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ARTICLE

Heterogeneous Carbon Nitrides Photocatalysis C-C Bond Oxidative Cleavage of Vicinal Diols in Aerobic Micellar Medium

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A green and efficient visible-light promoted aerobic oxidative C-C bond cleavage of vicinal diols in micellar medium has been developed. This protocol used nitrogen vacancies introduced graphitic carbon nitrides (CN620) as a metal-free recyclable photocatalyst and CTAB as surfactant in water. Controlled experiments and ESR result indicated superoxide radicals and valence band holes played an important role in the reaction. Further isotope experiments suggested both β-scission/HAT pathway and oxidation/hydrolysis/dehydration pathway in the reaction which is different from previous reports. The semiconductor/micellar catalyst system is fully recyclable at least 10 times without significant reducing activity. Furthermore, this reaction could be carried out under solar light irradiation and applicable for large-scale reaction with conserved results.

Introduction

The oxidative cleavage of the C-C bond of vicinal diols is of significant interest to organic chemists due to its fundamental importance in chemical industry.[1] In the earlier days, Pb(OAc)$_4$, a highly toxic compound was employed as the catalyst (Scheme 1a).[2] At the same time, periodic acid and its salts also have been explored.[3] Although these two methods remain the most widely used for 1,2-diols cleavage, the intrinsic problem related to the use of stoichiometric amount oxidants, and most of these reagents suffer from the drawbacks in terms of toxicity, selectivity, storage, handling, cost and solubility which cannot meet the current environmental sustainable development needs. Therefore, a large effort has been dedicated to the development of catalytic oxidation processes with green oxidants and catalysts.

Molecular oxygen is a cheap and clean oxidant, currently, noble metal heterogeneous catalysts such as Pt-,[4] Ru-,[5] Au-,[6] and Ag[7] based complexes have been utilized in oxygen oxidative cleavage of 1,2-diols (Scheme 1b). From economic viewpoint, using inexpensive catalytic systems is more cost-effective. Thus, Mn-[8], V-[9], Mo-[10], Fe-[11], Cu-[12] and Co[13] based catalysts have been demonstrated as inexpensive catalytic systems. Although these methods can be used to synthesize the corresponding carbonyl compounds with high yields and excellent regioselectivity, most of them are still suffering from drawbacks such as harsh conditions, toxic organic solvent or no reusability of the catalyst. Designing green, efficient and reusable catalytic method for generation of fine chemicals is crucial to future advances in
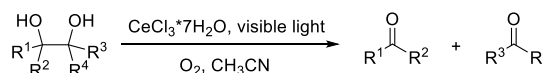

a) Classical method
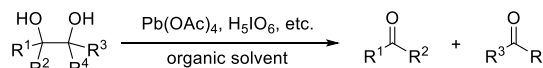
b) Metal catalysis
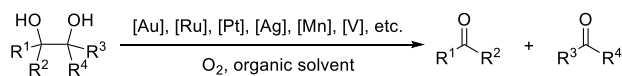
c) Homogeneous photocatalysis

d) This work
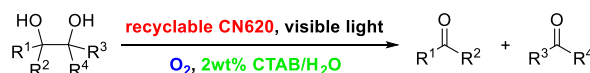
Scheme 1 Methods for oxidative cleavage of vicinal diols

synthetic organic chemistry. In the past years, visible-light promoted oxygen oxidation plays a unique role in this context and has received much attention due to its low cost, facile execution, and environmental friendliness.[14] So far, various homogeneous photoredox catalysts such as ruthenium- or iridium-based transition metal complexes[15] or organic dyes[16] have been developed. Recently, König and co-works reported a visible light promoted C–C bond cleavage of 1,2-diols to carbonyls by homogeneous cerium-photocatalysis[17] (Scheme 1c). Notwithstanding the novelty of this approach, challenges still remain. The homogeneous photocatalysts are usually difficult to recover from the reaction mixture and the using organic solvents are inconsistent with green chemistry development requirements. The search of a simple and metal-free heterogeneous photocatalytic reaction using

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environmentally solvent for oxygen oxidation cleavage of 1,2-diols in mild condition is still highly desirable.

In this context, polymeric carbon nitride (C_3N_4) has been considered as a cheap, metal-free, non-toxic and easily recyclable photocatalysts which exhibit remarkable activity in solar water splitting, degradation of pollutants and CO_2 reduction.[18] Moreover, because of its high thermal, chemical, and photo-stability, as well as favorable conduction and valence band positions, very recently, C_3N_4-base photocatalyst expand the reaction range to organic transformations such as oxidation reaction, C-H bond activation, and C-C bond forming reactions.[19] On the other hand, it is well known that water is a cheap, non-toxic, non-flammable and should be the most environmental-friendly solvent for organic synthesis.[20] However, few examples have been reported involving photocatalysis conducted solely in pure water due to the poor substrate solubilization.[21] Micellar catalysis is one of the solutions to disperse water-insoluble organic compounds in aqueous medium, which depends on the surfactants to form supramolecular aggregates.[22] In particular, surfactant contains amphiphiles could spontaneously self-aggregate to form nanomicelles in water, that could provide a unique interface effect and stabilize the reaction atmosphere, leading to excellent conversion and selectivity which may also provide a solution for photo reaction.[23] Herein, we developed a visible light promoted oxidative cleavage of the C-C bond of vicinal diols in micellar using nitrogen vacancies introduced C_3N_4 (CN620) as recyclable photocatalyst at room temperature (Scheme 1d).

Results and discussion

According to the recent reports, nitrogen vacancies could enhance photocatalytic activities of C_3N_4 due to the gradual enhancement of light harvesting and efficient charge separation and transportation.[24] Thus, our initial studies began with the reaction by using nitrogen vacancies introduced CN620 as photocatalyst when (R, R)-hydrobenzoin (**1a**) introduced as model substrate and water as solvent, under Xe lamp (250 W) irradiation at oxygen atmosphere (1 atm). However, only trace amount of desired product was observed (Table 1, entry 1), perhaps due to the poor solubility of the reagent. In order to obtain the optimum yield, a wide variety of surfactants was screened. To our delight, when 2wt% cationic surfactant cetyltrimethyl ammonium bromide (CTAB) was added, the highest yield was obtained (Table 1, entry 6). Other surfactants such as nonionic surfactant polyoxyethylene lauryl ether (Brij L4), polyethylene glycol monooleyl ether (Brij O20), polyoxyethylene (20) cetyl ether (Brij C20) and anionic surfactant sodium dodecyl sulfate (SDS) gave inferior results (Table 1, entries 2-5). Tuning the catalyst and surfactant amount did not improve the performance (Table 1, entries 7-9), and only a low yield was obtained. Besides, when the reaction was carried out at open air, a decrease of yield was observed (Table 1, entry 10). In addition, other C_3N_4 based photocatalysts such as porous graphite phase carbon nitride (p-g-C_3N_4) and metal-doped @g-C_3N_4 such as Fe@g-C_3N_4 and Cu@g-C_3N_4 were

Table 1 Optimization of reaction conditions[a]
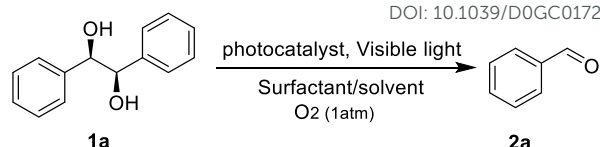
Entry	Catalyst	solvent	Conv. /%	Sel./%[b]
1	CN620 (20 mg)	H_2O	8	75
2	CN620 (20 mg)	2wt% Brij L4/H_2O	84	90
3	CN620 (20mg)	2wt% Brij O20/H_2O	62	13
4	CN620 (20mg)	2wt% Brij C20/H_2O	74	66
5	CN620 (20mg)	2wt% SDS/H_2O	66	47
6	**CN620 (20mg)**	**2wt% CTAB/H_2O**	**94**	**90**
7	CN620 (20mg)	1wt% CTAB/H_2O	92	77
8	CN620 (20mg)	4wt% CTAB/H_2O	86	90
9	CN620 (30mg)	2wt% CTAB/H_2O	95	79
10[c]	CN620 (20mg)	2wt% CTAB/H_2O	84	85
11	p−g-C_3N_4 (20 mg)	2wt% CTAB/H_2O	84	61
12	Fe$_2$O$_3$@g-C_3N_4 (20 mg)	2wt% CTAB/H_2O	73	54
13	CuO@g-C_3N_4 (20 mg)	2wt% CTAB/H_2O	80	63
14	Acr$^+$–Mes (2 mol%)	2wt% CTAB/H_2O	trace	−
15	Eosin Y (2 mol%)	2wt% CTAB/H_2O	trace	−
16	Ru(bpy)$_3$Cl$_2$ (2 mol%)	2wt% CTAB/H_2O	trace	−
17	Rhodamine B (2 mol%)	2wt% CTAB/H_2O	trace	−
18	NO	2wt% CTAB/H_2O	NR	NR
19[d]	CN620 (20mg)	2wt% CTAB/H_2O	NR	NR

[a] Reaction conditions: substrate **1a** (1 mmol), CN620 under Xe lamp (250 W) irradiation or homogeneous PC under blue LED (5W), at room temperature, solvent (3 mL), O_2 atmosphere, reaction for 5 hours. [b] Conversion and selectivity determined by HPLC. [c] reaction carried out at open air. [d] reaction without light.

screened, however lower catalytic activities results were obtained (Table 1, entries 11-13). For comparison, homogeneous photocatalysts such as 9-Mesityl-10-methylacridinium perchlorate (Acr$^+$–Mes), Eosin Y, Ru(bpy)$_3$Cl$_2$ and Rhodamine B were also tested under the same experimental conditions and only trace amount of the desired product was observed. (Table 1, entries14–17). Finally, no desired product was observed when the reaction was carried out in absence of photocatalyst or visible light (Table 1, entry 18, 19). It is notice that, compared with the organic solvent, the micellar medium gave higher conversion and selectivity which fully reflected the advantages of micelle reaction system (Supporting information, Table S1). Thus, the best yield was obtained when nitrogen vacancies introduced CN620 was used as photocatalyst and 2wt% CTAB/H2O as solvent under 250 W Xe lamp irradiation at oxygen atmosphere (Table 1, entries 6).

To investigate the nature of surfactant and CN60 in water, the reaction mixture has been analyzed by TEM (Supporting information, Figure S6). As we have seen, the nature of the micelles formed by CTAB was found to be spherical in shape. TEM also revealed that the micelle size distribution of CTAB aqueous solution is within 50 nm and CN620 is much larger than the micelle size. Therefore, the micelle is probably on the surface of the catalyst rather than the catalyst in the micelle.

Table 2 Aerobic oxidative cleavage of internal 1,2-diols[a]

Substrate	Product/%	Substrate	Product/%
1a	2a (75%)	1l	2l (67%)
1b	2b (70%)	1m	2m (63%)
1c	2c (67%)	1n	2n (35%)
1d	2d (74%)	1o	2o (86%)
1e	2e (73%)	1p	2p (83%)
1f	2f (74%)	1q	2q (83%)
1g	2g (65%)	1r	2r (86%)
1h	2h (85%)	1s	2a (72%)
1i	2i (87%)	1t	2e (70%) / 2a (63%)
1j	2j (89%)	1u	NR
1k	2k (63%)		

[a] Reaction conditions: substrate **1** (1 mmol), CN620 (20 mg) under Xe lamp (250 W) irradiation at room temperature, 2wt% CTAB/H_2O (3 mL), O_2 atmosphere, reaction for 5 hours. [b] isolated yield.

Table 3 Aerobic oxidative cleavage of monosubstituted 1,2-diols[a]

Substrate	Product/%	Substrate	Product/%
3a	2a (71%)	3n	4c (80%)
3b	2b (68%)	3o	4d (73%)
3c	2e (85%)	3p	2q (61%)
3d	2f (83%)	3q	4e (64%)
3e	2g (77%)	3r	4f (62%)
3f	2h (83%)	3s	4g (51%)
3g	2i (85%)	3t	4h (70%)
3h	2j (83%)	3u	4i (67%)
3i	2l (83%)	3v	4j (47%)
3j	4a (79%)	3w	4k (62%)
3k	4b (73%)	3x	4l (70%)
3l	2m (78%)	3y	4m (72%)
3m	2n (51%)	3z	4n (56%)

[a] Reaction conditions: substrate **3** (1 mmol), CN620 (20 mg) and Na_2CO_3 (2 equv.) under Xe lamp (250 W) irradiation at room temperature, 2wt% Brij L4/H_2O (3 mL), O_2 atmosphere, reaction for 5 hours. [b] isolated yield.

With the optimal reaction conditions in hand, a variety of internal aromatic 1,2-diols were subjected to the photo-catalyzed aerobic cleavage. As can be seen from Table 2, all the corresponding aldehydes were obtained in good to excellent yields at very mild condition. The catalyst tolerated the presence of both electron-withdrawing (**1b**–**1k**) and electron-donating (**1l**, **1m**, **1n**) substituents with satisfactory yields except **1n**, which gave the corresponding product in only 35% yield, while 47% yield of by-product 1,2-bis(4-methoxyphenyl)-

ethane-1,2-dione was obtained. The position of the substitutes on the benzene ring has no obvious effect on the oxidative
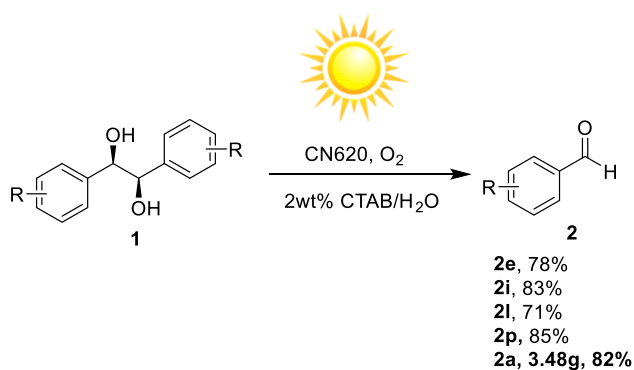
Reaction conditions: **1** (1 mmol), CN620 (20 mg), 2wt% CTAB/H_2O (3 mL), O_2 atmosphere, ambient temperature (24°C), under sunlight irradiation, reaction for 5 hours (from 10 a.m. to 3 p.m). For large-scale performance **1a** (20 mmol), CN620 (300 mg), 2wt% CTAB/H_2O (40 mL), O_2 atmosphere, ambient temperature (24°C), under sunlight irradiation, reaction for 7 hours (from 9 a.m. to 4 p.m). Isolated yield.

Scheme 2 Visible-light-promoted oxidative cleavage reaction of vicinal diols by sunlight and scale-up reaction

^{a} standard condition for **1a**：**1a** (1 mmol), CN620 (20 mg) under Xe lamp (250 W) irradiation at room temperature, 2wt% CTAB/H_2O (3 mL), O_2 atmosphere, reaction for 5 hours. standard condition for **3a**：**3a** (1 mmol), CN620 (20 mg) and Na_2CO_3 (2 equv.) under Xe lamp (250 W) irradiation at room temperature, 2wt% Brij L4/H_2O (3 mL), O_2 atmosphere, reaction for 5 hours.

Scheme 3 Controlled experiments

cleavage of C–C bond under the optimized conditions, substituents in the para-, ortho- and meta-positions gave similar yields (**1b**-**1g**). Moreover, hetero derivatives **1o** and **1p** also performed well in this condition, the desired products 2-Pyridinecarboxaldehyde **2o** and 2-Furaldehyde **2p** were obtained in high yields. Besides, the tertiary hydroxy groups **1q**

and **1r** also participated well in this reaction and gave the desired ketones in 83% and 86% isolated yields respectively. The results indicated that the steric hindrance of the substrates have no effect on the reaction. Furthermore, unsymmetrical 1,2-diaryl diols such as **1s** and **1t** were also suitable for this reaction and gave corresponding aryl aldehydes in moderate yields. The aliphatic 1,2-diols such as **1u**, however, were inert toward this transformation.

To further expand the substrate scope of this catalytic system, terminal 1,2-diols were also examined. Although, the best results were generally achieved for internal 1,2-diols without other additives, terminal 1,2-diols required base to afford the corresponding aldehydes and ketones in satisfactory yields, and more optimization details are provided in the Supporting Information Table S2. As shown in table 3, aromatic 1,2-diols containing functional groups such as F, Cl, Br, methy, CN, NO_2 and MeO were well tolerated under the standard conditions. Both electronic effect and steric hindrance of the substituents had a slightly influence on the reaction, all the desired products were obtained in satisfactory yields. Besides, α-substituted terminal 1,2-diols (**3p**-**3z**) also could participate to this reaction, but the corresponding ketones was afforded in moderated yields, probably due to steric hindrance.

Furthermore, this visible-light-promoted C-C bond oxidative cleavage reaction of vicinal diols could be driven by sunlight (Supporting information, Figure S7) with conserved results compared with the model reaction condition irradiation by Xe light. The use of solar energy makes it suitable for large-scale performance. The reaction of **1a** (20 mmol scale) in proceeded smoothly under the optimized conditions to provide the product **2a** in 82% yield (3.48 g) using 300mg of CN620 within 7 h irradiation under sunlight (Scheme 2).

To further explore the mechanism of the reaction, a group of controlled experiments has been conducted. First, for internal 1,2-diol **1a** when replacing H_2O by D_2O under the standard conditions, about 52% of yield of D-labeled product was detected [scheme 3a, Eq. (1)]. While replacing H_2O by H_2O^{18} under the standard conditions, about 28% of yield of O^{18}labeled product was detected [scheme 3b, Eq. (1)]. To our spurious, when O_2^{18} was used instead of O_2, trace amount of O^{18}labeled product was detected [scheme 3c, Eq. (1)]. On the contrary, similar result as scheme [scheme 3b, Eq. (1)] was obtained when O_2^{18} was used in anhydrous MeCN [scheme 3d, Eq. (1)]. These results implied the oxygen may react with vicinal diols to generate H_2O in this process and both hydrogen atom and oxygen atom in the product originate from internal vicinal diols or H_2O. Then terminal 1,2-diol **3a** was used for the isotope experiments. The results showed that when D_2O instead of H_2O under the standard conditions, however, no D-labeled product was detected [scheme 3a, Eq. (2)]. While only 9.6% of yield of O^{18}labeled product was detected when replacing H_2O by H_2O^{18} [scheme 3b, Eq. (2)]. Similarly, when O_2^{18} was used instead of O_2, trace amount of O^{18}labeled product was observed [scheme 3c, Eq. (2)]. And only 6.3% yield of O^{18}labeled product was detected when O_2^{18} was used in anhydrous MeCN [scheme 3d, Eq. (2)]. These results indicated all of the hydrogen atom and more than 90% of the oxygen atom in the product originate

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Table 4. Active species trapping reactions for the photocatalyzed oxidative cleavage reaction system[a]

Entry	Quencher	Quenching group	Conv. (%)	Sel. (%)
1	_	_	94	90
2	Hydroquinone	Free radicals	50	52
3	*p*-Benzoquinone	$\cdot O_2^-$	100	32
4	CCl_4	e^-	90	20
5	$HCOONH_4$	Hole	39	82
6	Tertiary butanol	$\cdot OH$	93	83

[a] Reaction conditions: substrate **1** (1 mmol), CN620 (20 mg) under Xe lamp (250 W) irradiation at room temperature, 2wt% CTAB/H_2O (3 mL), O_2 atmosphere, reaction for 5 hours.

from terminal 1,2-diols which is different from the result of internal vicinal diols, suggesting two reaction pathways may existed. Moreover, both of **1a** and **3a** could carry out without O_2, although only 40% and 46% yields of the desired product were obtained respectively (scheme 3e). It was also worth noting that the anaerobic reaction solution was weakly acidic for **1a** (pH = 5-6), while the standard reaction solutions for internal vicinal diols were neutral. In addition, the solution of tertiary hydroxy substrates **1r** and **1s** after reaction also showed slightly acidic. Besides, no product was observed, when the reaction carried out without O_2 in anhydrous MeCN (scheme 3f). Finally, no H_2O_2 was detected by potassium iodide-starch test paper in these reactions.

Then the subsequent active species trapping experiments were carried out to gain more insight into the mechanism. As shown in table 4, both conversion and selectivity were obviously inhibited by adding free radical scavengers such as hydroquinone (table 4, entry 2), which indicated that the reaction involved a free radical process. When the superoxide radical quencher *p*-benzoquinone was added (table 4, entry 3), low selectivity of the product was observed, while the conversion basically unchanged. Further ESR result confirmed the superoxide radical. In addition, the selectivity also decreased gradually when electrons were quenched by the tetrachloromethane (table 4, entry 4). These results suggested that the generated superoxide radicals were the major oxidative species. Besides the superoxide radicals and electrons, valence band holes also had an important effect on the oxidative cleavage reaction. Quenching of valence band holes dramatically decrease the conversion (table 4, entry 5). While the quenching of hydroxyl radical had almost no influence on the reaction (table 4, entry 6). These results revealing that the substrates were active by valence band holes.

Based on the previous reports and experimental results, a plausible mechanism was proposed (Figure 1). Initially, electrons and holes are produced by excitation of the CN620 under visible light irradiation. Consequently, hole oxidizes the hydroxyl of 1,2-diols to produce radical intermediate Ⅰ and H^+. At the same time, electron reduces molecular oxygen to produce superoxide radical. Then, there are two possible reaction pathways for this reaction. In pathway A, intermediate Ⅰ undergo β-scission to corresponding aldehyde or ketone and an α-hydroxy radical. Then hydrogen atom transfer (HAT) from this α-hydroxy radical to the solvent or another alkoxy radical
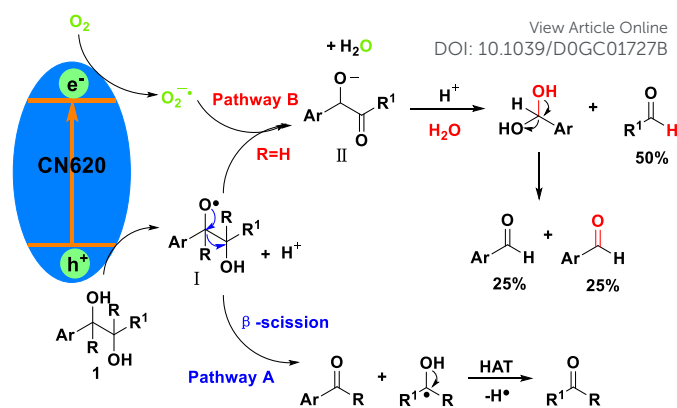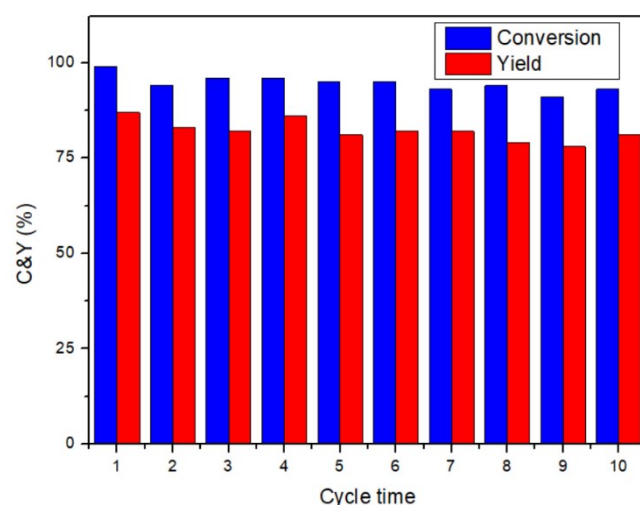
Figure 1 Plausible reaction mechanism

Figure 2 Recyclability of CN620 for the oxidative cleavage reaction of vicinal diols **1a**

would give the second aldehyde or ketone.[17] In pathway B, intermediate Ⅰ react with superoxide radical to generate intermediate Ⅱ and water. Subsequent hydrolysis of intermediate Ⅱ generates geminal diol and desired aldehyde which both oxygen and hydrogen atoms comes from 1,2-diols. Finally, dehydration of gemal glycol furnishes the other half of product which quarter of the aldehyde's oxygen and hydrogen atoms are from 1,2-diols, while the other quarter of the product's oxygen atom comes from water, and the hydrogen atom comes from water 1,2-diols. The controlled experimental results indicated that tertiary hydroxy substrates **1r** and **1s** and about 80% of terminal 1,2-diols may be classified as a type A mechanism, while the internal 1,2-diols and about 20% of terminal 1,2-diols may be classified as a type B mechanism. It is worth noting that, the mechanism of pathway B is different from previous reports.[8b, 9C, 17] In previous work, the oxygen atom of product aldehydes comes from 1,2-diols or oxidant, however, in pathway B of this reaction, the oxygen atom of product comes from 1,2-diols or water, while the oxygen only reacts with vicinal diols to generate H_2O_2 in reaction process.

Finally, the micellar catalyst system has been reused for the oxidative cleavage reaction of vicinal diols **1a** successfully. Once the reaction was finished under standard condition, the final product was obtained by extracting with ethyl acetate. The

separated aqueous medium containing CN620 could be recycled directly for 10 runs with the products in HPLC yields from 74 to 85% (Figure 2).

Conclusions

In summary, an environmentally-friendly and effective metal-free aqueous photocatalytic C-C bond oxidative cleavage of vicinal diols has been developed using CN620 as a recyclable photocatalyst and CTAB as the surfactant. A series of vicinal diols could be efficiently cleaved and converted into the corresponding aldehydes or ketones. TEM revealed that the micelle is probably on the surface of the catalyst. Preliminary mechanism revealed that both the superoxide radicals and valence band holes played an important role in the reaction process. Further isotope experiment confirmed β-scission/HAT process and oxidation/hydrolysis/dehydration process in the reaction which is different from previous reports. Notably, the CN620/micellar catalyst system could be recycled and reused 10 times with satisfactory yield. Moreover, this reaction could be carried out under solar light irradiation and is applicable for large-scale reactions. These features make this reaction a potential green and sustainable approach for both academic and industrial applications.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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Heterogeneous Carbon Nitrides Photocatalysis C-C Bond Oxidative Cleavage of Vicinal Diols in Aerobic Micellar Medium
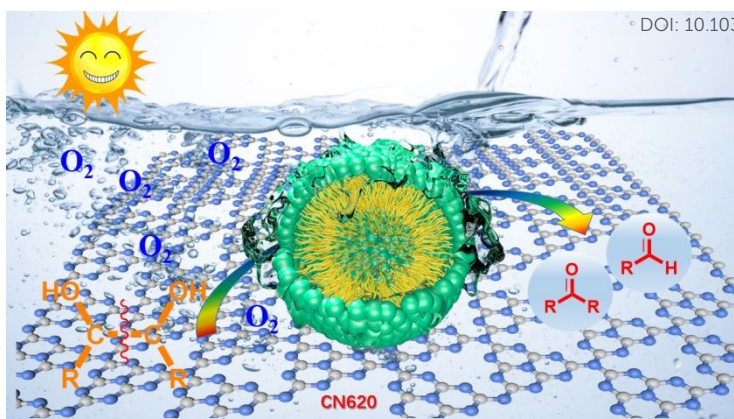
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A visible-light promoted oxidative cleavage of vicinal Diols by using CN620 as recyclable photocatalyst in in aerobic micellar medium has been developed.

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