but now obviously can be extended to a broad variety of related problems including O_2 activation, organic photosynthesis, or reductive CO_2 fixation.

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Supporting Information Available: Experimental details and more characterization and reaction results. This material is available free of charge via the Internet at http://pubs.acs.org.

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