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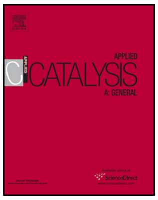

Carbon nitride-catalyzed oxidative cleavage of carbon–carbon bond of α-hydroxy ketones with visible light and thermal radiation

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ABSTRACT

Mesoporous carbon nitride (mpg-C_3N_4) as a photocatalyst showed higher photocatalytic activities in organic synthesis. Herein we reported a mpg-C_3N_4-catalyzed oxidation of α-hydroxy ketones to synthesize benzoic acids with visible light. This reaction represented a green and facile route to synthesize benzoic acids for which catalytic approaches were scarce.

1. Introduction

Transition metal-catalyzed oxidation cleavages of carbon–carbon bond [1–8] have been widely used as powerful tools for the preparation of carbonyl compounds and carboxylic acids in both industrial applications and academic research [9–11]. These compounds are also important starting material and intermediate in the synthesis of fine chemicals [12,13]. The protocol to achieve this goal is a critical part of much organic synthesis and remains a continuing challenge in organic synthesis. In the past decades, selective oxidation [14,15] cleavages of benzils to synthesize a-diketone and carboxylic acids have been achieved with a variety of oxidant regents such as periodic acid [16], alkaline hydrogen peroxide [17], and triperoxovanadate(V) trihydrates [18]. However, these catalysts, in general, suffer from the deficits in recovery, toxic and expensive of catalyst. In addition, some of them are difficult to prepare and handle. These results encouraged us to develop an inexpensive, environmentally friendly and nontoxic catalytic system [19–23] and design new method to prepare carbonyl compounds and carboxylic acids by oxidation cleavages.

Mesoporous carbon nitride (mpg-C_3N_4) is functionally not only a semiconductor but also a solid state organic reagent is one of the hottest topics in photocatalysis at present [24–32]. And it has been widely used in organic synthesis. Recently, many elegant and novel transformations have been reported by mpg-C_3N_4-catalyzed. Park's group has reported mpg-C_3N_4-catalyzed cycloaddition of CO_2 to propylene oxide and conversion of benzene to phenol [33]; Blechert and Wang's group has reported that mpg-C_3N_4 can function as a metal-free photocatalyst to activate O_2 for oxidation of benzyl alcohols [34] and amines [35] to form carbon–carbon bond via C—H activation with visible light. In this context, we anticipated to describe mpg-C_3N_4-catalyzed oxidation cleavage of carbon–carbon bond of benzils to form carbonyl compounds and carboxylic acids.

2. Experimental

2.1. Materials

NMR spectra were recorded using a Bruker Avance 400 MHz NMR spectrometer (100 MHz for carbon) and respectively referenced to 7.26 and 77.0 ppm for D-chloroform solvent with TMS as internal standard. Mass spectra were recorded on a Shimadzu GCMS-QP5050A at an ionization voltage of 70 eV equipped with a DB-WAX capillary column (internal diameter = 0.25 mm, length = 30 m). TLC was performed using commercially prepared 100–400 mesh silica gel plates (GF254), and visualization was effected at 254 nm.

2.2. General procedure for synthesis of benzil (**2a**)

In a typical procedure, mpg-C_3N_4 (60 mg) and 2-hydroxy-1,2-diphenylethanone (**1a**, 1.0 mmol) were added to CH_3CN (10 mL)

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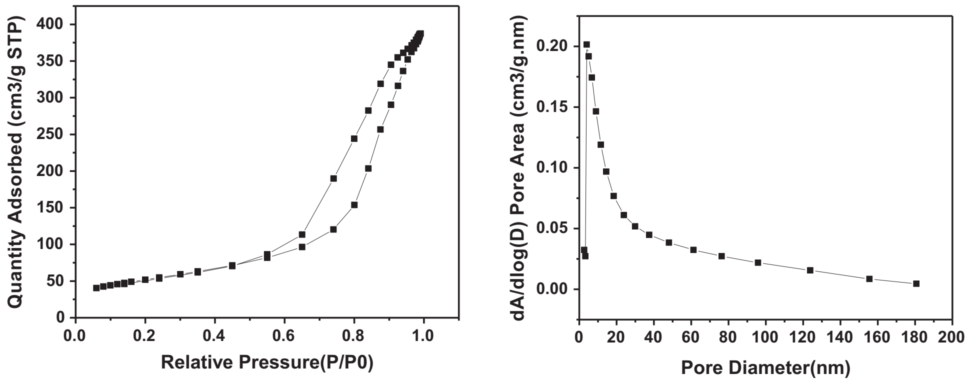


Fig. 1. Nitrogen adsorption–desorption isotherms (A) and the corresponding pore size distribution curves (B) of g-C_3N_4.

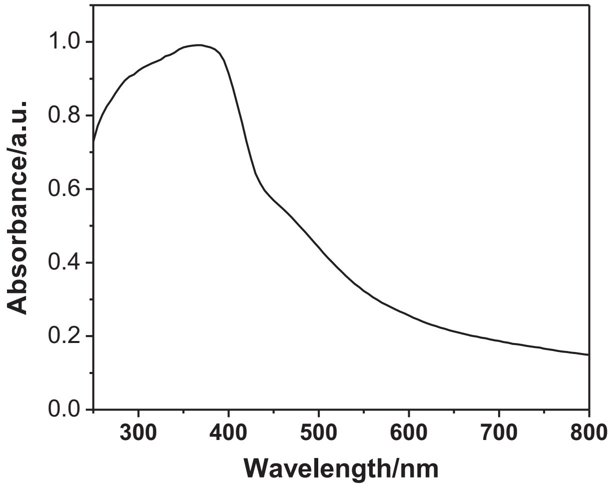


Fig. 2. UV–visible absorption spectra of g-C_3N_4.

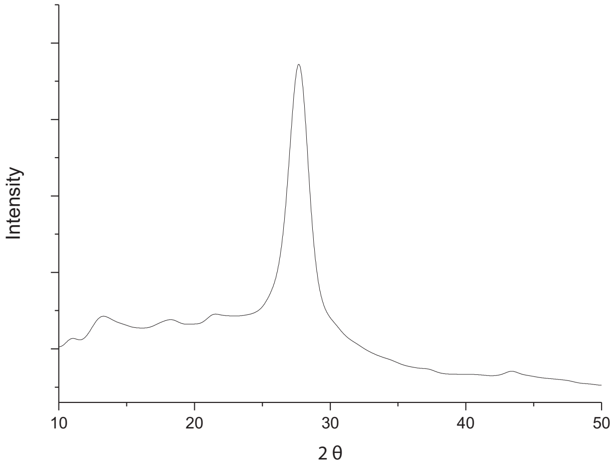


Fig. 3. XRD pattern of g-C_3N_4.

in a 100 mL stainless steel autoclave. The O_2 (3 bar) source was introduced and the closed autoclave was heated to 100 °C, followed by visible light irradiation for 16 h. The reaction mixture turned clear and the catalysts were deposited on the button, which was recovered by filtration. And then the solvent was removed, and the residue was separated by column chromatography to give the pure sample **2a**.

3. Results and discussions

3.1. Catalyst characterization

As shown in Fig. 1, mpg-C_3N_4 exhibits enhanced photocatalytic activity in the reaction due to their large surface area (ca. 200 m^2/g) for more possible reaction sites. And it has also indicated that mpg-C_3N_4, whose pores of with diameters are between 5 and 40, is an exemplary mesoporosity material. UV–visible absorption spectra of g-C_3N_4 showed absorption peaks between 250 and 450 nm, which demonstrated that g-C_3N_4 can be favorable for photocatalytic reaction (Fig. 2). The graphitic nature of carbon nitride material was confirmed by XRD in Fig. 3.

3.2. Catalytic study

2-Hydroxy-1,2-diphenylethanone **1a** was chosen as model substrates to optimize the reaction conditions such as amount of O_2 source, additive, time, and solvent (Table 1). As shown in Table 1, the products **2a** and **3a** could not be formed as treatment of **1a** in the absence of mpg-C_3N_4 using O_2 (1) in CH_3CN (Table 1, entry 1).

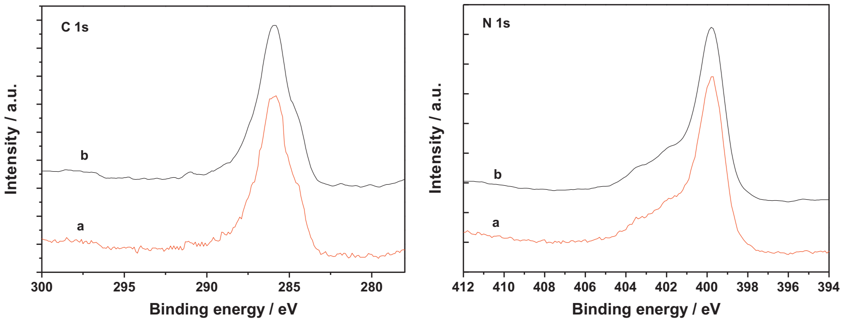
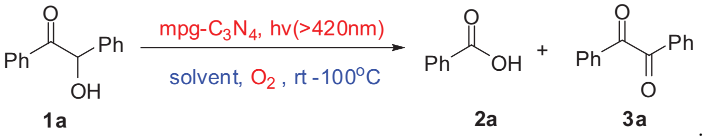


Fig. 4. XPS spectra of C 1s and N 1s in g-C_3N_4 before (a) and after (b) reaction.

Table 1
Optimization of reaction conditions.[a]



Entry	Solvent	Additive	Air/O_2 (atm)	*t* (h)	Yield[b] (%)	
					2a	**3a**
1[c]	CH_3CN	–	O_2 (1)	8	–	–
2	CH_3CN	–	O_2 (1)	8	14	45
3	DMF	–	O_2 (1)	8	13	41
4	1,4-Dioxane	–	O_2 (1)	8	8	22
5	Toluene	–	O_2 (1)	8	5<	36
6	Benzene	–	O_2 (1)	8	5<	30
7	CH_3CN/H_2O (10:1)	–	O_2 (1)	8	21	29
8	CH_3CN/H_2O (6:1)	–	O_2 (1)	8	28	25
9	CH_3CN/H_2O (3:1)	–	O_2 (1)	8	24	21
10	CH_3CN/H_2O (1:1)	–	O_2 (1)	8	13	17
11	CH_3CN/H_2O (6:1)	CH_3CO_2H	O_2 (1)	8	54	12
12	CH_3CN/H_2O (6:1)	L-proline	O_2 (1)	8	10	37
13	CH_3CN/H_2O (6:1)	NBu_4Br	O_2 (1)	8	24	33
14	CH_3CN/H_2O (6:1)	CH_3CO_2H	Air (1)	8	–	5<
15	CH_3CN/H_2O (6:1)	CH_3CO_2H	O_2 (2)	8	59	8
16	CH_3CN/H_2O (6:1)	CH_3CO_2H	O_2 (3)	8	62	7
17	CH_3CN/H_2O (6:1)	CH_3CO_2H	O_2 (3)	6	50	10
18	CH_3CN/H_2O (6:1)	CH_3CO_2H	O_2 (3)	12	67	5<
19	CH_3CN/H_2O (6:1)	CH_3CO_2H	O_2 (3)	16	72	–
20	CH_3CN/H_2O (6:1)	CH_3CO_2H	O_2 (3)	24	72	–
21[c]	CH_3CN/H_2O (6:1)	CH_3CO_2H	O_2 (3)	16	–	–
22	CH_3CN/H_2O (6:1)	CH_3CO_2H	N_2	16	–	–
23[d]	CH_3CN/H_2O (6:1)	CH_3CO_2H	O_2 (3)	16	–	–

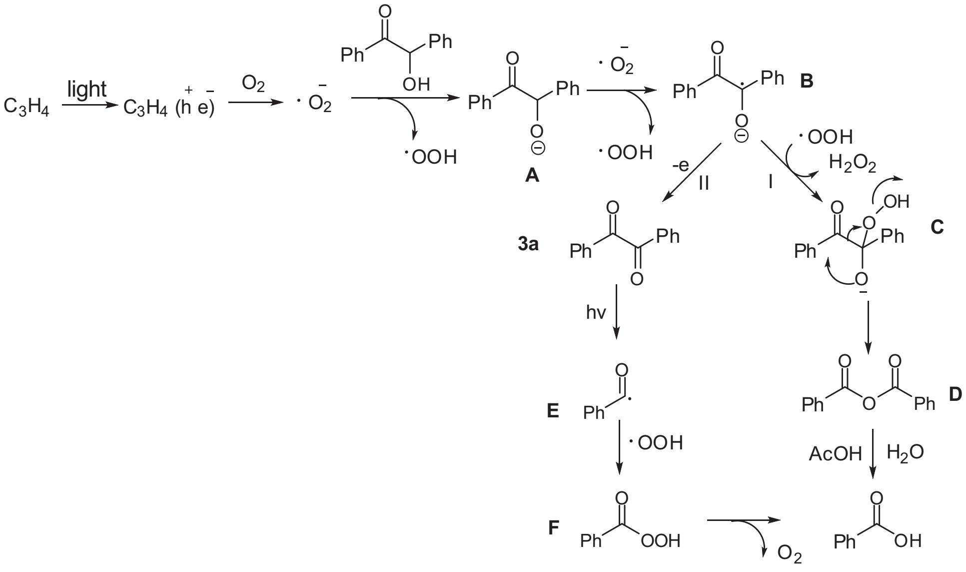
[a] In a typical reaction mpg-C_3N_4 (60 mg) was added to the desired solvent (10 mL) in a 100 mL stainless steel autoclave. The O_2 or air source was introduced and the closed autoclave was heated to 100 °C, followed by visible light irradiation for 6–24 h.

[b] GC-yield.

[c] In the absence of mpg-C_3N_4.

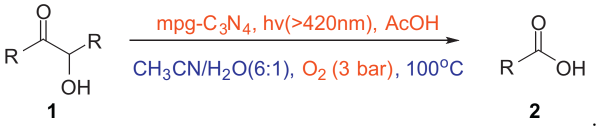
[d] Without visible light.

It was found that the desired products **2a** (14%) and **3a** (45%) were detected in the presence of mpg-C_3N_4 (Table 1, entry 2). A variety of solvents were examined, such as N,N-dimethylformamide (DMF), 1,4-dioxane, toluene, benzene and the mixture solvent CH_3CN/H_2O (entries 2–10). Interestingly, the yield of **2a** increased to 28% when the mixture solvent CH_3CN/H_2O was tested. We then attempted to improve the yield by adjusting the ratio of the mixture solvent. The results showed that the ratio of mixture solvent CH_3CN/H_2O reached 6:1 was the best solvent systems. Subsequently, our study focused on oxidation cleavages of **1a** by testing various additives, such as CH_3COOH, L-proline, NBu_4Br (entries 11–13). The use of CH_3COOH as an additive significantly improved the catalytic efficiency, yielding 54% of **2a**. And then we tried to improve the yields by using air substituted oxygen, increasing oxygen pressure and



Scheme 1. A possible reaction mechanism.

Table 2
Mpg-C_3N_4 catalyzed synthesis of 1,2-diketones with visible light.[a]



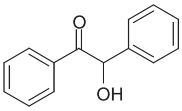
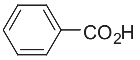
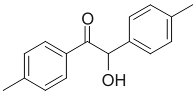
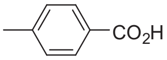
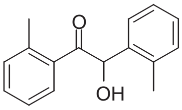
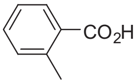
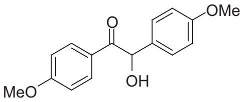
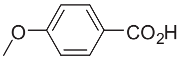
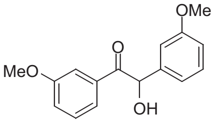
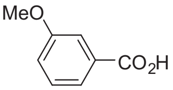
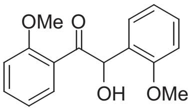
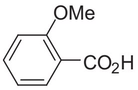
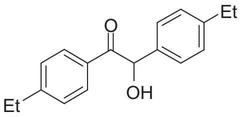
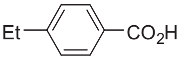
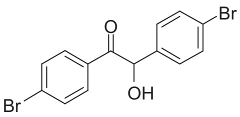
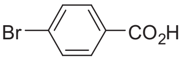
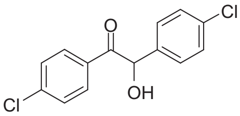
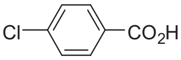
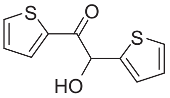
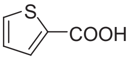
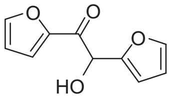
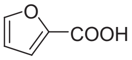
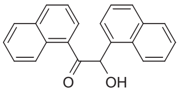
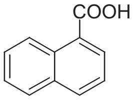
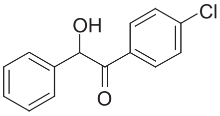
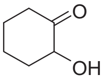
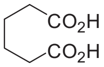
Entry	Benzoins	Product (Yield %)[b]
1	 **1a**	 **2a** 73
2	 **1b**	 **2b** 69
3	 **1c**	 **2c** 70
4	 **1d**	 **2d** 61
5	 **1e**	 **2e** 64
6	 **1f**	 **2f** 60
7	 **1g**	 **2g** 71
8	 **1h**	 **2h 74**
9	 **1i**	 **2i** 75
10	 **1j**	 **2j** 59

Table 2 (*Continued*)

Entry	Benzoins	Product (Yield %)[b]
11	 **1k**	 **2k** 55
12	 **1l**	 **2l** 49
13	 **1m**	**2i**, **2a** 70, 71
14	 **1n**	 **2n 53**

[a] Isolated yield.

[b] GC yield.

the time (entries 14–20). And the results clearly indicated that the yield of **2a** increased to 72% and **3a** would not be detected. Finally, control experiments revealed that no product could be formed in the absence of any condition in the following: mpg-C_3N_4 (entry 21), oxygen (entry 22) and visible light (entry 23).

With this optimized protocol in hand, we explored the scope of mpg-catalyzed oxidation cleavage with differently substituted α-hydroxy ketones derivatives and the results are summarized in Table 2. The reactions bearing electron-donating groups (entries 2 and 7) and electron-withdrawing substituents at the aromatic ring of α-hydroxy ketones (entries 8 and 9) proceeded to give the desired products in moderate to good yields. Notably, the corresponding products were also isolated in good yields, when the reactions were used 2-hydroxy-1,2-di(thiophen-2-yl)ethanone (**1j**), 1,2-di(furan-2-yl)-2-hydroxyethanone(**1k**), 2-hydroxy-1,2-di(naphthalen-1-yl)ethanone(**1l**) as substrates under optimal conditions. Further, the asymmetric substrate 1-(4-chlorophenyl)-2-hydroxy-2-phenylethanone (**1m**) was also tested and the desired products **2h** and **2i** were obtained in 70% and 71% respectively. All these results indicated that this photo catalysis process proved extensively applicable and tolerated various valuable functional groups on the aromatic ring such as CH_3, OCH_3, C_2H_5, Br, Cl.

We next turned our attention to catalyst recycling and reuse. After completion of the reaction, the catalyst was recovered by filtration and washed 2–3 times with ethanol. And then the catalyst was dried overnight in a vacuum oven at 100 °C and reused in the next reaction. It was found that the catalytic activity was still maintained even when the catalyst was reused for 3 times. The surface chemical composition and chemical states of g-C_3N_4 catalysts were analyzed by means of XPS (Fig. 4).

A plausible reaction mechanism is shown in Scheme 1. A similar mechanism has been mentioned in previous reports. The electron (e^-) was combined with the oxygen to generate the superoxide radical anion, which formed by the irradiation of mpg-C_3N_4, ($O_2^{\bullet-}$). Abstraction of the hydrogen atom of **1a** was occurred in the presence of $O_2^{\bullet-}$ to give intermediate **A.** And then the same deprotonation of **A** took place to form hydroperoxide ($OOH^{\bullet}$), while intermediate **B** could give product by two possible path. Path I: intermediate **B** underwent nucleophilic attack by hydroperoxide to gernate **C**. The intermediate **D** is formed through 1,2-insertion of the negative oxygen to the neighboring carbonyl group and simultaneous elimination of hydroxide. Finally, the product is obtained wih the help of H_2O and AcOH. Path II: intermediate product **3a** was observed, which was possibly produced by electron transfer of intermediate B. Consequently, intermediate **E** was formed from **3a** with visible light. This radical would be recombined with the superoxide radical and giving the perbenzoic acid **F** which would give the final product with the help of formal liberation of O_2.

4. Conclusion

In conclusion, we have reported on the first mpg-catalazed oxidation cleavages of carbon–carbon bond of α-hydroxy ketones with visible light. Mesoporous carbon nitride appears to play a vital role as a driving force in this transformation. This catalytic system proved boardly applicable and tolerated various valuable functional groups on the aromatic ring. In addition, this transformation represents a green and environmentally friendly process. Further applications of this approach are currently underway in our laboratories.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apcata.2013.08.008.

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