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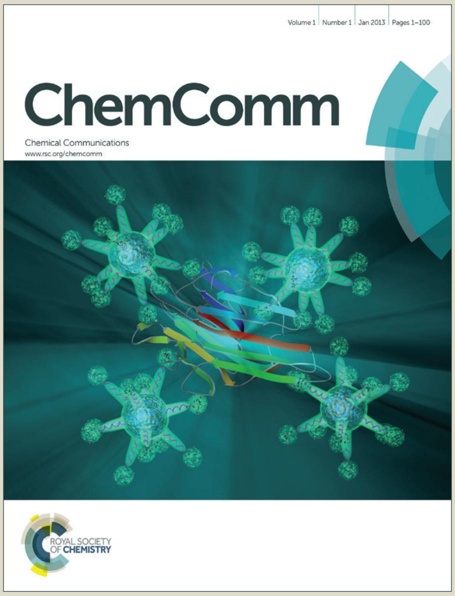

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ARTICLE TYPE

Post-Functionalization of Graphitic Carbon Nitride by Grafting Organic Molecule: Toward C-H Bond Oxidation Using Atmospheric Oxygen

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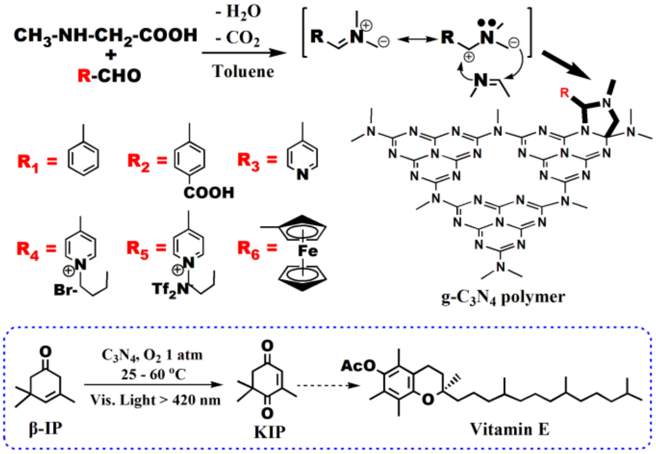
Described here is the feasible modification of graphitic carbon nitride polymer by Prato's reaction with in situ formed azomethine ylides. Those novel carbon nitrides with designable organic functional groups, and tailorable surface and structure properties illustrated excellent performance in the selective oxidation of 3, 5, 5-trimethylcyclohex-3-en-1-one with atmospheric oxygen.

Graphitic carbon nitrides (g-C_3N_4) are attracting global interest, mainly due to their unique physical and chemical properties with excellent performance in various fields, such as metal-free oxidation, photocatalytic water splitting, fuel cell and photoelectric conversion. [1] In comparison to two-dimensional graphene with sp^2-hybridized carbon atoms arranged in six-membered rings, g-C_3N_4 possesses a stacked layer architecture yet with high N-substitution (~60 wt%), and most recent works energetically favor its defect-rich, N-bridged "poly(tri-s-triazine)" network. [2] The "nitrogen pots" with six nitrogen lone-pair electrons on the surface could act as strong Lewis base sites for coordinating to metal species or strengthening the interaction with organic substrate. [1f, 1g] Being different with the metal-like conductor of graphene, electrochemical studies of g-C_3N_4 revealed its organic semiconductor property with medium band gap of ~ 2.69 eV, corresponding to a blue light absorption up to 450 nm. [1c] All above-mentioned features argue the direct use of g-C_3N_4 in sustainable chemistry as heterogeneous catalyst. [3] Indeed, Antonietti and co-workers recently illustrated the visible-light promoted oxidation of alcohols, amines and sulfides by g-C_3N_4, however, there is still large room for improvement, respecting to the catalytic activity. [4]

In the past five years, g-C_3N_4 derivates with various heteroatom dopants (e.g., B, F, S, P, O, I), have been prepared by co-thermal condensation of suitable additives with the precursor of g-C_3N_4. [5] In comparison, post-functionalization of g-C_3N_4 has the extra advantage of introducing much more functional groups or dopants into g-C_3N_4 after the lattice is formed at elevated temperatures. However, the high chemical stability and bad solubility in common solvents of g-C_3N_4 constitute a vast barrier to post-modify g-C_3N_4 material. In this contribution, we present the chemical functionalization of mesoporous g-C_3N_4 (mpg-C_3N_4) with organic groups, via 1, 3-dipolar cycloaddition of azomethine ylides (Prato's reaction), in situ generated by thermal condensation of the α-amino acid N-methylglycine and an aldehyde containing R group (Scheme 1). Though the reactivity of mpg-C_3N_4 (-C=N-) differs from that of pure carbon material (-C=C-, e.g., fullerenes, carbon nanotubes, graphenes and mesoporous carbon), [6] the 1, 3-dipolar cycloaddition can undergo efficiently and yield highly functionalized carbon nitrides with diverse organic groups, including aryl, aryl acid, pyridine, ionic liquids and ferrocene. The essence of our strategy was adjusting the electronic structure of g-C_3N_4, at the same time introducing organic functional group with specific task.



Scheme 1. The 1, 3-dipolar cycloaddition reaction for carbon nitride modification, and the industrial route for Vitamin E production via selective oxidation of β-isophorone to keto-isophorone.

The mpg-C_3N_4 material used in this investigation was prepared by thermal condensation of cyanamide in the presence of a silica template, 12 nm SiO_2 nanoparticles. [1] The template was subsequently removed by 4 M NH_4HF_2 aqueous solution to obtain mpg-C_3N_4 frameworks. The surface modifications of mpg-C_3N_4 were carried out with α-amino acid N-methylglycine (3 mmol), an aldehyde (2 mmol) and mpg-C_3N_4 (300 mg) in toluene at 120 °C for 21 h. After filtration and thoroughly washing, functionalized products from yellow to dark brown were obtained, labelled by C_3N_4-R1 *etc.*, where the "R1" corresponded to the group in the aldehyde.

The Fourier transform infrared (FT-IR) spectra of modified mpg-C_3N_4 materials show typical C-N heterocycle stretches in the ~ 1200-1600 cm^{-1} region together with the breathing mode of the triazine units at ~ 810 cm^{-1}, which are related to the poly(tri-s-triazine) network (Figure S1). These results indicate that the surface modifications do not alter the bulk structure or the basic skeleton of mpg-C_3N_4 in large degree and we infer that the organic group density is relatively low.

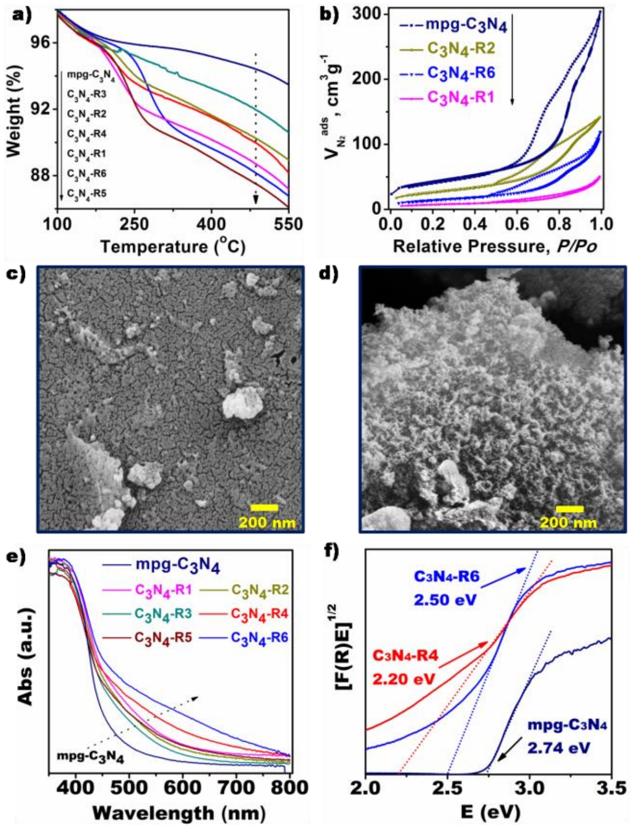


Figure 1. a) TGA plots of carbon nitride polymers in N_2 atmosphere; b) N_2 sorption isotherms of carbon nitrides at 77 K; c) SEM image of mpg-C_3N_4 sample; d) SEM image of C_3N_4-R1 sample; e) UV-Vis diffuse reflectance spectra of carbon nitride polymers; f) Tauc plots of respective samples.

The presence of different organic groups on the mpg-C_3N_4 material was further investigated by thermo gravimetric analysis (TGA) under N_2 atmosphere. There is acceptable weight loss during thermal treatment of mpg-C_3N_4 to 550 °C, mostly induced by the loss of chemically/physically adsorbed species, and the decomposition of terminal amino groups and bridging nitrogen atoms. With mpg-C_3N_4 as a reference sample, TGA plots of modified products show pronounced weight loss of 2.9%-7.4% during 100-550 °C, and we attribute it to the decomposition of organic groups attached on the carbon nitride surface by covalent bonds (Figure 1a). The grafting densities of those products are roughly estimated to ~ 3 - 9 functional groups in per 100 tri-s-triazine units (0.16-0.47 mmol/g), which could be comparable with those of modified mesoporous carbon material (Table S1).[6b]

Carbon and nitrogen stoichiometry of the samples were then determined by elemental analysis (Table S1). The as-made mpg-C_3N_4 sample holds a C/N molar ratio of 0.74 (A slightly defective carbon nitride polymer), very close to the theoretical value of 0.75 for C_3N_4. Comparing with mpg-C_3N_4, these modified ones afford higher C/N molar ratios (0.76-0.81), another proof for the successful introduction of organic groups, as those linked organic groups have much higher C/N molar ratios (4-13).

It was also found that the chemical functionalization process changed not only the chemical composition of mpg-C_3N_4 polymers, but also the pore structure and its sorption characteristics. N_2 sorption isotherms of all modified mpg-C_3N_4 samples show typical type IV curves with distinct hysteresis loops, similar to the pristine mpg-C_3N_4 sample, suggesting the existence of abundant mesopores (Figure 1b). Further analysis of sorption isotherm by BJH method suggests that the covalent attachment of functional group into carbon nitrides do not alter the pore size distribution in large degree (Figure S2). However, the introduction of organic groups leads to a decrease in BET surface area. It is reasonable as those organic groups are essentially nonporous (Table S1), and would block some pores in mpg-C_3N_4.

High resolution SEM image shows the typical slate-like texture of mpg-C_3N_4, where the chapped surface is smooth with few small aggregations (Figure 1c). In sharp contrast, the picture of the post-treated C_3N_4-R1 shows the rough surface covered by coral-like wrinkle (Figure 1d). Due to the development of organic group branch on mpg-C_3N_4 texture, the characteristic sheet-like surface might be broken up. In principle, the "surface villus" structure would benefit the interaction between reactant molecules and catalytic active sites, somewhat like the promotion effect of intestinal villi on food digestion. In addition, the surface chemistry of C_3N_4-R6 sample with ferrocene group was characterized by elemental mapping technology, which clearly visualized the homogeneous incorporation of Fe into the mpg-C_3N_4 (Figure S3).

As shown in the UV-Vis diffuse reflectance spectra, the absorbance of the carbon nitride materials with linked organic groups is significantly red shifted, in comparison with typical mpg-C_3N_4 (Figure 1e). The broader absorption band should be the consequence of linked organic aromatic rings, which enlarges the *p*-electron delocalization in the conjugated system, and thus changes the intrinsic optical/electronic properties of carbon nitride polymers. It should be emphasized that C_3N_4-R6 containing ferrocene favorably moves the absorption edge to >700 nm, covering most sunlight spectrum on the earth. Moreover, the optical band gaps of modified samples are significantly narrowed, for instance: C_3N_4-R4 with N-butylpyridinium bromide group has a band gap of 2.20 eV (Figure 1f). The current modification, leading to carbon nitrides with narrowed band gap and extended visible light absorption range, in principle would contribute to its photocatalytic activity.

The aerobic oxidation of β-isophorone (β-IP) to keto-isophorone (KIP) is a selective allylic C-H oxidation, and in particular KIP is a widely-used chemical and intermediate in preparing foodstuffs, vitamins and carotenoids.[7] Here, the β-IP oxidation using atmospheric oxygen was investigated with carbon nitride polymers by light irradiation. Under visible light illumination (>420 nm), the oxidation of β-IP occurred at room temperature, while the main product located at 4-hydroxy-3, 5, 5-trimethyl-2-cyclohexen-1-one (HIP), an intermediate for KIP, and we attribute it to the insufficient oxidation by original mpg-C_3N_4 (Table 1).[7a] When those modified carbon nitrides (C_3N_4-R4, C_3N_4-R6) were used for this process, both higher β-IP conversion

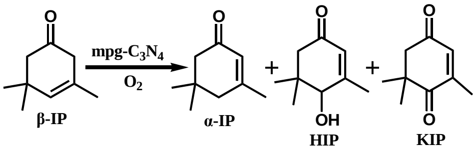


Table 1. The selective oxidation of β-IP by carbon nitrides. [a]

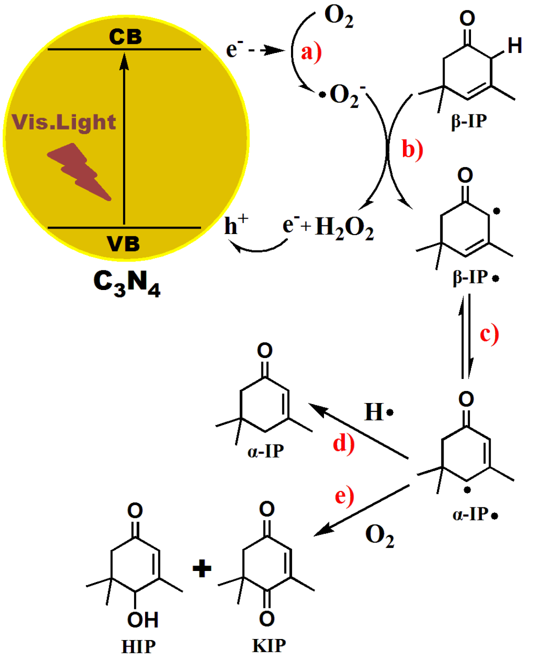
Catalyst	Additives [b]	T (°C)	Conv. (%)	Sel. (%) α-IP	Sel. (%) HIP	Sel. (%) KIP
mpg-C_3N_4	-	25	9	-	60	28
C_3N_4-R4	-	25	24	-	4	92
C_3N_4-R6	-	25	30	2	6	84
[BPy]Br[c]	-	25	<1	-	-	-
$Fe(C_5H_5)_2$[c]	-	25	<1	-	-	-
C_3N_4-R6	-	60	96	10	4	82
C_3N_4-R6	AQ	25	10	-	57	27
C_3N_4-R6	IBA	25	56	1	10	82
C_3N_4-R6	NHPI	25	88	-	3	93
-	NHPI	25	3	-	-	-
$Fe(C_5H_5)_2$[c]	NHPI	25	<1	-	-	-

[a] Reaction condition: β-IP 0.5 mmol, n-decane 75 μL (internal standard), catalyst 50 mg, pyridine 3 mL, O_2 4 mL/min, visible light (λ > 420 nm), 4 h. [b] AQ (anthraquinone): 20 mg, IBA (isobutylaldehyde): 20 mg, NHPI (N-hydroxyphthalimide): 16 mg. [c] N-Butylpyridiniumbromide ([BPy]Br) 10 mg, $Fe(C_5H_5)_2$ (Ferrocene) 10 mg.

and KIP selectivity were achieved. We noticed that a satisfying KIP yield (Conv.: 96%; Sel.: 82%) was reached as the reaction temperature increased to 60 °C. As a heterogeneous photocatalyst, C_3N_4-R6 successfully drives aerobic oxidation of β-IP to KIP.

Previous works on mpg-C_3N_4-promoted photooxidations revealed that light-irradiated electrons from the conduct band (CB) of mpg-C_3N_4 with large reduction potential could reduce O_2 to the •O_2^- radical, an active specie that has been captured by electron spin resonance (ESR) measurement (Scheme 2a). [4a,4b,4d,4e] Thereby, it is reasonable to consider that the H-abstraction in β-IP by the •O_2^- radical with medium oxidation ability could occur, because the C-H bond at 2 site of β-IP holds a relatively low bond dissociation enthalpy (75.78 kcal mol^{-1}) and the resulting β/α-IP• radicals are significantly stabilized by allylic resonance (Scheme 2b, 2c). [7a] Following a radical route, the O_2 kinetic addition could then happen on the α-IP• radical, the one with favourable dioxygen-binding affinity, and finally main products (KIP and HIP) form via the decomposition of α-IP peroxide (Scheme 2e). [7a] Therefore, the generation of superoxide radical anion - •O_2^- is a vital step for the whole oxidation. In comparison to mpg-C_3N_4, an enhanced Lorentzian line (Centering at g=2.0031) from C_3N_4-R6 was observed in ESR spectra, revealing more unpaired electrons on conjugated C_3N_4-R6 aromatic rings, which would contribute to more •O_2^- anions, and this should be considered as the origin of higher catalytic activity of C_3N_4-R6.

To complete this process at room temperature, several organocatalysts including anthraquinone (AQ), isobutyraldehyde (IBA) and *N*-hydroxyphthalimide (NHPI), have been coupled with C_3N_4-R6 as an alternative strategy. As expected, radical initiator IBA and *N*-oxyl radical precursor NHPI promoted this process in large degree; for instance, the combination of NHPI and C_3N_4-R6 afforded 88% β-IP conversion with 93% selectivity for KIP at 25 °C. Control experiments with NHPI alone or NHPI-ferrocene (R6 group) did not afford any detectable products. Hence, the enhanced oxidation activity should be attributed to the interaction between carbon nitride polymers and NHPI, that is the oxidation of NHPI to active phthalimide *N*-oxyl (PINO) radical by the •O_2^- radical, as suggested in pervious literature. [4e]



Scheme 2. A purposed mechanism for the oxidation of β-IP by carbon nitride polymers.

Conclusions

In summary, the use of 1, 3-dipolar cycloaddition with commercially available chemicals under a controlled environment allows for the simple, scalable and designable functionalization of carbon nitrides and the grafting densities of organic groups could reach 0.47 mmol/g. The current strategy distinctly adds a number of wrinkles into the smooth surface, significantly broadens the light sorption range, and at the same time narrows the band gap. Importantly, the derivative illustrated exceptional performance in the activation of atmosphere oxygen for the selective oxidation of β-IP to KIP. Further post-modifications of carbon nitride polymers can be easily envisioned, such as: introduction of photoexcitable donor-acceptor groups for photoinduced charge-transfer studies in oxidation.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Experimental details, Figure S1-S4 and Table S1. See DOI: 10.1039/b000000x/

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