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# Metal-free Photocatalytic Aerobic Oxidative Cleavage of C-C Bonds in 1,2-Diols

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Abstract: The preparation of carbonyl compounds by the aerobic oxidative cleavage of C-C bonds in 1,2-diols under mild reaction conditions is a very significant reaction and it is widely employed in various scenarios. Avoiding the use of harmful stoichiometric oxidants and adopting a greener chemical process are still the challenge for this reaction to date. In this manuscript, a heterogeneous metal-free photocatalytic strategy without any additive was developed for aerobic oxidative cleavage of C-C bonds in 1,2-diols at ambient conditions with visible light. The reaction mechanism was further studied through a series of control experiments and DFT (Density Functional Theory) calculations. In addition, the catalytic system has a broad substrates scope, including aliphatic (linear or cyclic) 1,2-diols, benzylic, alkenyl 1,2diols and  $\alpha$ -hydroxy acids (such as lactic acid). Thus, this strategy could serve as a method for the transformation of 1,2-diols to corresponding carbonyl compounds by the aerobic oxidative cleavage of C-C bonds.

### Introduction

The aerobic oxidative cleavage of C-C bonds in 1,2-diols to prepare corresponding carbonyl compounds (carboxylic acid, aldehyde, ketone) is a very significant fundamental reaction in synthetic organic chemistry. This reaction is widely employed in various scenarios, such as organic synthesis<sup>[1]</sup>, biomass valorization<sup>[2-4]</sup>, analytical studies in biochemistry<sup>[5]</sup> and so on. In the early 20th century, the Malaprade reaction<sup>[6]</sup> and the Criegee oxidation<sup>[7]</sup> were the classical methods to transform 1,2-diols to aldehydes or ketones. Traditional methods for effective cleavage of C-C bonds in 1,2-diols require the consumption of stoichiometric or excess amount of oxidants, such as high-valent iodine<sup>[8-</sup> <sup>10]</sup> and lead<sup>[11]</sup>. These toxic reagents not only damage human health, reduce atom economy, but also generate equimolar quantities of hazardous waste, which is harmful to the environment. Hence, a catalytic system with high atom economy and green reaction process is urgent to be developed. In this context, many improved catalytic systems have been proposed using the widely accepted clean oxidant molecular oxygen[12-17]. Some of these protocols were able to selectively cleave the C-C bond in specific 1,2-diols, but most of them required the use of toxic metal reagents or harsh reaction conditions. Driven by the need for low-cost conversion and high atomic economy, a heterogeneous catalyst, sodium-manganese layered mixed oxide (Scheme 1b), was developed by Anastas and coworkers in 2017<sup>[18]</sup>, and a homogeneous vanadium catalyst was developed by Licini and co-workers in 2018<sup>[19]</sup>. These two catalytic systems are capable of efficiently cleaving C-C bonds in 1,2-diols under 80-100 °C using ambient pressure of O2. However, these two noble metal-free catalytic systems were still limited to reaction temperatures and posttreatments for product collection. Another recent work was reported by Gao and co-workers<sup>[20]</sup>, in which cobaltbased heterogeneous catalyst exhibited excellent performance on the oxidative cleavage of some 1,2-diols into corresponding aldehydes or carboxylates (Scheme 1b). It should be noted that the work of  $Anastas^{\left[18\right]}$  and  $Gao^{\left[20\right]}$ was not applicable to a wide scope of substrates, which limited to benzyl diols. In addition, Li and co-workers<sup>[21]</sup> reported that the silver (I)-based catalyst could efficiently cleave C-C bonds in 1,2-diols under mild conditions (Scheme 1c). However, the critical drawbacks persisted as the usage of excess amount of base and a complicated post-processing. Although many catalytic strategies<sup>[22-26]</sup> have also been developed to achieve this catalytic reaction, there are still many limitations. Hence, a catalytic strategy of high atomic economy with broad applicability, mild reaction conditions and simple process needs further development.

Previous work:

This work:



limited substrates

`R⁴

c) 
$$R^{1}$$
  $R^{2}$   $R^{3}$   $R^{3}$   $R^{2}$   $R^{3}$   $R^{2}$   $R^{3}$   $R^{2}$   $R^{3}$   $R^{2}$   $R^{3}$   $R^{2}$   $R^{3}$   $R^{2}$   $R^{3}$ 

excessive base; complex after-treatment

d) 
$$\begin{array}{c} HO \\ R^1 \\ R^2 \\ R^2 \end{array} \xrightarrow{R^4} R^3 \end{array} \xrightarrow{mpg-C_3N_4} P^1 \\ O_2 \text{ balloon, r.t.} \\ visiable light \end{array} \xrightarrow{O} P^1 \\ R^2 \\ R^3 \\ R^4 \end{array}$$

no base: no metal: mild reaction conditions

Scheme 1. Methods for the oxidative cleavage of 1,2-diols to corresponding carbonyl compounds.

In recent years, semiconductor materials have been extensively studied<sup>[27]</sup>. These photosensitive materials were attempted to conduct photocatalytic reactions in various organic synthesis driven by the need of clean and synthesis renewable organic strategy. In these semiconductor materials, graphitic carbon nitride has attracted much more attention in the field of hydrogen evolution reaction<sup>[28]</sup>, biomass valorization<sup>[29]</sup> and organic synthesis<sup>[30-31]</sup>. Properties of large surface area, low cost, easy functionalization, visible light adsorption, plenty of nitrogen atoms or vacancies and high photocatalytic activity make C<sub>3</sub>N<sub>4</sub> one of the most promising catalysts for visible light photoredox catalysis, and the flexible organo twodimension character of C3N4[42] may provide an ideal surface for many substrates<sup>[29]</sup>. In this work, a base-free and metal-free strategy (Scheme 1d) was proposed for the aerobic oxidative cleavage of C-C bonds in 1,2-diols to corresponding carbonyl compounds catalyzed by mesoporous carbon nitride (mpg-C<sub>3</sub>N<sub>4</sub>) under mild conditions (visible light, room temperature, O<sub>2</sub> balloon). Reaction conditions were optimized and the reaction mechanism was further investigated through a series of control experiments and DFT (Density Functional Theory) calculations, exhibiting the interaction between the catalyst and the substrate. The catalytic system also has a broad substrate scope, including aliphatic 1,2-diols, benzylic 1,2diols, alkenyl 1,2-diols and  $\alpha$ -hydroxy acids, such as lactic acid

### **Results and Discussion**

Initially, a series of semiconductor materials were adopted for photocatalytic oxidative cleavage of a model substrate 1,2-diphenylethane-1,2-diol (1a) at room temperature with a 390 nm light source. As shown in Figure 1a, using CH<sub>3</sub>CN as the solvent and O<sub>2</sub> as the oxidant, mpg-C<sub>3</sub>N<sub>4</sub> showed the best activity on the conversion of **1a** (95%) and yield of 2a (28%) and 3a (34%). Under identical conditions, 1a conversion decreased to about 40-60% over WO<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> catalysts. In addition, SnO<sub>2</sub>, CdS, and Mo<sub>2</sub>S showed about 10% conversion of 1a. When Al<sub>2</sub>O<sub>3</sub> or TiO<sub>2</sub> were used as the catalyst, 1a could hardly react and the conversion was lower than 5%. It is speculated that the photocatalytic activity of a catalyst is closely related to its absorbance of light, as electrons will be emitted under the interaction with photons. Therefore, UV-visible (UV-Vis) absorption spectra were obtained for all the tested semiconductor materials, as shown in Figure S2d. As anticipated, Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> had poor absorbance at wavelength of 390 nm. Therefore, it is reasonable that these two catalysts showed rare activity in the photocatalytic oxidative cleavage. WO3, CdS, Fe2O3 and mpg-C<sub>3</sub>N<sub>4</sub> had excellent absorbance at 390 nm light source. While compared with mpg-C<sub>3</sub>N<sub>4</sub>, their activity on 1a conversion was significantly lower. The UV-Vis results indicated that for a photocatalyst, a good absorbance for specific light source was necessary for a high photocatalytic activity. However, the catalytic performance of a strong absorbent material might be poor, which suggested the nature of the catalyst, like activity sites, was another determining factor on its photocatalytic activity.



Figure 1. Catalytic oxidative cleavage of 1a to 2a and 3a with different catalysts. Reaction conditions: 0.2 mmol 1a, 10 mg catalyst, 1 mL MeCN, 390 nm LED,  $O_2$  balloon, room temperature, 12 h. The conversion and yield of this reaction were detected by gas chromatography (GC).

A series of solvents were adopted to investigate the solvent effect on the photocatalytic oxidative cleavage of 1a. As shown in Figure 2, DCM  $(CH_2CI_2)$  was the optimal solvent obtaining 99% conversion of 1a and 81% yield of 3a. Although a conversion of higher than 90% was obtained when using CH<sub>3</sub>CN and dimethyl sulfoxide (DMSO), the yield of 3a was lower, and a considerable amount of byproduct 2a was detected. As DMSO itself could be oxidized in some photocatalytic reaction system<sup>[32]</sup>, it was not suitable to be employed as the solvent in this reaction system. In the alcohol solvents (such as MeOH), a few of carboxylates were detected, leading to a low yield of target product 3a. In addition, the alcohol solvent, MeOH, could be activated to alkoxy radicals in some photocatalytic systems<sup>[33]</sup>. The alcohol solvents have the potential to compete with 1,2-diols under light conditions. Therefore, alcohols are also not suitable as the solvents in this reaction system. In addition, we speculated that the interaction between the substrate, catalyst, and solvent is also one of the factors that affect the experimental results. In the following, through theoretical calculations, we find that the active sites on the surface of the catalyst can transfer electrons or holes through the interaction with the hydroxyl group of the substrate, thereby catalyzing the reaction. When the solvent used contains groups that are likely to interact with hydroxyl groups, the interaction between the substrate and the active site of the catalyst may be affected, thereby reducing the catalytic activity of the catalyst. In addition, when the solvent used is likely to interact with the active site of the catalyst, the same effect would be produced. As we all know, the hydroxyl group of the substrate easily forms hydrogen bonds with atoms (such as O, N, S) with large electronegativity, thereby affecting the interaction between the substrate and the

90 100 /// Ph-COOH 80 90 Ph-CHO 70 80 7060 Conversion [%] Yield [%] 60 50 50 40 40 30 30 20 20 10 10 0 0 MeCN MeOH DCM GVL 120 DMFDMSO THE EA Solvent

Figure 2. The aerobic oxidative cleavage of 1a to 2a and 3a with different solvents. DCM=  $CH_2Cl_2$ , MT= methanol, EA= ethyl acetate, THF= tetrahydrofuran, DMF= N,N-dimethylformamide, DMSO= dimethyl sulfoxide, GVL=  $\gamma$ -Valerolactone.

catalyst. Therefore, when we used MeOH, ethyl acetate (EA), DMSO, N,N-dimethylformamide (DMF),  $H_2O$ , etc. as the reaction solvent, we did not get the ideal experimental results. In addition, when different solvents were used, the product distribution of benzaldehyde (2a) and benzoic acid (3a) was different. From the following kinetic studies, we knew that substrate 1a was first converted to benzaldehyde (2a), and then benzaldehyde (2a) was oxidized to benzoic acid (3a). Both of these reactions were radical processes, and both required the participation of catalysts. Therefore, the above solvation effects seem to be applicable to both processes.

In addition, the effect of light source irradiation wavelength on the photocatalytic activity was explored (Figure 3). A variety of light radiation sources were screened including 370 to 467 nm LEDs and sunlight, with black condition as comparison. As shown in Figure 3, with LED wavelengths ranging from 390 to 440 nm, a high conversion of 1a with a good selectivity towards 3a was achieved. As the wavelength increased to 456 and 467 nm, the conversion and yield decreased continuously. These results were aligned with the UV-Vis results, which suggested that  $mpg-C_3N_4$  had high absorbance for wavelengths between 259 nm and 442 nm (Figure S2c). It should be noted that under 370 nm light source, the conversion and yield were much lower than those from 390-440 nm, which was not consistent with the UV-Vis results. This might be because that the glass tube used for this reaction had inhibiting effect on 370 nm light source, leading to a low transmittance of radiation source. Under black condition, the conversion and yield were determined as lower than 5%, indicating that this catalytic process was indeed triggered by photons. In addition, when sunlight was used as the radiation source, 22% 2a and 7% 3a were obtained with a conversion of 63%. At the same time, we also tested the quantum efficiency of the catalyst under different light sources. The results also showed that the



Figure 3. The aerobic oxidative cleavage of 1a to 2a and 3a with different light sources.



Figure 4. The aerobic oxidative cleavage of **1a** to **2a** and **3a** with different reaction time. Reaction conditions: 0.2 mmol **1a**, 10 mg catalyst, 1 mL DCM, 390 nm LED,  $O_2$  balloon, room temperature. The conversion and yield of this reaction were detected by gas chromatography (GC).

catalyst has the best quantum efficiency under a light source with a wavelength of 390 nm (Table S1).

The effect of reaction time on the generation of **3a** from substrate **1a** was also investigated for further understanding the reaction mechanism, as shown in Figure 4. With the progress of reaction, conversion of **1a** increased monotonously in the first 6 hours, accompanied by an increasing amount of **2a** generated. At the full conversion of **1a**, **2a** was gradually converted into **3a** under catalytic conditions. Therefore, the yield of **2a** decreased while the yield of **3a** increased. For the total yield of **2a** and **3a**, a distinct drop was detected between the sixth hour and seventh hour. This might be due to the conversion of **2a** into an undetected intermediate. In order to analyze the possible intermediates, we performed ESI-MS (Figure S2f) detection on the in-situ reaction solution. We could see from

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[a] Reaction conditions: 0.2 mmol substrate, 10 mg mpg-C<sub>3</sub>N<sub>4</sub>, DCM 1 mL, 390 nm LED, O<sub>2</sub> balloon, room temperature, 12 h. [b] The yield was isolated yields. [c] The yield was determined by <sup>1</sup>H NMR spectroscopy with the biphenyl as the internal standard in D<sub>6</sub>-DMSO. [d] The yield was determined by GC.

the figure that there were obviously characteristic peaks of benzaldehyde (m/z = 105) and benzoic acid (m/z = 121). At the same time, we also detected characteristic peaks of other substances (such as m/z = 227, 301 etc.). From this ESI-MS, we speculated that the acetal (m/z = 301) formed by the reaction of produced aldehyde and substrate diol could be the intermediate. And the ester compound (m/z = 227) formed by the produced radical II (Scheme 3) and activated benzoic acid during the reaction may also be an intermediate of the reaction. Overall, the kinetics study indicated that 3a was converted from 2a under this catalytic condition, and 2a was an intermediate for the entire reaction. In addition, the recyclability test of this catalyst was performed under five consecutive runs utilizing identical conditions (Figure S2h). The slightly reduced product yield was mainly caused by the loss of catalyst during the catalyst transfer process. Nevertheless, the high product yields observed herein indicated that the catalysts could be recycled and reused several times.

With the optimal reaction conditions on hand ( $O_2$  balloon, room temperature, mpg- $C_3N_4$  as the photocatalyst, 390 nm light, DCM as the solvent), the substrate scope of this photocatalytic system for a variety of 1,2-diols was examined, with results tabulated in Table 1. The mpg- $C_3N_4$  photocatalytic system was effective for a wide range of substitute and non-substitute 1,2-diols. Generally, 1,2-diols with electron withdrawing groups could be converted into corresponding acids in higher yields compared with those bearing electron donating groups (**1b–1f**). The electron-donating aromatic 1,2-diols (**1b–1c**) gave the target

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Figure 5. Optimized interaction patterns (top view and side view) and adsorption energies of substrate 1a and 1y adsorbed on catalyst surface (Pattern A: a and d for H atom on hydroxyl group of substrate 1a; Pattern B: b and e for O atom on hydroxyl group of substrate 1a; Pattern C: c and f for O atom on carbonyl group of substrate 1y).

products (3b-3c) in good yields, giving 4-methylbenzoic acid (3b) in 78% yield and 4-methoxybenzoic acid (3c) in 70% yield respectively. The electron-withdrawing aromatic 1,2-diols (1d-1f) afforded the target products (3d-3f) in excellent yields, giving 4-trifluoromethylbenzoic acid (3d) in 78% yield, 4-fluorobenzoic acid (3e) in 88% yield, 4chlorobenzoic acid (3f) in 85% yield. Due to the steric hindrance effect, yield of 3g was lower than 3f. The polysubstituted 1h, 1i and 1j was converted into corresponding ketone (3i) in 96%, 92% and 91% yield respectively. In addition, it should be emphasized that this mpg-C<sub>3</sub>N<sub>4</sub> catalyzed system was also effective for aliphatic (linear and cyclic) 1,2-diols (1k-1q) in good yields. Particularly, a novel strategy for the synthesis of adipic acid (3I) was verified with substrate 1I, with a yield of 48% being obtained. It should be noted that when mono-substituted odiols (substrate 10-1q) were used as the reaction substrates, another product was formic acid (Figure S2g). In addition, this catalytic system was also applicable to the structure of α-hydroxy acids (1r-1t), such as mandelic acid and lactic acid, giving benzoic acid (3r). cyclohexyl(phenyl)methanone (3s) and acetic acid (3t) in 83%, 88% and 43% yield respectively.

The reaction mechanism was further explored through a series of control experiments (Scheme 2). Under optimal reaction conditions, almost full conversion of the model substrate **1a** was achieved. The main product was **3a** in 81% yield with a tiny amount of **2a** (entry a). When using  $\alpha$ -hydroxy ketone structure **1x** as the model substrate, under identical conditions, the conversion was only 64%, with the yield of main product **3a** being 56% (entry b). Further, with o-dione structure **1y** as the model substrate, the reaction almost did not occur, resulting in a conversion lower than 5% and trace amount of products being detected (entry c).

For heterogeneous catalysis, the effective interaction between catalyst surface and substrate is the most key



Scheme 2. Control experiments.

point. In the skeleton of mesoporous carbon nitrides, a variety of nitrogen functional groups would be the sites for adsorption of substrate molecules<sup>[34]</sup>. To illustrate the interactions between substrate molecules (1a and 1y) and catalyst surface, DFT (Density Functional Theory) calculations using a three-layer model were conducted, as shown in Figure S3. A 4×4 C<sub>3</sub>N<sub>4</sub> sheet was used as the model of catalyst. The geometry optimization result suggests that a corrugated conformation is the most stable structure of C<sub>3</sub>N<sub>4</sub> sheet. With optimized catalyst model, surface interactions were further investigated as shown in Figure 5 (other adsorption conformations can be found in the Supporting Information, Figure S4). Interaction pattern A demonstrates the H atom on hydroxyl group of 1a approaching N atom on the edge of catalyst surface, with the two benzene rings of 1a being nearly perpendicular. Pattern B shows the O atom on hydroxyl group of 1a approaching the central N atom on  $C_3N_4$  surface, while the two benzene rings are nearly parallel. The adsorption energy is -0.55 eV and -0.47 eV respectively, indicating that substrate 1a has stable chemical adsorption states on C<sub>3</sub>N<sub>4</sub> by H atom or O atom on the hydroxyl group. While for substrate 1y, the adsorption energy of O atom on catalyst surface is -0.28 eV, which might be attributed to the lack of hydroxyl H atom on 1y structure compared with 1a. As the adsorption energy is lower than 40 kJ/mol, an instable physical adsorption of 1y on  $C_3N_4$  structure can be inferred. The weak interaction between 1y and catalyst is not beneficial for the electron transfer from catalyst to substrate, which might be the reason for the trace conversion of 1y.

The yield of acids from these three substrates are in sequence of o-diol, α-hydroxy ketone and o-dione (Scheme 2). Therefore, it can be concluded that the photocatalytic reaction pathway was not the conventional process of first oxidation into ketone<sup>[30]</sup> followed by C-C bond cleavage. Combining with the kinetics study (Figure 4), it is speculated that the direct radicalization of o-diol compound first occurred, followed by the  $\beta$ -scission, which resulted in the C-C bond cleavage to generate the corresponding aldehyde compound. The aldehyde compound then underwent further oxidation under identical conditions forming corresponding carboxylic acid. At the same time, we also found that the oxygen was critical to the cleavage of C-C bonds in 1,2-diols. When using argon instead of oxygen (entry d in Scheme 2), the substrate 1a could hardly react, and the product benzoic acid 3a could rarely be detected in the reaction system. In addition, to verify this conjecture of radical reaction process, excessive amount of radical scavenger TEMPO was added for 1a conversion under optimal conditions (entry e). As TEMPO captured the radicals that generated in the photocatalytic process, trace amount of products 2a and 3a was detected although 1a was almost fully converted. This result confirmed that the photocatalytic oxidation of 1a followed the radical mechanism. In addition, photocatalytic conversion of 2a was also performed for mechanism study (entry f). With a full conversion of 2a, the yield of corresponding carboxylic acid product 3a was 92%, proving that the hypothesis of first oxidation to aldehyde then forming acid was reasonable, which was consistent with the speculation from kinetics study that 2a was the intermediate of 1a conversion to 3a.



Scheme 3. a) Detection of Superoxide Radical ( $O_2^{-}$ ) formed by irradiated mpg- $C_3N_4$  using the spin-trap method. b) Proposed mechanism for the photocatalytic cleavage of C-C bonds in 1,2-diols with mpg- $C_3N_4$ .

In order to confirm the active species of oxygen involved in the present reaction, electron paramagnetic resonance (EPR) experiments were performed with 5,5-dimethyl-1pyrroline N-oxide (DMPO) as the spin trapper. The spectra (Scheme 3a) indicated the formation of O2<sup>-- [43]</sup>. No EPR signal was detected in the dark, indicating that light was necessary for the formation of O2 -. Those data indicated that O2<sup>--</sup> was the reactive oxygen species. Therefore, based on the above results, a possible reaction mechanism was proposed in Scheme 3b. This reaction was an oxidation process driven by light radiation. Firstly, the photocatalyst was excited by light radiation source, generating holes and electrons separately in the valence and conduction band. Under the effect of photocatalyst, O2 was catalytically converted into O2-. Simultaneously, the hydroxyl group was radicalized with releasing a hydrogen for substrate 1a interacting with the photocatalyst, which then combined with the oxygen radical forming HOO. The formed radical I was then cleaved through  $\beta$ -scission<sup>[35]</sup> in this reaction conditions, generating a molecule of 2a and the radical II. Hydrogen atom transferred from radical II to the solvent or combined with HOO• to be converted into HOOH and the second benzaldehyde would be generated simultaneously. Subsequently, the generated 2a was further oxidized into **3a**. The conversion of benzaldehyde to benzoic acid was a radical-induced oxidation process, which was a classic fundamental reaction, thus was omitted in this manuscript.

## Conclusion

In summary, we have developed a heterogeneous metalfree photocatalytic strategy to achieve aerobic oxidative cleavage of C-C bonds in 1,2-diols at ambient conditions with visible light using O2 as the oxidant. Reaction conditions were optimized, achieving the excellent yields of corresponding products without any additive. Significantly, this metal-free catalytic strategy has a broad substrate scope, including aliphatic (linear or cyclic) 1,2-diols, benzylic, alkenyl 1,2-diols and  $\alpha\text{-hydroxy}$  acids, such as lactic acid. In addition, the reaction mechanism was further investigated through a series of control experiments and DFT calculations. Mechanistic investigations revealed that H or O atom on the hydroxyl group could be adsorbed on mpg-C<sub>3</sub>N<sub>4</sub> and generated the alkoxy radical. This would be an approach that complements the method of other previous work. And further applications of this catalytic system to other oxidation processes are under investigation in our laboratory.

## **Experimental Section**

#### Materials and instrumentation

All of the reagents and solvents were of analytical grade, purchased from commercial sources (Alfa Aesar, sigma, Adamas-beta, Energy Chemical, TCI and Aladdin) and used without further purification. The Photo Reaction Setup was purchased from Anhui Kemi machinery technology Co., Ltd. Gas chromatographic (GC) analysis was acquired on a Shimadzu GC-2014 Series GC System equipped with a flame-ionization detector. 1H-NMR and 13C-NMR spectra were recorded on a Bruker Avance 400 spectrometer at ambient temperature. The following abbreviations are used to explain the multiplicities: s = singlet, d = doublet, t =triplet, q = quartet, and m = multiplet. The powder X-ray diffraction (XRD) patterns of the catalysts were measured by an X'pert (PANalytical) diffractometer, using CuKa radiation at 40 kV and 40 mA, with a 20 range of 20-80°. FTIR spectra were recorded on a FTIR/Raman Thermo Nicolet 6700 spectrometer, in ATR mode. UV-Vis spectrum was measured by UV-3600.

### Preparation of mpg-C<sub>3</sub>N<sub>4</sub> Catalysts

The mesoporous graphitic carbon nitride (mpg- $C_3N_4$ ) was synthesized according to a modified method in the previous work<sup>[36]</sup>. Briefly, about 40 g urea were dissolved in a solution of 0.2 M HCl solution (60 mL) and ethanol (52 mL) under vigorous stirring, and tetraethyl orthosilicate (32 mL) was then slowly added to the above solution drop by drop. After stirring vigorously at room temperature for 3 h, the mixture was heated under vacuum for the solvent evaporation and then dried at 100 °C for about 12 h. The obtained white solid was calcined in a muffle furnace at 550 °C for 4 h (heating rate: 2.5 °C/min) under nitrogen atmosphere. Subsequently, hydrofluoric acid was used to remove SiO<sub>2</sub> through stirring with the above material for 24 h. Then, after the following filtration, water and ethanol washing for several times, and drying at 80 °C for about 12 h, the pale-yellow solid (about 4 g) was finally obtained and denoted as mpg-C<sub>3</sub>N<sub>4</sub>.

Other semiconductor materials (shown in Figure 1a) are purchased and used directly without any further treatment in this work.

#### General procedure for Photocatalytic Reactions:

To a 10 mL reaction tube with a stir bar was added the substrate lactone (0.2 mmol) and then 10 mg catalyst mpg-C<sub>3</sub>N<sub>4</sub> was added to the reaction tube. Substrately, 1 mL CH<sub>2</sub>Cl<sub>2</sub> was added as the solvent. The reaction mixture was stirred for 12 h at room temperature with a 390 nm light source at 1 atm O<sub>2</sub> pressure (O<sub>2</sub> Balloon). After completion of the reaction, the mixture was subjected to purification. Evaporation of the solvent and short column chromatography of the resulting crude material over silica gel afforded the pure products. The conversion of substrates and the products yield were calculated according to the following formula :

Conversion =  $(n_0-n_1)/n_0 * 100\%$ 

Yield = n(actual yield)/n(theoretical yield) \* 100%

 $n_0$  : mol of substrate before reaction

 $n_1$  : mol of substrate after reaction

The apparent quantum efficiency (QE) was measured under the same photocatalytic reaction condition. The QE was calculated according to the following formula<sup>[37]</sup>:

$$QE = \frac{number of reacted electrons}{number of incident electrons} \times 100\%$$

 $= \frac{\text{number of converted substrates}}{\text{number of incident electrons}} \times 100\%$ 

### General information for DFT calculations

Gaussian 16 package<sup>[38]</sup> were used for all DFT calculations. The B3LYP functional<sup>[39-40]</sup> and 6-31G<sup>\*[41]</sup> basis set were employed for geometry optimization of reactants, intermediates, and products. For the 4×4 ONIOM model of catalyst, B3LYP/6-31G\* was used for high layer calculation, HF/6-31G\* was used for medium layer, and PM6 was used for the low layer. Then frequency analysis was performed at the same level. The adsorption energy was calculated as follows: Eads = E(reactant + catalyst) – E(free reactant molecule) – E(free catalyst). In addition, the vibrational frequencies were used to compute zero-point energy (ZPE) corrections.

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## Entry for the Table of Contents



A heterogeneous metal-free photocatalytic system was developed for oxidative cleavage of C–C bonds in 1,2-diols at mild conditions (visible light, room temperature, no base,  $O_2$  balloon). The reaction mechanism was studied through a series of control experiments and DFT calculations. In addition, the catalytic system has a broad substrate scope, including aliphatic, benzylic, alkenyl 1,2-diols and  $\alpha$ -hydroxy acids, such as lactic acid.