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Flower-like Bi₂O₂CO₃-mediated selective oxidative coupling processes of amines under visible light irradiation



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ABSTRACT

The photocatalytic selective transformation of amines is a green and cost-effective technology to obtain value-added products in chemical industry. In this work, a series of bismuth-based photocatalysts including Bi_2MOG_6 , Bi_2WO_6 , Bi_5O_7CI , Bi_5O_7Br , Bi_5O_7I , $BiPO_4$, $BiVO_4$, Bi_2O_3 and various morphology $Bi_2O_2CO_3$ (flower-like, sponge-like, plate-like and spherical) were synthesized and employed in the aerobic oxidative coupling of benzylamine. It is found that flower-like $Bi_2O_2CO_3$ exhibited the highest photocatalytic activity, in which a 100% conversion of benzylamine with 99.0% selectivity of *N*-benzylidenebenzylamine was obtained at room temperature. Moreover, the photocatalytic oxidative coupling processes of various aromatic and aliphatic amines were further investigated, and excellent yields and selectivities of corresponding products are attained. Then, based on characterization results (XRD, SEM, BET and XPS, etc.) of catalyst, high photocatalytic activity of flower-like $Bi_2O_2CO_3$ is attributed to thin nanopetals, low band gap, the morphology and large specific surface area. Finally, a possible reaction mechanism is proposed for the photocatalytic oxidative coupling of benzyl amine.

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1. Introduction

Developing renewable clean energy has become one of the most promising topics of the 21st century [1,2]. Solar energy is abundant, clean, and renewable on earth. At present, researchers have paid great attentions on the efficient utilization of solar energy. In the chemical field, photocatalysis is considered as one of the most desirable technologies for the conversion of solar energy; of particular note is that photocatalysis can take advantage of solar energy to trigger chemical reaction [3,4]. Correspondingly, the application of the semiconductors as photocatalysts including metal oxides TiO₂ [5], ZnO [6], SnO₂ [7], ZrO₂ [8], metal sulfides CdS [9], ZnS [10] and bismuth oxides BiOX [11–13], Bi₂O₃ [14], BiVO₄ [15] have showed high photocatalytic activity in UV and/ or visible regions.

Although photocatalysis has been studied extensively, the research and application of photocatalysis now mainly focuses on photolysis of water to produce hydrogen and degradation of organic pollutants. The application of photocatalysis on organic synthesis is limitedly reported, and some efforts have been made toward expansion the scope of organic reactions [16–18]. In recent years, the oxidation of amines to imines is often chosen as a model reaction to investigate the activity of photocatalyst, where the generated imines

have a wide range of applications in the synthesis of pharmaceutical intermediates or biologically active organic compounds [19,20]. Notablely, from the standpoint of green chemistry, using molecular oxygen as oxidant to carry out the oxidation of amines is an attractive approach in which the activation of oxygen is a key point [21– 24]. In traditional, the aerobic oxidative coupling of amines was often performed under thermal conditions with precious metallic ruthenium and gold catalysts. For example, the RuCl₃ [25], Ruporphyrin [26], Ru/Al₂O₃ [27], Au/Al₂O₃ [28], Au/CeO₂ [29] and Au/ graphite [30] have been found to be active catalysts for this reaction. However, these processes need high temperature and high pressure, resulting in large number of energy consumption despite the use of precious metal. On the contrary, along with the rapid development of photocatalytic technology, the aerobic oxidative coupling of amines to imines with photocatalysts can be achieved at a low temperature and low pressure. In the previous investigations, TiO₂ [31] and Nb₂O₅ [32] have exhibited relatively high photocatalytic activities under light irradiation. However, the disadvantage of these systems is requiring a long reaction time (greater than 24 h) to obtain a high yield of imines. In addition, Jin et al. also reported the use of homogeneous cobalt thioporphyrazine as photocatalyst to accelerate the oxidation of amines to form imines [33]; however, the recycling and reuse of cobalt catalyst still keeps a problem.

In the photocatalytic researches, bismuth oxides including $WO_3@Bi_2WO_6/NiWO_4$ [34], $BiVO_4/FeVO_4$ [35] and $Bi_2O_3-V_2O_5$ [36] were mainly used for photo-degradation of organic pollutants,





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and there have been few reports on the application of organic synthesis. Recently, Samanta et al. employed a $BiVO_4/g-C_3N_4$ composite catalyst to accelerate the oxidation of benzylamine, benzyl alcohol and aniline, and achieved a desired product yield after 16 h reaction time [37]. Han et al. reported that the bismuth oxyhalide could promote the oxidative coupling of amines to imines with molecular oxygen [38]. Therein, the catalytic efficiency and the introduction of halogen were not still quite satisfactory, so exploring a new and green bismuth oxide catalyst is attractive and promising in the photocatalytic synthesis.

 $Bi_2O_2CO_3$, as a newly developed green photocatalyst, has showed a good photocatalytic activity in the degradation of organic pollutants. For example, the $Co_3O_4/Bi_2O_2CO_3$ catalyst was used to accelerate the degradation of naphthalene [39], and CuS- $Bi_2O_2CO_3$ was employed on the photocatalytic chlorpyrifos degradation [40]. In addition, the single $Bi_2O_2CO_3$ was also found to be efficient for the purification of dye-containing wastewater [41]. Also, different morphologies BiO_2CO_3 catalysts such as flowerlike, sponge-like, plate-like and spherical were also successfully prepared with the simple methods [41–43].

Considering a series merit of using $Bi_2O_2CO_3$ as the photocatalyst, in this article, the $Bi_2O_2CO_3$ was first employed as photocatalyst to promote the selective oxidative coupling of amines with molecular oxygen. Especially, $Bi_2O_2CO_3$ catalysts of different morphologies including the flower-like, sponge-like, plate-like and spherical ones were studied in detail on the oxidation of benzylamine. As a result, it is found that the flower-like $Bi_2O_2CO_3$ showed the highest photocatalytic activity with a 100% conversion of benzylamine and 99.0% selectivity to *N*-benzylidenebenzylamine. Moreover, the oxidative coupling processes of different aromatic and aliphatic amines have also been successfully performed at room temperature. Furthermore, the recycling experiment exhibited that the $Bi_2O_2CO_3$ catalyst still keeps a high active after being reused for 5 times.

2. Experimental

2.1. Materials and instruments

Bismuth nitrate (Bi(NO₃)₃·5H₂O), sodium tungstate (Na₂WO₄·2H₂O), ammonium metavanadate (NH₄VO₃), potassium molybdate (K₂MoO₄), Sodium dihydrogen phosphate (NaH₂PO₄), sodium carbonate (Na₂CO₃) and potassium chloride (KCl) are purchased from Aladdin Chemistry Co., Ltd. Cetyltrimethylammonium bromide (CTAB), sodium hydroxide (NaOH), sodium citrate, citric acid, potassium bromide (KBr), potassium iodide (KI) and ammonium carbonate are commercially available from Tianjin Guangfu Fine Chemical Research Institute. All the solvents and chemicals are of analytical grade and used received without further purification.

The quantitative analyses of the products are performed on a GC apparatus with FID detector. The capillary column is HP-5, 30 m \times 0.25 mm \times 1.0 μ m. The qualitative analysis for the product is carried out on the Agilent 6890/5973 Gas Chromatography-Mass Spectrometer (GC–MS) instrument. The light source is a CEL-HXF300 Xe lamp purchased from Beijing China Education Aulight Co., Ltd with different cutoff filters.

2.2. Catalyst preparation

2.2.1. The preparation of Bi₂O₂CO₃

a) The preparation method of flower-like Bi₂O₂CO₃ is similar with the reference 41. In a typical process, 4.85 g Bi (NO₃)₃·5H₂O (10 mmol) was dissolved in 10 mL HNO₃ (1 mol/L) (a transparent solution named as solution A) and 1.0 g CTAB and 8.45 g Na₂CO₃ (80 mmol) were added to 90 mL distilled water (a transparent solution named as solution B). When solution A was added dropwise to solution B with constant stirring, there was the immediate formation of a milk-like suspension. After being stirred for 10 min, the mixture was subject to filtration and the resulting white precipitate was collected and then washed several times with distilled water and absolute alcohol. After drying at 60 °C for 4 h, the flower-like Bi₂O₂CO₃ samples were obtained.

- b) The preparation method of sponge-like Bi₂O₂CO₃ is similar with the reference 42. Firstly, 0.5 mmol Bi(NO₃)₃·5H₂O and 0.75 mmol tri-sodium citrate were added to 25 mL deionized water with stirring at room temperature, and then the solution was subjected to an ultrasonic process (10 min) and vigorous stirring (3 h). Then the PH value of the solution was adjusted to about 9 using 25% (mass weight) NH₃·H₂O solution. After another 2 h of stirring, the final transparent solution was transferred into a 30 mL Teflon-sealed autoclave with about 85% of the total volume and maintained at 180 °C for 24 h. After being cooled to room temperature, milk-white precipitates were collected and washed with deionized water and ethanol several times and finally dried in a vacuum at 60 °C for 5 h.
- c) The synthesis of plate-like $Bi_2O_2CO_3$ is near to that of sponge-like one,which was obtained by replacing trisodium citrate with 1 mmol ammonium carbonate, with the other conditions unchanged.
- d) The preparation method of spherical Bi₂O₂CO₃ is similar with the reference 43. In a typical procedure, 4.5 mmol of Bi(NO₃)₃·5H₂O was dissolved in 40 mL of dilute HNO₃ solution (1 mol/L) and stirred for 10 min. Then, 3 mmol of citric acid was added to the solution to ensure complete dissolution. Next, a certain amount of NaOH aqueous solution was added dropwise into the solution, setting the PH value of the solution to 4–5. Later, the solution was transferred into a 100 mL Teflon lined stainless steel autoclave, and milkywhite precipitates were obtained by a hydrothermal reaction at 180 °C for 24 h. Finally, the precipitate was centrifuged and washed with deionized water and ethanol several times before being dried at 75 °C for 8 h.

2.2.2. The preparation of Bi₅O₇X

In general, the synthesis of Bi_5O_7X is similar with the method in previous work [44]. For the preparation of Bi_5O_7I , firstly, 4 mmol of $Bi(NO_3)_3$ ·5H₂O and 4 mmol of KI was dissolved in 20 mL distilled water to form a transparent solution under stirring. Then, the mixed solution was adjusted to PH = 13 with an appropriate concentration of NaOH solution. After being stirred for 10 min, the aforementioned solution was then transferred into a Teflon lined stainless steel autoclave, sealed and maintained at 160 °C for 16 h. Subsequently, the as-prepared product was centrifuged, washed with distilled water and ethanol several times and finally dried at 60 °C in air overnight. The syntheses of Bi_5O_7CI and Bi_5O_7 -Br were similar with that of Bi_5O_7I except for replacing KI with KCI or 4 mmol of KBr, respectively.

Moreover, the preparation of Bi_2O_3 , $BiVO_4$, Bi_2WO_6 and Bi_2MOO_6 catalysts are provided in the supporting information.

2.3. The characterization of catalyst

IR spectra were recorded in the range of 4000–400 cm⁻¹ on a Perkin-Elmer spectrometer with KBr pellets. X-ray powder diffraction (XRD) intensities of the different samples were measured on a Rigaku D/max-IIIA diffractometer (Cu K α , λ = 1.54056 Å) in the range from 5° to 80° (20). TG experiments were performed in flowing N₂ on a NETZSCH TG 209 instrument with a heating rate of 10 °C/min. The morphology of catalytic materials was determined by the scanning electron microscope (SEM: JSM-6301F, JEOL) equipped with a JED-2300 (JEOL) EDXS spectrometer for chemical element analysis. X-ray photoelectron spectra (XPS) were recorded on a KRATOS AXIS 165 with a dual X-ray anode (Mg and Al) and all XPS spectra were recorded using the Mg K α line. The BET surface areas, pore volumes, and average pore diameters of the prepared samples were obtained from N₂ adsorption measurement using a Micro-meritics ASAP2020M system.

2.4. Photocatalytic oxidative coupling process of amines

All photocatalytic experiments are performed in a 120 mL autoclave equipped with a glass window and magnetic stirring. A typical procedure for the oxidative coupling of benzylamine is as follows: 0.1 g of benzylamine, 0.025 g of flower-like Bi₂O₂CO₃ catalyst and 10 mL of CH₃CN solvent were charged into the reactor, and the atmosphere inside was replaced with oxygen for three times after the reactor was sealed. Then, pure oxygen was charged to 0.3 MPa at room temperature. Subsequently, the mixed solution was irradiated through the window of autoclave with a Xe lamp, and then was kept for 6 h under stirring. After reaction, the excess gas was purged. The mixture was transferred into a 100 mL volumetric flask, in which the reactor was washed with ethanol for 3–5 times in order to transfer completely. The obtained products were analyzed with internal standard technique by GC with a flame ionization detector (all products were determined on GC-MS with an Agilent 6890N GC/5973 MS detector).

3. Results and discussion

3.1. Characterization

The phase structure of different bismuth oxides were investigated by means of XRD and the patterns are shown in Fig. 1. It can be seen that the diffraction peaks of the $Bi_2O_2CO_3$ samples are sharper, indicating that $Bi_2O_2CO_3$ has better crystal form than those of other bismuth oxides. In addition, for the XRD pattern of $Bi_2O_2CO_3$ with different morphologies, the diffraction peaks of the flower-like $Bi_2O_2CO_3$ matched those of tetragonal $Bi_2O_2CO_3$



Fig. 1. XRD patterns of different bismuth-based catalysts.

(JCPDS card No. 41-1488) and other morphology of $Bi_2O_2CO_3$ samples can be assigned to orthorhombic $Bi_2O_2CO_3$ (JCPDS card No. 84-1752). The sharp and narrow diffraction peaks indicated that the $Bi_2O_2CO_3$ samples are of high crystallinity, and there is no any sight of impurity phases.

Moreover, it is found that the specific surface area and pore volume of flower-like $Bi_2O_2CO_3$ are 20.2 m²/g and 0.104 cm³/g, respectively (Shown in Table 1), which are much larger than most of other bismuth oxides (Table S1). For different morphology of Bi₂O₂CO₃ materials, although band gap of the sponge-like is slightly lower than the flower-like, the pore volume is smaller than that of the flower shape. In case of the plate-like Bi₂O₂CO₃ material, both the specific surface area and pore volume are much smaller than the flower-like Bi₂O₂CO₃ material, however, its band gap is much larger than that of the flower-like one. As for the spherical Bi₂O₂CO₃ material, all the surface area, pore volume and band gap are much larger than the flower-like Bi₂O₂CO₃ material. Furthermore, thermogravimetric analysis of the flower-like Bi₂O₂CO₃ showed that it can keep stable between room temperature to 300° (Fig. S2). On the other hand, there was no significant change in the structure as well as in phase after 4 photocatalytic runs (Fig. S3), indicating that the flower-like Bi₂O₂CO₃ showed good stability during the catalytic process.

In the following, the surface composition of the flower-like Bi₂O₂CO₃ sample was further investigated by XPS technique. Fig. 2 presents the detection results of the high-resolution XPS spectra. As shown in Fig. 2a, the relative peaks of the Bi, C and O elements have been successfully detected. Therein, the C1s peak at a binding energy of 284.6 eV can be attributed to contaminant carbon, and the peak observed at 288.5 eV should be ascribed to the carbon of carbonate in Bi₂O₂CO₃ material (Shown in Fig. 2b). Moreover, the peaks located at 158.7 and 164.0 eV are assigned to Bi $4f_{7/2}$ and Bi $4f_{5/2}$ of the Bi³⁺ component, respectively (Shown in Fig. 2c). In other words, the bismuth of Bi₂O₂CO₃ exists as the Bi³⁺ form. Also, the IR spectrum of Bi₂O₂CO₃ exhibites two obvious characteristic peaks at 1400 cm⁻¹ and 800 cm⁻¹, respectively, due to the stretching vibration of Bi-O bond and C—O bond (Fig. S4). For the UV-Vis spectra of different catalysts, the Bi₂O₂CO₃ material has two significant absorption peaks which are at 210 nm and 300 nm, respectively (shown in Fig. S5).

The SEM images of the as-prepared Bi₂O₂CO₃ samples are displayed in Fig. 3. From the image of magnification, it can be seen that the Bi₂O₂CO₃ materials with different preparation methods have the flower-like (a, b), sponge-like (d), plate-like (e) and spherical (f) structure. In the flower-like Bi₂O₂CO₃ material, with the intercrossing of nanosheets, there is the formation of open pores that allow reactant access to reach the inner surface of the catalyst. What is more, the open pores could promote multiple scattering of the UV-vis light, resulting in greater light-harvesting capacity. It is suggested that the excellent photocatalytic activity of the flowerlike Bi₂O₂CO₃ material is possibly due to the flower-like morphology, thin nanopetals, low band gap, and large specific surface area. During the cycling experiment, the morphology of the flower-like $Bi_2O_2CO_3$ catalyst was basically unchanged (Fig. 3(c)), which proved that the prepared catalyst could keep stable and recyclable in the reaction. Furthermore, the results of EDX analysis of the

Table 1 Results of BET surface areas and band gaps of $Bi_2O_2CO_3$ sample.

Bi ₂ O ₂ CO ₃ samples	Surface area (m²/g)	Pore volume (cm ³ /g)	Band gap (eV)
Flower-like	20.2	0.104	2.90 [41]
Sponge-like	29.6	0.093	2.87 [42]
Plate-like	3.8	0.013	3.34 [42]
Spherical	37.1	0.150	3.25 [43]



Fig. 2. XPS spectra of Bi₂O₂CO₃ samples: (a) survey scan, (b) C1s core and (c) Bi4f core.

flower-like $Bi_2O_2CO_3$ indicated that only the Bi, O and C exist on the catalyst surface, which confirms that the material is of high purity (Fig. 3 (g)).

3.2. Photocatalytic oxidation of amines

3.2.1. The oxidation of benzylamine with different catalysts

The photocatalytic oxidation of benzylamine (1) was carried out at room temperature with molecular oxygen as the oxidant. The reaction equation is given in Scheme 1. The generated reaction products include *N*-benzylidenebenzylamine (2), benzaldehyde (3) and *N*-benzylbenzamide (4). In the absence of catalyst, only 18.6% conversion of benzylamine was obtained (Table 2, entry 1), indicating that benzylamine (1) is not easily reacted under the light irradiation. In particular, no reaction occurs when the oxidation is performed in dark (Table 2, entry 2) which demonstrates that light irradiation is very important for the oxidation of 1. Firstly, a series of bismuth-based catalysts were employed to promote the oxidation of **1**. Therein, the conversion was respectively 65.0%, 62.7% or 37.4% with Bi_5O_7Cl , Bi_5O_7Br or Bi_5O_7l as the catalyst (Table 2, entries 3-5), proving that the catalytic ability of Bi_5O_7X for the oxidation of 1 was decreased with the decreasing of electronegativity of the halide atom. Then, the flower-like Bi₂O₂CO₃ was used as the catalyst for the oxidation of 1 (Table 2, entry 6). To our surprise, a 95.3% conversion of 1 and more than 99% selectivity of **2** are obtained after 6 h. Moreover, when the BiVO₄, Bi₂-WO₆, Bi₂MoO₆, BI₂O₃ and BiPO₄ were employed, less than 44.0% conversion of **1** was attained though the selectivity of **2** can reach more than 99% (Table 2, entries 7-11). These results showed that the Bi₂O₂CO₃ is the most efficient to accelerate the photocatalytic aerobic oxidation of **1**. Furthermore, the catalytic performances of various morphology Bi₂O₂CO₃ materials are also studied, and a 70.4%, 65.8% and 53.2% conversion of **1** were acquired in the presence of sponge-like, plate-like and spherical Bi₂O₂CO₃ materials,

respectively. This proves that the morphology of Bi₂O₂CO₃ is a significant factor to affect the catalytic reactivity. Therefore, the flower-like Bi₂O₂CO₃ exhibited the best photocatalytic activity in oxidative coupling of amine to imine.

3.2.2. Effects of different reaction conditions

The effects of different solvents were investigated in the oxidative coupling process of 1 with flower-like Bi₂O₂CO₃ as the catalyst, and the corresponding results are presented in Table 3. It can be seen that a 94.3% conversion of 1 was obtained after 6 h in DMF solvent, while the selectivity of 2 was 92.0% (entry 2). With DMSO as the solvent, the conversion of 1 and the selectivity of 2 was respectively 78.2% and 94.0% under the similar conditions (entry 3). In THF, the conversion of 1 was 96.9% whereas the selectivity of **2** was 62.9% (entry 4), limiting its usage due to the noticeable amount of by-products. Moreover, using benzotrifluoride and dichloromethane (DCM) as solvents, both the conversion and selectivity were lower than those in acetonitrile. where the conversion of 1 was 57.1% and 72.4%, respectively (entries 5 and 6). It was therefore concluded that acetonitrile is the most suitable solvent for the catalytic oxidation reaction. Moreover, when the wavelength was controlled at more than 400 nm with the filter, the conversion of **1** was decreased to 60% in acetonitrile for 6 h (entry 7); however, a 100% conversion of 1 in a 99% selectivity of 2 was obtained when the time was further prolonged to 21 h at room temperature (entry 8). It shows that the oxidative coupling process should be driven by the visible light.

In addition, the effects of O₂ pressure and reaction time were also investigated and the obtained data are provided in the Table S2 and Fig. S6 of supporting Information.

3.2.3. The recycling experiment of catalyst during the oxidation

After the oxidative coupling reaction, Bi₂O₂CO₃ catalyst was filtered, and washed with deionized water and ethanol and then was



Fig. 3. SEM images of Bi₂O₂CO₃ samples: (a–b) flower-like sample, (c) recycled flower-like sample, (d) sponge-like sample, (e) plate-like sample, (f) spherical sample and (g) EDX spectrum of flower-like sample.



Scheme 1. The equation for the selective oxidation of benzylamine by O₂.

Table 2

The oxidation of benzylamine using the Bi-containing photocatalyst.^a

Entry	Catalyst	Conversion (%) ^b	Selectivity (%) ^b	
			2	3+4
1.	no	18.6	>99	<1
2 ^c	Bi ₂ O ₂ CO ₃ (flower)	<0.5	0	0
3	Bi ₅ O ₇ Cl	65.0	>99	<1
4	Bi ₅ O ₇ Br	62.7	>99	<1
5	Bi ₅ O ₇ I	37.4	>99	<1
6	Bi ₂ O ₂ CO ₃ (flower)	95.3	>99	<1
7	BiVO ₄	31.2	>99	<1
8	Bi ₂ WO ₆	43.5	>99	<1
9	Bi ₂ MoO ₆	33.4	>99	<1
10	Bi ₂ O ₃	7.9	>99	<1
11	BiPO ₄	17.3	>99	<1
12	Bi ₂ O ₂ CO ₃ (sponge)	70.4	>99	<1
13	Bi ₂ O ₂ CO ₃ (plate)	65.8	>99	<1
14	Bi ₂ O ₂ CO ₃ (spherical)	53.2	98.7	1.3

^a Reaction condition: 0.1 g benzylamine, 25 mg catalyst, in 10 mL acetonitrile, under 0.3 MPa of oxygen, Xe lamp with a light intensity of 160 mW/cm², 6 h, 25 °C. ^b The data are obtained by GC with internal standard technique.

The data are obtained by Ge with interna

^c Reaction was performed in dark.

Table 3		
Effects of different reaction	conditions on oxidative	coupling of benzylamine. ^a

Entry	Solvent	Conversion(%) ^b	Product distribution (%) ^b	
			2	3 + 4 + Others
1	CH ₃ CN	95.3	>99	<1
2	DMF	94.3	92	8
3	DMSO	78.2	94.0	6.0
4	THF	96.9	62.9	37.1
5	Benzotrifluoride	57.1	95.2	4.8
6	DCM	72.4	>99	<1
7 ^c	CH₃CN	60.0	>99	<1
8 ^d	CH ₃ CN	100	>99	<1

^a Reaction condition: 0.1 g benzylamine, 25 mg catalyst, in 10 mL acetonitrile, under 0.3 MPa of oxygen, Xe lamp with a light intensity of 160 mW/cm², 6 h, 25 °C. ^b The data are obtained by GC with internal standard technique.

^c The wavelength is controlled at more than 400 nm with the filter and light intensity of Xe lamp is 260 mW/cm².

^d The condition is same with that of entry 7 except that the reaction time is 21 h.





employed for next cycle. As shown in Fig. 4, both the conversion of 1 and selectivity of 2 still kept more than 95.0% even after being reused for five times. It indicates that the $Bi_2O_2CO_3$ was recyclable and stable during the photocatalytic oxidation process.

3.2.4. The investigation on reaction mechanism

Upon visible light irradiation, electron-hole pairs are generated in Bi₂O₂CO₃. In order to clarify the role of electron and holes in the oxidation of 1, the silver nitrate or ammonium oxalate solution was added during the oxidation to suppress electron effect and hole effect, respectively. The experimental results exhibited that the conversion of 1 was drastically reduced to 31.1% when 1 mmol/L silver nitrate solution was added into reaction system (Table 4, entry 1), which showed that electron plays a key role during the oxidation. When 1 mmol/L ammonium oxalate solution was added, the conversion of 1 was also greatly reduced, which was reduced to 43.0% (entry 2). This provides evidence that holes are also involved during the oxidation. In the following, tertbutanol was used to capture hydroxyl radical. The result showed that the conversion of **1** was reduced to 46.7% (entry 3), indicating that hydroxyl radical species also promote the oxidative coupling reaction.

In general, there are two ways to activate oxygen in which one is that the BiO₂CO₃ photocatalyst as sensitizer to create energy transfer to O_2 to form 1O_2 species, and another is that electron is excited from the HOMO of the BiO₂CO₃ and jump to the corresponding LUMO, and further transferred to O_2 to produce O_2^- [45]. In order to further confirm the activation of oxygen, TEMPO and β -carotene were added as scavengers for O_2^{-} and 1O_2 during catalytic oxidation, respectively. As shown in entry 4 of Table 4, when 0.1 mmol of TEMPO was added, the conversion of 1 was slightly reduced to 61.0%, indicating that the O₂⁻ species is helpful for oxidation of 1. Moreover, both the conversion of 1 and the selectivity of 2 were reduced to 49.4% and 35.7%, respectively when 0.1 mmol of β -carotene was added into reaction system (entry 5). The decrease of product selectivity was considered as the formation of benzoic acid and compound 4 as by-products during the oxidation. This provides evidence that ${}^{1}O_{2}$ also has a crucial effect on oxidative coupling of 1. Finally, when both 0.1 mmol of TEMPO and β-carotene were added to reaction mixture, it is found that the conversion of **1** was reduced to 23.7%, and the selectivity of 2 was 92.4% (Table 4, entry 6). These data indicated that there are two forms of O₂ activation mode during the reaction, and the activation mode of producing ¹O₂ is dominant. When the formation of ${}^{1}O_{2}$ is suppressed, the compound **1** is excessively oxidized to

Table 4

The control experimental result for studying reaction mechanism with ${\rm BiO_2CO_3}$ catalyst. $^{\rm a}$

Entry	Additive	Conversion (%) ^b	Product distribution (%) ^b	
			2	3 + 4 + Others
1	Silver nitrate	31.1	97.5	2.5
2	Ammonium oxalate	43.0	97.6	2.4
3	t-butanol	46.7	>99	<1
4	TEMPO	61.0	>99	<1
5	β-carotene	49.4	35.7	64.3
6	TEMPO + β-carotene	23.7	92.4	7.6
7 ^c	Benzaldehyde	95.0	98.9	1.1
8 ^d	β-phenylethylamine	32.8	49.5	50.5

^a Reaction condition: 0.1 g of **1**, 25 mg catalyst, in 10 mL acetonitrile, under 0.3 MPa of oxygen, Xe lamp with a light intensity of 160 mW/cm², 6 h, 25 °C.

^b The data are obtained by GC with internal standard technique.

^c The compound **1** was reacted with benzaldehyde in the dark for 10 h.

^d 0.1 g of β-phenylethylamine was added to verify the intermediate benzaldehyde; therein, generated by-products include **3**, **4** and **N**-benzylidenephenethylamine.

benzoic acid with O_2^- species, resulting in the decrease of compound **2** during oxidation. In order to verify the reaction mechanism of oxidative coupling of **1**, several control experiment were carried out. When the compound **1** and benzaldehyde were reacted



Fig. 5. Proposed mechanism for the oxidative coupling of 1 in the presence of $Bi_2O_2CO_3$ catalyst.

Table 5 The selective oxidation of different aromatic amines with ${\rm Bi_2O_2CO_3}$ as catalyst.

in the dark, the conversion of **1** and selectivity of **2** were 95.0% and 98.9%, respectively (entry 7). Moreover, when same amount of **1** and β -phenylethylamine were added into the reaction system (entry 8), both the compound **2** and *N*-benzylidenephenethylamine were generated. These results further showed that benzaldehyde was an intermediate during oxidative coupling of **1**, and the role of visible light is to promote the oxidation of **1** to benzaldehyde during the reaction.

Based on above investigations and catalytic principle, the possible reaction mechanism for oxidation of **1** with flower-like Bi₂O₂CO₃ as photocatalyst is proposed. As seen in Fig. 5, the Bi₂O₂CO₃ catalyst firstly produced electrons and holes under visible light irradiation, and then the photogenerated electron transmitted to O_2 to form O_2^{-} and 1O_2 species. Meanwhile, the α -H bond of compound 1 was attacked to produce reactive intermediate I. The generated intermediate I reacted with O₂⁻ species to form intermediate II during reaction. Next, the intermediate II removed NH₂OH to generate benzaldehyde with the help of proton. Finally, another molecule 1 was dehydrated with in situ generated benzaldehyde to obtain product 2 (route 1). In addition, there exists a second pathway, in which the compound 1 was firstly activated to form intermediate III, and then reacted with ¹O₂ to produce intermediate IV and hydroxyl radical. In the following, the intermediate IV is further oxidized to generate benzaldehyde, and dehydrated with another molecular 1 to attain product 2 (route 2).

3.2.5. The oxidative coupling processes of different amines

Selective oxidative coupling reactions of different amines were further investigated with the flower-like $Bi_2O_2CO_3$ as the catalyst,

Entry	Amine	Product	Conversion (%) ^b	Selectivity (%) ^b
1	NH ₂		95.3	>99
2	NH ₂	() Y)	89.0	>99
3	NH ₂		97.5	>99
4	F NH2		87.4	>99
5	F NH2	F' V V F	97.6	>99
6	CI ² NH ₂		97.8	>99
7	Br ² NH ₂	Br Br	97.4	>99
8	NH ₂		100	>99
9	Ń NH ₂		94.9	>99
10	NH ₂		94.2	>99
11	F NH ₂	F F F	82.7	>99
12	ř N H	ŕ ŕ	100	69.4
13			31.0	>99
14			100	87.9
15	^I NH ₂	^V √√√ ^N ∧∕∼∕ ^N N	51.4	>99

^a Reaction condition: 0.1 g substrate, 25 mg catalyst (flower-like $Bi_2O_2CO_3$), in 10 mL acetonitrile solvent, under 0.3 MPa of O_2 , Xe lamp with a light intensity of 160 mW/cm², for 6 h, at 25 °C.

^b The data are obtained by GC with internal standard technique.

and the results are presented in Table 5. It was found that all the o-, m- and p- fluorine substituted benzyl amines can be efficiently transformed to the corresponding oxidative coupling products, in which the selectivities of target products kept more than 99% and the conversions of o-, m- and p- fluorine substituted benzyl amines were 89.0%, 97.5% and 87.4%, respectively. Moreover, for the oxidative coupling reaction of p-chloro benzylamine and pbromobenzyl amine, the substrate conversions were respectively 97.6% and 97.8% with more than 99% product selectivity. These data showed that the Bi₂O₂CO₃ catalyst is very efficient to the photocatalytic oxidative coupling processes of halide-substituted amines in which there is a little electron and position effects of the substituent groups. Moreover, when the o-, m- or p-methoxy substituted benzyl amines was employed as the reactant, the conversion was respectively 97.4%, 100% or 94.9%, where the selectivity of oxidative coupling product retains >99%. Similarly, a 94.2% or 82.7% substrate conversion with a more than 99% selectivity of product was obtained in the oxidative coupling reactions of 4methyl benzylamine and 4-trifuoromethyl benzylamine. In the case of dibenzylamine, the conversion and selectivity were 100% and 69.4%, respectively, where a relatively low product selectivity is due to the formation of quite a few benzaldehyde as the byproduct. Moreover, for the oxidation of N-benzylaniline, the selectivity of N-benzylideneaniline also keeps as high as more than 99% although only a 31.0% conversion was attained. It was demonstrated that the first step in the reaction system is to activate the α -H of the amine. This can be confirmed on the oxidation of 1, 2, 3, 4-tetrahydroisoquinoline, where the conversion and product selectivity were 100% and 87.9%, respectively. On the other hand, when the aliphatic amine such as butylamine was used as the reaction substrate, a 51.4% conversion and more than 99% selectivity of target product was obtained, respectively. It also exhibits that the catalyst is promising for the oxidative coupling of aliphatic amines with oxygen.

4. Conclusions

A systematic study was carried out on the selective photocatalytic oxidative coupling of benzylamine to *N*- benzylidenebenzylamine in the presence of bismuth series of photocatalysts. It was found that flower-like $Bi_2O_2CO_3$ exhibited an excellent activity, where 100% conversion and 99.0% selectivity was attained after 6 h under visible light irradiation at room temperature. The flower-like $Bi_2O_2CO_3$ sample also showed very high catalytic activity for the oxidation of various amines. This approach provides an environmental friendly, low price, and green heterogeneous photocatalytic technology for the synthesis of imines in the presence of oxygen.

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Appendix A. Supplementary material

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