

# Photocatalytic Reduction of $CO_2$ to $CH_3OH$ Coupling with the Oxidation of Amine to Imine

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## Abstract

The photocatalytic reduction of  $CO_2$  to organic molecules is one promising approache for both decreasing  $CO_2$  concentration in the atmosphere and storing energies. However, most of the photocatalytic reduction of  $CO_2$  cannot avoid the utilization of sacrificial agents, which are not atomic economy and restricts the practical application of the photocatalytic reduction of  $CO_2$ . In this contribution, an atomic economy photocatalytic reduction of  $CO_2$  to  $CH_3OH$  coupling with the oxidation of amine to imine by  $Cu/TiO_2$  was reported, which can avoid using the sacrificial agents in the reaction systems.  $CO_2$  was reduced to  $CH_3OH$  by photo-induced electrons; meanwhile benzylamine was selected as the reductant to react with photo-generated holes and converted into imine with high selectivity. The results showed that the maximum conversion of benzylamine to imine is 88.7% with selectivity of 98%, and the highest yield of  $CH_3OH$  is 961.4 µmol g<sup>-1</sup> using ca.0.5 wt% Cu/TiO<sub>2</sub> as the catalyst. And also, the reaction mechanism was also investigated by DFT calculation, which would give a detailed explanation for the reaction process.

## **Graphical Abstract**

Schematic illustration is that maximum conversion of benzylamine to imine is 88.7% with selectivity of 98%, and the highest yield of CH<sub>3</sub>OH is 961.4  $\mu$ mol g<sup>-1</sup> using ca.0.5 wt% Cu/TiO<sub>2</sub> as the catalyst



Keywords Photocatalysis  $\cdot$  Reduction of CO<sub>2</sub>  $\cdot$  DFT  $\cdot$  Schiff base  $\cdot$  Oxidation

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# **1** Introduction

An intriguing research found that the  $H_2$  and  $O_2$  derived from water-slipping with a weak external voltage under the light condition in 1972 [1]. Over the past few years, more and more attentions were paid to the study of photocatalysis [2–4]. With the development of photocatalytic technology, it can not only produce hydrogen by photocatalytic water-splitting [5, 6], but also prepare a series of chemical

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raw materials and small organic molecules by photocatalytic reduction of  $CO_2$  [7–10]. To a certain extent, photocatalytic reduction of  $CO_2$  can solve both the energy crisis and the greenhouse effects caused by the accumulation of  $CO_2$  in the atmosphere [11–14].

Motivated by the the above-mentioned advantages of photocatalytic reduction of  $CO_2$ , an increasing number of researchers launched out into the studies [15–23]. Inoue et al. reported the photocatalytic reduction of  $CO_2$ to HCHO, CH<sub>3</sub>OH, CH<sub>4</sub> using TiO<sub>2</sub>, ZnO, CdS, SiC and WO<sub>3</sub> as the photocatalysts in 1979 [24]. Li et al. found CO<sub>2</sub> could be photocatalytically transformed into HCOO<sup>-</sup> under visible light over a photoactive Ti-containing MOF, NH<sub>2</sub>-MIL-125(Ti) [25]. However, the beforementioned photocatalytic reduction of CO<sub>2</sub> cannot avoid the utilization of sacrificial agents, which is not atomic economy and would restrict the practical application of the photocatalytic reduction of CO<sub>2</sub>.

In order to address this issue, an atomic economy photocatalytic (AEPC) reduction of  $CO_2$  is in urgent need. In our previous work, photocatalytic reduction of  $CO_2$ into  $CH_3OH$  coupling with aromatic alcohol high selective oxidation to aromatic aldehyde was carried out under ambient conditions [10]. In order to improve the photocatalytic reduction efficiency of  $CO_2$ , in this paper, benzylamine that has high ability of producing hydrogen, was selected as reductant to react with photo-generated holes and transfers to the imine. The product imine plays an important role in the fields of medicine, catalysis, analytical chemistry, and photochromism [26–29]. This kind of catalytic reactions can avoid using the sacrificial agents and increase the atom utilization efficiency.

Photocatalyst titanium dioxide (TiO<sub>2</sub>) has always been the first choice of photocatalyst, due to its well-known advantages of abundance, nontoxicity, strong catalytic activity and chemical and biological stability [30–33]. However, the photocatalytic activity of TiO<sub>2</sub> nanoparticles is higher under ultraviolet (UV) light irradiation and it is widely used to photocatalytic reduction CO<sub>2</sub> to CH<sub>3</sub>OH  $(CH_3OH)$  [34–36]. Recently, Some new paths to solve the above-mentioned problems are bubbling by alien ion doping to enhance photocatalytic activity, such as nonmetal doping [37–40], self-doping [41–43], rare-earth metal doping [44-47], transitional metal doping [48, 49] and noble metal doping [50–52]. Copper loading crystalline titania (Cu/TiO<sub>2</sub>) is actually exploited for the improvement of the conversion efficiency of CO<sub>2</sub> to CH<sub>3</sub>OH from under certain conditions [53]. In this paper, a sequence of different concentrations for copper loading crystalline titania (Cu/TiO<sub>2</sub>) were prepared by the emblematic sol-gel method. These photocatalysts were devoted to photocatalytic reduction of CO<sub>2</sub> to CH<sub>3</sub>OH coupling with the oxidation of amine to imine.

#### 2 Experiments

## 2.1 The Preparation of Copper Loading Crystalline Titania (Cu/TiO<sub>2</sub>) Nanoparticle

The preparation of copper loading crystalline titania (Cu/  $TiO_2$ ) nanoparticle was according with a representative synthesis process. 10 mL tetrabutyl titanate was dissolved in 40 mL anhydrous ether at room temperature. A volume of 12 mL acetic acid (CH<sub>2</sub>COOH) was added to the abovemention solution by the intensively stirring. A volume of 5 mL acetic acid was added to 10 mL deionized water (or a predetermined concentration of Cu(NO<sub>3</sub>)<sub>2</sub> aqueous solution) as hydrolysis inhibitor solution in the meantime. When the precursor solution was adequately stirred for half an hour, the hydrolysis inhibitor solution was slowly added to the precursor solution. When the hydrolysis inhibitor solution was added, a large amount of white precipitate was forming in the mixed solution. After stirring for 2 h under airtight condition, the suspension was aged in the same temperature for 24 h. The supernatant was removed, and the underlayer white deposition was dried at 100 °C under vacuum for 24 h. In order to remove the residual organic compounds, the solid was alternately washed with deionized water and ethanol, and dried at 100 °C to remove moisture. And then, the sample was calcined at various temperatures for 2 h in muffle furnace. The final sample was grinded into powder.

#### 2.2 Photocatalysts Characterization

The crystalline phases of the photocatalyst were characterized on a D8 diffractometer from Bruker instruments inc by X-ray diffractometer (XRD, Cu Ka radiation,  $\lambda = 0.15406$  nm, at 40 kV and 25 mA). The diffract grams were obtained at  $2\theta$  range from  $15^{\circ}$  to  $85^{\circ}$  in steps of  $0.02^{\circ}$ /s. The crystalline phases of the photocatalysts with different Cu loading content were performed from diffraction peak intensities of rutile and anatase corresponding to (101), (110) and (120), respectively. According to the Debye–Scherrer equation, the average crystalline size was obtained. Morphology of the photocatalyst was investigated by a scanning electron microscope (SEM, Quanta 200F FEI). The microstructures of the photocatalyst was determined by the transmission electron microscopy (TEM, JEM-2010F, at 200 kV) equipped with EDX. The fluorescence lifetime spectrum of the photocatalysts were examined by Fluoro-Max-4 ( $\lambda = 365$  nm) at room temperature. XPS spectrum of ca.0.5 wt% Cu/TiO2 was investigated on THERMO SCI-ENTIFIC K-Alpha surface analysis system, equipped with 650 µm Mono at Al Ka 1486.6 eV.

# 2.3 Photocatalytic Reduction of CO<sub>2</sub> Coupling with Benzylamine to the Corresponding Imine Test

The reactions of photocatalytic CO<sub>2</sub> reduction into CH<sub>3</sub>OH coupling with benzylamine into N-benzylidenebenzylamine were carried in 40 ml anhydrous acetonitrile with 0.06 g photocatalyst, 1 mmol benzylamine (purified by distilled before using). In order to adequately remove diminutive quantities of oxygen, the reactor was evacuated and highly purified by adding dry CO<sub>2</sub> swiftly. The CO<sub>2</sub> was purified to remove small quantities of H<sub>2</sub>O and O<sub>2</sub> through asbestos, allochroic silica gel and activated carbon introducing the reactor. Subsequently, the suspension was stirred at a high rate of speed for an hour under the complete darkness. Then, the high pressure mercury lamp ( $\lambda = 365$  nm) was turned on (10 cm from the reactor). After the reactor was irradiated for 10 h, gas chromatography (GC) with flame ionization detector (FID) was applied to quantitatively analyze the product. And the liquid products were also determined by a Bruker Avance 400 MHz spectrometer (NMR). The GC-MS [equipped with a HP-5 capillary column  $(30 \text{ m} \times 0.25 \text{ mm} \times 0.25 \text{ mm})]$ , was applied to identify the component of products.

## 2.4 Computation Method

First-principle calculations for the reaction on the anatase  $TiO_2$  (101) surface were carried out by using the Vienna ab initio simulation package (VASP) based on the all-electron projected augmented wave (PAW) method [54, 55]. The k-points sampling was generated following the Monkhorst–Pack procedure with a  $2 \times 3 \times 1$  mesh for anatase  $TiO_2$  (101) surface. The generalized gradient approximation (GGA) with the spin-polarized Perdew-Burke-Ernzerhof (PBE) functional was used for all of the calculations. During structural optimization, the bottom layers of the slab were fixed at the bulk truncated position, while the top two layers and the adsorbates were fully relaxed. To prevent the artificial interaction between repeated slab along z-direction, 15 Å vacuum was introduced with correction of the dipole moment. All calculation for the formation of imine were performed using Gaussian 09 package [56]. Theoretical calculation for the geometrical optimizations was performed by density functional theory (DFT) using B3LYP method. The 6-311G (d, p) basis sets were employed for C, H, O and N atoms. The vibrational frequency was calculated at the same level to characterize the nature of the stationary points as true minima (with no imaginary frequency) or transition states (with unique imaginary frequency).

# **3** Results and Discussions

## 3.1 Catalyst Characterization

The microstructure of Cu/TiO<sub>2</sub> nanoparticles was shown in Fig. 1 and Fig. S1 (see supporting information). From Fig. 1a, this kind of photocatalyst is obviously nanoparticles. The average particle size of the photocatalyst was about 20 nm that was the same as the diameter calculated by Debye-Scherrer equation from XRD results (Fig. S2), which indicated that the photocatalyst was well crystallized. From Fig. S1e and f, there are some shadows (copper nanoparticles) on the surface of the photocatalyst which show that CuO nanoparticles and TiO<sub>2</sub> nanoparticles were clearly distinguished from each other. And Cu, Ti, O elements are almost uniformly distributed, forming a series of CuO/TiO<sub>2</sub> nanocomposites. In fact, the uniform distribution of copper nanoparticles on the surface of TiO<sub>2</sub> nanoparticles would be beneficial to improve photocatalytic activity. A bathochromic shift absorption was observed with the increasing of copper content, and it's the well-absorbed in the visible region, which may be caused by the Cu plasmonic effect (Fig. S3a). XPS analyses of  $Cu_{2n}$  were showed in Fig. S3b, Based on the appearance of the satellite feature, existence of CuO could be confirmed [57, 58].

Furthermore, a polycrystal diffraction ring was observed for ca. 0.5 wt% Cu/TiO<sub>2</sub> nanoparticles, which can attribute to the (101) crystalline phase of TiO<sub>2</sub> as shown in Fig. S1a. And also, HR-TEM was used to investigate the interfacial structures between CuO and TiO<sub>2</sub> (Fig. 1c, d). In Fig. 1c, d, the lattice fringes of CuO and TiO<sub>2</sub> showed a surfacejunction. The (110) lattice fringe of the CuO nanoparticles was 0.278 nm, and the (101) lattice fringe of anatase was 0.356 nm. To demonstrate the success of the Cu loading, EDX spectrum of ca.0.5 wt% Cu/TiO<sub>2</sub> nanoparticles was determined, and the results were shown in Fig. S1f. Ti, O and Cu elements were detected on the surface of ca.0.5 wt% Cu/TiO<sub>2</sub> nanoparticles, which indicates that the photocatalyst was consist of TiO<sub>2</sub> and CuO.

# 3.2 Catalytic Performance of Photocatalytic Oxidation of Amine to Imine Coupling with the Reduction of CO<sub>2</sub> to CH<sub>3</sub>OH

The photocatalytic oxidation of amine to imine coupling with the reduction of CO<sub>2</sub> to CH<sub>3</sub>OH was carried out at 0.1 Mpa CO<sub>2</sub> pressure under ultraviolet light ( $\lambda$  = 365 nm) irradiation. The liquid products were determined by GC (Fig. S4) and with flame ionization detector. At the same time, liquid products have also been confirmed by <sup>1</sup>H



Fig. 1 a Representative SEM and b TEM image of ca.0.5 wt% Cu/TiO<sub>2</sub> nanoparticles. c, d HR-TEM image of ca.0.5 wt% Cu/TiO<sub>2</sub> nanoparticles

NMR spectroscopy (Fig. S5) and GC-MS (Fig. S6). All these indicate that the  $CO_2$  was reduced to  $CH_3OH$ , and benzylamine was converted to the corresponding imine with high selectivity.

The detailed results for photocatalytic reductions of  $CO_2$  to  $CH_3OH$  coupling with of amine to imine catalyzed by  $TiO_2$ -base catalysts were showed in Table 1. From Table 1, it is found that the  $CO_2$  was reduced to  $CH_3OH$ , and benzylamine was converted to the corresponding imine with the high selectivity for all catalysts. The yield of  $CH_3OH$  is 201.8 µmol g<sup>-1</sup>, and the conversion of benzylamine is 16.5% catalyzed by pure  $TiO_2$ . However, the yield of  $CH_3OH$  and conversion of benzylamine showed a tremendous growth catalyzed by  $Cu/TiO_2$  nanoparticles, which turned out that the copper loading can effectively improve the photocatalytic activity. Moreover, two blank reactions were studied as well, which showed that the conversion of benzylamine with the low selectivity is 23.7 and 9.5% oxidized by  $O_2$  in the absence and presence of catalyst.

The effects of copper loading content on photocatalytic activity of Cu/TiO<sub>2</sub> were evaluated. The catalytic activity of ca.0.1–0.5 wt% Cu/TiO<sub>2</sub> nanoparticles was improved with

increasing copper loading content in standard reaction condition. The photocatalytic conversion of benzylamine into *N*-benzylidenebenzylamine and the yields of CH<sub>3</sub>OH were enhanced with the increasing of copper loading content. It was found that the ca.0.5 wt% Cu/TiO<sub>2</sub> was optimal to attain the maximum conversion of benzylamine (67.9%) and the highest yield of CH<sub>3</sub>OH (837.8 µmol g<sup>-1</sup>) after irradiating for 10 h. It could be interpreted that the CuO nanoparticles can inhibit the recombination of photogenerated charge and carrier to enhance the photocatalytic activity under ultraviolet light irradiation [57, 58].

However, the photocatalytic activity decreases when copper loading exceeds ca.0.5 wt% Cu/TiO<sub>2</sub>. With the increasing copper loading content from 0.5 to 1.0%, the conversion of benzylamine and the yield of CH<sub>3</sub>OH were declined from 67.9 to 34.8% and from 837.8 to 410.8 µmol g<sup>-1</sup>, respectively. It might be interpreted that superfluous copper nanoparticles cover the surface of TiO<sub>2</sub> activity sites that could absorb UV photon. Therefore, absorption photon capacity of the photocatalyst was reduced. Meanwhile, when the concentration of loading metal were higher, the exceeding copper nanoparticles Table 1 The yields of the reduction of  $CO_2$  coupling with the conversion of benzylamine to *N*-benzylidenebenzylamine with high selectivity under UV light irradiationa after 10 h

Entry	Catalyst	Gas	CH <sub>3</sub> OH	Amine		ME/SB <sup>e</sup>
			(µmol/g)	Conv. (%) Sel. (%)		
1	TiO <sub>2</sub>	CO <sub>2</sub>	201.8	16.5	99	1/6.6
2	TiO <sub>2</sub>	$N_2$	_	5.3	99	0
3	P25	$CO_2$	285.5	24.7	99	1/7.3
4	0.1%Cu/TiO <sub>2</sub>	$CO_2$	317.6	28.3	99	1/7.2
5	0.2%Cu/TiO <sub>2</sub>	$CO_2$	342.7	30.5	99	1/7.4
6	0.3%Cu/TiO <sub>2</sub>	$CO_2$	396.2	34.4	99	1/7.2
7	0.4%Cu/TiO <sub>2</sub>	$CO_2$	505.6	43.8	99	1/7.2
8	0.5%Cu/TiO <sub>2</sub>	$CO_2$	837.8	67.9	99	1/6.7
9	0.6%Cu/TiO <sub>2</sub>	$CO_2$	764.9	57.4	99	1/6.2
10	0.7%Cu/TiO <sub>2</sub>	$CO_2$	563.7	46.7	99	1/6.9
11	0.8%Cu/TiO <sub>2</sub>	$CO_2$	458.4	40.9	99	1/7.4
12	0.9%Cu/TiO <sub>2</sub>	$CO_2$	429.6	36.1	99	1/7
13	1.0%Cu/TiO <sub>2</sub>	$CO_2$	410.8	34.8	99	1/7.1
14	0.5%Cu/TiO <sub>2</sub>	N <sub>2</sub>	_	7.8	99	0
15 <sup>a</sup>	_	$CO_2$	_	_	-	0
16 <sup>b</sup>	0.5%Cu/TiO <sub>2</sub>	$CO_2$	145.1	11.3	99	1/6.4
17 <sup>c</sup>	0.5%Cu/TiO <sub>2</sub>	$CO_2$	_	_	_	0
18	0.5%Cu/TiO <sub>2</sub>	0 <sub>2</sub>	_	23.7	63	_
19 <sup>d</sup>	_	$O_2$	-	9.5	57	-

1 mmol benzylamine; 40 mL CH<sub>3</sub>CN, 60 mg catalyst

<sup>a</sup>Without catalyst

<sup>b</sup>40 mL benzylamine without CH<sub>3</sub>CN

<sup>c</sup>40 mL CH<sub>3</sub>CN without benzylamine

<sup>d</sup>Without catalyst

<sup>e</sup>The molar ratio of the formation of CH<sub>3</sub>OH and imine

could also act as recombination centers of electron and hole, which also gave rise to the declining of the catalytic activity of Cu/TiO<sub>2</sub> nanocomposites. The above-mentioned conclusions can be proved by the UV-Vis diffuse reflectance spectroscopy and photoluminescence spectra of the photocatalysts showed in Fig. S3a and S7. From this Fig. S7, when the copper loading content was lower than 0.5 wt%, the fluorescence intensity of the photocatalyst were decreases with the increase of copper loading content. However, when the copper loading content was higher than 0.5 wt%, the fluorescence intensity of the photocatalyst was gradually increasing with the increasing of copper loading content. It was well known that the photocatalytic activity of the photocatalyst is negative correlation with the fluorescence intensity of the photocatalyst, which were consistent with experimental conclusions. In order to know the stoichiometry of this reaction, the ratio of the formation of CH<sub>3</sub>OH and imine has been calculated (the last column in Table 1). The result shows that the ratio will be keep in a range from 1:6.5 to 1:7.5 for all catalysts, which is smaller than the reaction stoichiometry (1:3). The first reason is that side-products are formed, such as H<sub>2</sub>, CH<sub>4</sub>, HCOOH, HCHO etc. The second reason is that with the progression of the reaction, the  $CH_3OH$  also reacts with photo-generated holes to produce  $H_2$  and  $CO_2$ .

In order to compare with above results, a series of blank experiments were carried out under the above-mentioned conditions. When N<sub>2</sub> was used to replaced CO<sub>2</sub>, the conversion of benzylamine are only 5.3 and 7.8%, and there are no small organic molecule to be observed, catalyzed by TiO<sub>2</sub> and ca.0.5 wt% Cu/TiO<sub>2</sub>, respectively. These indicated that the CO<sub>2</sub> was able to be conversed to CH<sub>3</sub>OH in standard reaction condition. Moreover, without benzylamine in reaction system, no product is observed catalyzed by ca.0.5 wt% Cu/TiO<sub>2</sub> in CH<sub>3</sub>CN. These results certificated that CO<sub>2</sub> can be reduced to CH<sub>3</sub>OH coupling with the conversion of benzylamine to the corresponding imines.

Furthermore, the photocatalytic reductions of  $CO_2$  coupled with selective oxidation of various amines to imines have been performed over ca.0.5 wt% Cu/TiO<sub>2</sub> under the same reaction conditions. The results were shown in Table 2. The photocatalytic oxidation of the benzylamine to the corresponding imines and the conversion of  $CO_2$  into CH<sub>3</sub>OH were observed. It indicated that the groups on the aromatic ring have an effect on the photocatalytic performance. There are 10.9–67.9% conversions for different kind of amines in

**Table 2** The yields of the reduction of  $CO_2$  coupling with the conversion of amine to corresponding imine with ca.0.5 wt% Cu/TiO<sub>2</sub> catalyst under UV light irradiation after 10 h

Entry	Reactant	Product	Yield <sup>a</sup>	Conv. [%] <sup>b</sup>	Sel.
					[%] <sup>b</sup>
1			027.0	(7.0	00
1		$(\mathcal{Y}^{v})$	837.8	67.9	99
2	~~~~uu		1.57.0	01.1	0.0
2			157.2	21.1	99
3	NH <sub>2</sub>	$\sim\sim\sim\sim$	213 7	30.2	98
5	$\mathbf{\mathbf{\mathbf{\mathbf{\mathbf{\mathbf{\mathbf{\mathbf{\mathbf{\mathbf{\mathbf{\mathbf{\mathbf{\mathbf{\mathbf{\mathbf{\mathbf{\mathbf{$	$\downarrow$ $\downarrow$	215.7	50.2	20
4	NH <sub>2</sub>		271.4	54.3	99
	$\swarrow$	N V			
5	NH2		135.9	18.9	98
		F~~ ~F			
6			221.5	34.5	98
		u u			
7			234.2	37.6	99
8	NH <sub>2</sub>	$\sim\sim\sim\sim$	247 1	41.2	99
0			247.1	71.2	,,,
9	S NH <sub>2</sub>	$\langle s \rangle \rangle \langle s \rangle$	193.7	29.8	98
10	0 NH <sub>2</sub>	$\langle \mathcal{A}, $	64.8	10.9	98
11	$\wedge \wedge$	_	_	_	_
11	/ V \ <sub>NH2</sub>	_	_	_	_
12		_	_	_	_



<sup>b</sup>Unit:  $[\mu mol g^{-1}]$ 

<sup>c</sup>Conversion of amine

<sup>d</sup>Selectivity of the corresponding imine

standard reaction condition. There are obvious differences both the conversion of amines and the yield of  $CH_3OH$ among three kinds of methyl substituted benzylamine (at ortho-, meta-, para-positions of the benzene ring, Table 2, entries 2–4). The orders for the conversion of amines and the yield of  $CH_3OH$  are both ortho- > meta- > para-, which indicated that space steric hindrance of substituted benzylamine had large effect on the catalytic activity. In order to know the electronic effect of substituted group, the electron-donating groups (CH<sub>3</sub>O- and CH<sub>3</sub>-) and the electrondrawing groups (F- and Cl-) benzylamine were investigated in detailed. The methoxy benzylamine could be converted into the corresponding imines with conversions of 37.6% and the yield of CH<sub>3</sub>OH of 234.2  $\mu$ mol g<sup>-1</sup> after reacting for 10 h, respectively. However, the conversion of 4-fluorobenzylamin is only 18.9% and the yield of CH<sub>3</sub>OH is lower  $(135.9 \ \mu mol \ g^{-1})$  under the same reaction conditions. The results showed the electron donating groups on the aromatic ring favor CH<sub>3</sub>OH production and benzylamine oxidation. However, the electron withdrawing groups on the aromatic ring resulted in a low conversion of benzylamine and the yield of CH<sub>3</sub>OH. Compared with 4-chlorobenzylamine, 2,4-dichlorobenzylamine were easy to be oxidated into the corresponding imine (entry 8). As can be seen from Table 2, the reaction of heteroatom-containing substrates amine derivatives were also converted to corresponding imine with high selectivity under photocatalysis (entries 9-10). However, there are no products to be observed when the aliphatic amine used in this reaction under same reacting conditions (entries 11-12).

The effect of irradiation time on photocatalytic reduction of  $CO_2$  into  $CH_3OH$  and the conversion of benzylamine were conducted on ca.0.5 wt% Cu/TiO<sub>2</sub> nanoparticles under the same reaction condition (Fig. 2). The conversion of benzylamine was clearly enhanced with the increasing of irradiation time. However, the selectivity was slightly declined due to the growth of by-products in the reaction system. At the same time, the yield of  $CH_3OH$  was gradually increased with the elongation of irradiation time. When the irradiation time reached 15 h, the yield of  $CO_2$  into  $CH_3OH$  was 961.4 µmol g<sup>-1</sup> (Fig. 2b), and the conversion of benzylamine to *N*-benzylidenebenzylamine was 88.7 with 98% selectivity (Fig. 2a).

In order to test the reusability of the Cu/TiO<sub>2</sub> nanoparticle, the used catalyst was recovered by centrifugation and thoroughly washed with anhydrous acetonitrile. The photocatalyst was recycled up to three times. As shown in Fig. 3, the photocatalytic activity of ca.0.5 wt% was only slightly deteriorated after three consecutive photocatalytic experiments. It could be interpreted that a small portion of copper nanoparticles were leached and aggregated after the photocatalytic experiment. So that photocatalytic activity was slightly decreased. In summary, these kinds of catalyst has high stability for photocatalytic reduction of CO<sub>2</sub> into CH<sub>3</sub>OH coupling with the conversion of benzylamine into *N*-benzylidenebenzylamine.

#### 3.3 Catalytic Mechanism

To understand the photocatalysis reaction process, the DFT calculations were carried out to study the reaction



**Fig.2 a** The influence of irradiation time on conversion of benzylamine and selectivity of corresponding imine with ca.0.5 wt% Cu/ TiO<sub>2</sub> catalyst. **b** The yields of CH<sub>3</sub>OH production (unit:  $\mu$ mol g<sup>-1</sup>) with the prolonging of irradiation time. (Reaction condition: 1 mmol benzylamine, 60 mg photocatalyst, 40 mL CH<sub>3</sub>CN)



Fig. 3 The conversion of benzylamine to *N*-benzylidenebenzylamine with ca.0.5 wt% Cu/TiO<sub>2</sub> catalyst in different recycling runs at 0.10 MPa CO<sub>2</sub> under UV light irradiation

mechanism. The mechanism for photocatalytic reduction of  $CO_2$  to  $CH_3OH$  coulping with the conversion of amine to corresponding imine was showed in Fig. 4 and as follows:

$$Catalyst + hv \rightarrow catalyst^* + e^-_{cond} + p^+_{val}$$
(1)

$$PhCH_2NH_2(aq) + 2p_{val}^+ \rightarrow PhCH = NH + 2H_{cond}^+$$
(2)

$$\text{CO}_2 + 2\text{H}^+_{\text{cond}} + 2e^-_{\text{cond}} \rightarrow \text{HCOOH}$$
 (3)

$$\text{HCOOH} + 2\text{H}^{+}_{\text{cond}} + 2e^{-}_{\text{cond}} \rightarrow \text{HCHO} + \text{H}_2\text{O}$$
(4)

$$\text{HCHO} + 2\text{H}^{+}_{\text{cond}} + 2\text{e}^{-}_{\text{cond}} \rightarrow \text{CH}_{3}\text{OH}$$
(5)

$$PhCH_2NH_2 + PhCH = NH \rightarrow PhCH = NCH_2Ph + NH_3$$

$$PhCH = NH_2 + H_2O \rightarrow PhCHO + NH_3$$
(7)

 $PhCHO + PhCH_2NH_2 \rightarrow PhCH = NCH_2Ph + H_2s$  (8)

Photogenerated holes in the VB of pholocatalyst oxidize benzylamine to corresponding imine and generating H<sup>+</sup> (Eq. 2), and CO<sub>2</sub> was reduced by photogenerated electrons in CB following the sequence of reactions to produce HCOOH, HCHO and CH<sub>3</sub>OH (Eqs. 3, 4, 5). The formed imine in step 2 was conversed to Schiff base via two possible reaction channels, the concerted (channel 1) and stepwise (channel 2) mechanisms. For the channel 1, the imine was reacted directly with benzylamine to form imine (step 6). The channel 2 was divided into two step, the first step was the hydrolysis of imine to give NH<sub>3</sub> and aldehyde that was then reacted with amine to produce the imine and H<sub>2</sub>O (step 7 and 8).

Figure 5 presents the calculated potential energy surface of the dissociation of benzylamine on anatase TiO<sub>2</sub> (101) (Fig. S9). The benzylamine can be adsorbed at Ti atom on TiO<sub>2</sub> (101) surface to form a monodentate adsorbate without an intrinsic transition state, where the N–Ti bond length was 2.31 Å and the adsorption energy was 22.50 kcal/mol. Then a hydrogen transfer was carried from N atom of benzylamine to the O atom on TiO<sub>2</sub> (101) surface, forming an O–H bond via TS1 with a reaction barrier of 27.91 kcal/mol. The



Fig. 4 The proposed mechanism of photocatalytic reduction of  $CO_2$  to  $CH_3OH$  coupling with the conversion of amine to corresponding imine



Fig. 5 The calculated potential energy of the dissociation of benzylamine on anatase  $TiO_2$  (101)

second hydrogen transfer step from C atom of benzylamine to O atom on  $\text{TiO}_2(101)$  surface takes place by overcoming reaction barrier of 18.33 kcal/mol at TS2, producing benzylimine with an endothermicity of 15.64 kcal/mol.

The formation of Schiff base from benzylimine was able to proceed via two channels (channel 1 and channel 2 in Fig. 4). The benzylamine was able to react with formed benzylimine via an electrophilic addition of N to C=N bond to form the intermediate (IN1a) by overcoming energy barrier of 11.29 kcal/mol (channel 1 in Figs. 4, 6a). Then, a hydrogen transfer step between two N atoms takes place via TS2b with energy barrier of 11.53 kcal/mol to attain the last product Schiff base.

If the existence of water, the reaction would take place via another reaction channel (channel 2 in Fig. 4). The calculated energy profile for this channel was showed in Fig. 6b, c. In the first step, the  $H_2O$  was reacted with benzylimine via transition state TS1a in that the hydrogen atom of  $H_2O$ was transferred to N atom of benzylimine, producing IN1b with an energy barrier of 10.48 kcal/mol. Then the second hydrogen of  $H_2O$  was continually transferred to N atom of benzylimine via TS2a with energy barrier of 7.71 kcal/mol, then the NH<sub>3</sub> and benzaldehyde was attained. Our experiments also indicate that the NH<sub>3</sub> was the main gas product base on GC analysis (Fig. S6), which is good agreement with the calculating results.

It is well know that the benzaldehyde is able to react easily with benzylamine to form Schiff base. Figure 6c presents the calculated potential energy of the reaction between benzaldehyde and benzylamine via two elementary reaction steps. For the first step, the N atom of benzylamine nucleophilicly attack the carbanyl group of benzaldehyde to produce IN1c in that the hydrogen atom on N atom was transferred to O atom of carbanyl group with a low energy barrier of 9.96 kcal/mol. Then the second H on N atom was transfer to O atom of carbanyl group via TS2b with energy barrier 10.67 kcal/mol to form the H<sub>2</sub>O and imine. Compare



**Fig. 6** The calculated potential energy for the producing imine from benzylimine via channel 1 (**a**) and channel 2 (**b**, **c**)

channel 1 with channel 2, it is found that the energy barrier in former is higher than that of the latter, which means that the introduction of  $H_2O$  can weakly accelerate the reaction process.

#### 4 Conclusions

In this paper, an reduction of  $CO_2$  into  $CH_3OH$  coupling with the conversion of aromatic amine into corresponding imine by a series of photocatalysts have been conducted under UV irradiation. This kind of catalytic reactions can avoid using the sacrificial agents and increase largely the atom utilization efficiency. The optimal photocatalyst was ca.0.5 wt% Cu/TiO<sub>2</sub> nanoparticles. The highest yield of the conversion of  $CO_2$  into  $CH_3OH$  is 961.4 µmol g<sup>-1</sup> after 14 h. Meanwhile, the maximum conversion of benzylamine to corresponding imine is 88.7% with high selectivity of 98%. Therefore, it provides a new route for photocatalytic reduction of  $CO_2$  to  $CH_3OH$ , and also to produce another kind of significant chemical products.

# **5** Supporting Information

The Supporting Information is available free of charge on The SEM, TEM, emission spectra, GC, GC-MS results and additional data.

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## **Compliance with Ethical Standards**

Conflict of interest The authors declare no conflict of interest.

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