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The preparation and photocatalytic activity of Ag-Pd/g-C₃N₄ for the coupling reaction between benzyl alcohol and aniline



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ABSTRACT

In this study, the carrier g-C₃N₄ was prepared by melamine, and the Ag-Pd/g-C₃N₄ catalyst was synthesized by the NaBH₄ reduction method. Different characterization techniques, including SEM, TEM, XRD, UV-vis DRS, XPS, photoluminescence spectra (PL) and BET, were employed to investigate the morphology and optical properties of the as-prepared samples. The Ag-Pd/g-C₃N₄ catalyst was used for the synthesis of imine from a benzyl alcohol and aniline. The results show that when the total loading of Ag and Pd is 2 wt%, and the mass ratio of Ag and Pd is 1:1, the activity of the catalyst is the highest (The highest conversion of aniline is 86.7% and the product selectivity is > 99%.). The reaction is optimized by changing the type of solvent, the type and amount of base, the type of catalyst, and the amount of reactants. The optimal reaction conditions are 6 ml of nhexane, 1.4 mmol of Cs₂CO₃, 50 mg of the Ag-Pd/g-C₃N₄ (2 wt%, 1:1), and 2:1 mol ratio of benzyl alcohol and aniline. Under optimal reaction conditions, alcohol derivatives and amine derivatives were investigated to determine the suitable range of the catalyst for alcohols and amines. Then, the effects of different light intensities and wavelengths on the reaction were explored. Additionally, the catalyst's recycling ability was tested, and it was found to be relatively stable. The effect of reactive groups on the mechanism shows that the reaction is mainly achieved by the synergy between h^+ , e^- and O_2^- .

1. Introduction

Imines are organic compounds containing the C=N bond. They are a class of important intermediates in organic synthesis reactions such as reduction, addition, condensation and cyclization. They are used in pharmaceuticals, perfumes, fungicides, dyes and pesticides. Imines are also a class of widely used intermediates [1-5]. In addition, imines are also common ligands in coordination chemistry. Conventional methods for synthesizing imines include the coupling of amine compounds with aldehydes or ketones. However, in recent years, a growing number of methods for the synthesis of imines under mild reaction conditions from the perspective of reactant species have been developed. Imine synthesis is mainly divided into the following three categories: (1) The reaction of an alcohol and amine to synthesize an imine: Chen et al. [1,2] found that CeO₂ can oxidize and catalyze this reaction at a low temperature (303 K). The reaction principle is based on the fact that the alcohol is oxidized to the corresponding aldehyde or ketone under the action of a catalyst and then coupled with aniline to form an imine. (2) The self-oxidative coupling of aromatic amines to synthetic imines: Yuan et al. [3] loaded RuO₂ on graphene oxide (RuO₂/GO) for the

synthesis of imines. In the reaction process of aniline self-oxidative coupling to a synthetic imine, no solvent is needed, and the activity of the imine can reach 95% under an air atmosphere at 373 K. (3) The reaction of nitrobenzene with alcohol to synthesize imines: Nakaia et al. [4] showed a synthesis of imines from benzylic alcohols with substituted groups and nitrobenzene over a CdS-TiO₂ photocatalyst under visible light irradiation at room temperature. The photocatalytic activity can be explained by the photocurrent efficiency and a shift in the flatband potentials of the CdS photoelectrode. In this paper, the first method is used to obtain an imine by the photocatalytic coupling of a benzyl alcohol and aniline.

The traditional photocatalyst is mainly composed of the semiconductor TiO₂, a wide-bandgap semiconductor, whose forbidden band width is 3.2 eV, therefore, TiO₂ can only use 3%~5% of the solar spectrum [6-10], which greatly limits its range of practical applications. Carbon nitride has been studied [11–14], and findings reveal that both the carbon and nitrogen atoms in g-C₃N₄ are sp² hybridized, which is a thermodynamically stable arrangement. It has the most stable structure and semiconductor properties at room temperature. Moreover, g-C₃N₄ possesses band gap energy of approximately 2.7 eV (which allows the

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absorption of certain visible light), an excellent photocatalytic performance, chemical stability, and a good resistance to corrosion by acid and alkali, making it a favorite in the field of photocatalysis. However, some flaws have also been exposed, such as a small specific surface area, a low degree of separation of electrons and holes, and a limited range of visible light for reactions. In this regard, researchers all over the world have developed various methods of modifying g-C₃N₄, and have made some progress in this pursuit. Among the most popular methods to increase photocatalytic performance is doping with a metal, forming a precious bimetal from Ag and Pd to improve the catalytic activity. Ag nanoparticles exhibit surface plasmon resonance (SPR) effect. Under visible light irradiation, Ag nanoparticles undergo intraband transitions in the 6sp orbital. Under ultraviolet light, inter-band transitions from the 5d or 6sp orbit occur [15]. Researchers have successfully loaded Ag nanoparticles onto g-C₃N₄. Pd, as a member of the platinum group, has strong hydrogen absorbing ability, but exhibits poor selective oxidation ability toward reactant molecules [16-19]. When Pd nanoparticles are diluted by Ag nanoparticles, as the isomerization active center, the isomerization activity promotes the oxidation of benzyl alcohols. The hydroxy group concentration decreases due to the decrease in the concentration of Pd, while on the hydrogenation active center, the synergistic effect with the Ag SPR effect promotes the dissociation of hydrogen and Ag [19,20]. The overflow of hydrogen atoms accelerates the reaction rate.

In this work, Pd/g-C₃N₄, Ag/g-C₃N₄, and Ag-Pd/g-C₃N₄ (with different loadings of Ag and Pd and different mass ratios of Ag and Pd) catalysts were prepared, and the catalysts were exmined by SEM, TEM, XRD, UV-vis DRS, XPS, PL, and BET techniques. The Ag-Pd/g-C₃N₄ catalyst was used to catalyze the reaction of a benzyl alcohol with aniline under visible light to form an imine. The solvent type, the type and amount of alkali, the mass ratio and the bimetallic loading, the amount of reactants, alcohol and amine derivatives, and the effect of the light intensity and wavelength on the reaction were discussed. Finally, the stability of the catalyst was determined by recycling, and the photocatalytic principle of the reaction was explored by adding a capture agent, which provided a basis for research into the catalyst and the design of an industrial device.

2. Materials and methods

2.1. Preparation of Ag-Pd/g-C₃N₄ photocatalyst

2.1.1. Preparation of $g-C_3N_4$

Melamine was quantitatively placed in a crucible using an analytical balance, then placed in a box-type electric resistance furnace, slowly heated to 550 °C at 2 °C/min, and calcined for 4 h to obtain g-C₃N₄.

2.1.2. Preparation of Ag-Pd/g- C_3N_4

- (1) In all, 1.5 g of the supporter was dissolved in 200 ml of deionized water, and sonicated for 30 min, 5 wt% of PEG2000 was added, followed by stirring for 10 min, and sonicated for 10 min.
- (2) A quantitative amount of $AgNO_3$ (0.1 mol·L⁻¹) was pipetted into a volumetric flask to prepare 100 ml of an $AgNO_3$ liquid. The prepared solution was slowly added dropwise to the above solution for approximately 20 min. Then, lysine (0.53 mol·L⁻¹) was taken with a pipette and added dropwise for 10 min. After the completion of the dropwise addition, the mixture was magnetically stirred for 30 min.
- (3) A quantitative amount of $PdCl_2$ was pipetted into a volumetric flask to prepare 100 ml of a $PdCl_2$ (0.01 mol·L⁻¹) liquid, and the prepared solution was added dropwise to the above solution for approximately 20 min. The lysine was taken with a pipette, added dropwise for 10 min, and magnetically stirred for 30 min.
- (4) NaBH₄ (0.135 g) was weighed and dissolved in 10 ml of water, added dropwise to the solution, and then 10 ml of HCl (0.3 mol·L⁻¹)

was added dropwise, finally stirred for 1 h and aged for 24 h.

(5) The resulting catalysts was washed three times with deionized water and ethanol, and dried at 60 °C for 12 h.

2.2. Characterization methods

Scanning electron microscopy (SEM, model S-4800, Japan Electron Optics Laboratory Limited Company, Hitachi) was used to characterize the morphology of the obtained composites. The morphology and structure of the samples were examined by transmission electron microscopy (TEM) using an FEI Tecnai G2 F20 S-Twin electron microscope, which was operated at an acceleration voltage of 200 kV. The crystal phases of the samples were analyzed by X-ray diffraction (XRD) with a Rigaku D/MAX-2500 X-ray diffractometer using Cu Kα radiation $(\lambda = 1.5405 \text{ Å})$ at 40 kV and 100 mA. The UV–vis diffuse reflectance spectra (UV-vis DRS) of the solid samples were obtained using a scanning UV-vis spectrophotometer (U-3900, Hitachi) equipped with an integrated sphere assembly with 100% BaSO₄ as the reflectance sample. X-ray photoelectron spectroscopy (XPS) with Al Ka X-ray $(h\nu = 1486.6 \text{ eV})$ radiation operating at 150 W (Escalab 250xi, ThermoFisher Scientific USA) was applied to investigate the surface properties. The photoluminescence spectra (PL) of the catalyst was determined using an Edinburgh Instruments FLS920 photoluminescence spectrometer with a pulsed xenon lamp (450 W) that possessed an excitation wavelength of 325 nm and a wavelength range of 450–650 nm. A multipoint BET method was applied to determine the Brunauer-Emmett-Teller (BET) specific surface areas. The reaction products were quantitatively analyzed with a gas chromatograph (GC-2014C). The identity of the product was confirmed with a Trace DSQ II gas chromatograph-mass spectrometer (GC-MS) at Inner Mongolia University.

2.3. Photocatalytic activity test

In this experiment, the reaction substrate was 1 mmol of benzyl alcohol and 1 mmol of aniline, 1.4 mmol of weakly basic cesium carbonate (Cs₂CO₃), 50 mg of catalyst, and 6 ml of solvent in a circular bottom flask under an air atmosphere. The substrate was stirred, and the light reaction was conducted for 10 h. The reaction temperature was 30 ± 3 °C.

2.4. Recycling test

About 50 mg of the catalysts is used in each experiment at the first time, 40 experiments are done in succession, there are some losses after each experiment (The catalysts are washed with deionized water for 3 times and with ethanol for 1 time, and then dried at 60 °C for 8 h.). Finally, the catalysts are not enough for the sixth recycling. Therefore, the catalysts are recycled for five times.

3. Results and discussion

3.1. Scanning electron microscopy (SEM) analysis

As seen from Fig. 1(a), the synthesized g- C_3N_4 is a stacked irregular sheet-like structure with partially stacked pores. As shown in Fig. 1(b–d), when modified with Ag and Pd, the surface of g- C_3N_4 becomes rough due to the presence of the noble metals, and it is also found that the precious metal particles are also deposited in the pores of g- C_3N_4 . Fig. 1(e) shows the elemental surface distribution of Ag-Pd/g- C_3N_4 (2 wt%, 1:1). It can be seen that the Ag and Pd nanoparticles reduced by NaBH₄ are uniformly dispersed on g- C_3N_4 . From the results in Fig. 1(f), the mass fractions of Ag and Pd are 0.87% and 0.74%, respectively, which are consistent with the theoretical additions. The metal mass ratio is also consistent, which indicates that we successfully prepared a catalyst of uniform dispersion.



Fig. 1. SEM images of the different catalysts (a) g-C₃N₄; (b)-(d) Ag-Pd/g-C₃N₄ (2 wt%, 1:1); (e) The element mapping of Ag-Pd/g-C₃N₄ (2 wt%, 1:1); (f) The EDX image of Ag-Pd/g-C₃N₄ (2 wt%, 1:1).



Fig. 2. TEM images of the different catalysts (a) g-C₃N₄; (b) Pd/g-C₃N₄ (1 wt %); (c) Ag/g-C₃N₄ (1 wt %); (d) and (e) Ag-Pd/g-C₃N₄ (2 wt %, 1:1); (f) TEM images of the recycled Ag-Pd/g-C₃N₄ (2 wt %, 1:1) catalyst.

3.2. Transmission electron microscopy (TEM) analysis

We can see from Fig. 2(a) that $g-C_3N_4$ possesses an irregular sheet structure. Seen from Fig. 2(b), (c), and (d), when modified with Ag and Pd, the Ag and Pd nanoparticles are present on the surface of g-C₃N₄, and the structure of g-C₃N₄ does not change. The Ag and Pd nanoparticles supported on g-C₃N₄ are well dispersed. By determining the particle size from the TEM image, the inset of Fig. 1(b1), (c1), and (d1) is obtained. When only the single metal Pd nanoparticles are supported, the particle size distribution of the nanoparticles is between 3-5 nm, and the measured average particle size of Pd is 4.24 nm. When only single metal Ag is supported, the Ag particles are easily agglomerated, and the measured particle size distribution is 8 nm. When Pd and Ag are simultaneously loaded on g-C₃N₄, the average particle diameter is 4.17 nm, which is smaller than the single metal particle sizes, and the dispersion of Ag particles is also better, which may be due to the synergy between the two metals. Fig. 2(e) is an HRTEM image of Ag-Pd/g- C_3N_4 (2 wt%, 1:1). The lattice fringes of two kinds of nanoparticles Ag and Pd can be seen in Fig. 2(e). The average lattice spacings are 0.237 nm and 0.219 nm, corresponding to the lattice fringes of the Ag (111) and the Pd(111) crystal planes [21]. Fig. 2(f) is a TEM image of the catalyst recovered after recycling. It can be seen that the g-C₃N₄ sheet structure remains intact, but a portion of the loaded Ag and Pd nanoparticles fell off.

3.3. X-ray diffraction (XRD) analysis

Fig. 3 shows the XRD patterns of the different catalysts. It can be seen from Fig. 3(a) that there are clear diffraction peaks at 2θ values of 12.8° and 27.4° , corresponding to the typical tri-triazine structural units of g-C₃N₄. The (100) crystal plane and the conjugated aromatic system are stacked to form a (002) crystal plane, thereby indicating that the structure of g-C₃N₄ is stable [22]; after loading the Ag and Pd nanoparticles, the structure is not changed. However, the characteristic peak

of Ag is not found after loading Ag, which may be because the loading of Ag nanoparticles is too low. The characteristic Pd(111) diffraction at a 2 θ of 40.2° indicates that Pd is loaded onto g-C₃N₄ [21]. It can be seen from Fig. 3(b) that as the loading of bimetallic Ag and Pt nanoparticles increases, the intensity of the characteristic diffraction peak of Pd is continuously strengthened. Due to the partial formation of the alloy, the characteristic diffraction peak of Pd is shifted to a lower angle. From the XRD spectrum of the catalyst after the cycle, we can conclude that the structure of the catalyst does not change significantly after 5 cycles, and the structure of the catalyst is stable.

3.4. UV-vis diffuse reflectance spectroscopy (DRS) analysis

Fig. 4 shows the UV–vis DRS spectra of the different catalysts. As seen from Fig. 4(a), g-C₃N₄ exhibits an absorption at 460 nm [23] (the band gap is approximately 2.7 eV [24]), while Ag/g-C₃N₄ has an absorption tail band at 500 nm, which is due to the SPR effect of the Ag nanoparticles. The absorption strength of the Pd/g-C₃N₄ catalyst is significantly enhanced over that of g-C₃N₄. The three-way catalyst with Ag and Pd loading has a red shift in its absorption wavelength and a stronger intensity than g-C₃N₄. When combined with data from Fig. 4(a) and (b), the strength and width of Ag-Pd/g-C₃N₄ (2 wt%, 1:1) are the largest, that is to say, its ability to utilize visible light is the strongest, and its reactivity is the best.

3.5. X-ray photoelectron spectroscopy (XPS) analysis

Fig. 5(a) shows the full spectrum of Ag-Pd/g- C_3N_4 (2 wt%, 1:1), and the characteristic peaks of C1 s, N1 s, Ag3d, and Pd3d can be seen. Fig. 5(b) is a 1 s high-resolution XPS spectrum of the C element in the Ag-Pd/g- C_3N_4 (2 wt%, 1:1) catalyst. As seen from Fig. 5(b), 284.6 eV is the binding energy of the C–C bond, and 287.8 eV corresponds to the binding energy of N–C = N in g- C_3N_4 [23]. Fig. 5(c) is a 1 s high-resolution XPS spectrum of the N element in the catalyst Ag/Pd/g- C_3N_4



Fig. 3. XRD of the different catalysts.

(2 wt%, 1:1). It can be seen from Fig. 5(c) that there are three characteristic peaks at 398.7 eV, 400.5 eV and 404.0 eV. The peak at 398.7 eV corresponds to the nitrogen atom in the triazine ring, which is hybridized by sp² orbitals; the characteristic peak at 400.5 eV corresponds to the nitrogen atom of the group N-(C) 3; and the weak characteristic peak at 404.0 eV is caused by positive charges in the carbon and nitrogen ring [25]. Fig. 5(d) is a high-resolution XPS spectrum of the Ag3d orbital in the Ag-Pd/g-C₃N₄ (2 wt%, 1:1) catalyst with two characteristic peaks at 367.8 eV and 373.8 eV, corresponding to Ag3d_{5/} $_{2}$ (Ag⁰) and Ag3d_{3/2} (Ag⁰) [21], indicating that the Ag nanoparticles are present in the metallic state. Fig. 5(e) is a high-resolution XPS spectrum of Pd3d orbital in the Ag-Pd/g-C $_3N_4$ (2 wt%, 1:1) catalyst, with two characteristic peaks at 339.9 eV and 334.4 eV [21], corresponding to the combined energies of the metallic Pd⁰. In summary, g-C₃N₄ was successfully prepared, and the noble metals were supported on the carrier in their metallic states.

3.6. Photoluminescence spectra (PL) analysis

As seen from Fig. 6, the prepared g-C₃N₄, Ag/g-C₃N₄, Pd/g-C₃N₄, and Ag-Pd/g-C₃N₄ (2 wt%, 1:1) catalysts possess a broad fluorescence at 460 nm. The signal peak of pure g-C₃N₄ is the strongest, while the multi-catalyst loaded with a single precious metal shows a weaker fluorescent signal peak, and Ag-Pd/g-C₃N₄ presents the lowest intensity. This result indicates that the loading of two precious metals can promote the photogeneration and separation of electrons and holes, while the synergy of Ag and Pd bimetals also inhibits the recombination of photogenerated electrons and holes. Based on the comprehensive PL and UV-vis DRS spectra, we know that the Ag-Pd/g-C₃N₄ catalyst not only increases the response range in the visible light, but also effectively suppresses the recombination of photogenerated electrons and holes.

3.7. N_2 adsorption/desorption isotherm (BET) analysis

Fig. 7(a) is the N₂ adsorption/desorption isotherm curves of pure g-C₃N₄, Ag/g-C₃N₄, Pd/g-C₃N₄, and Ag-Pd/g-C₃N₄ (2 wt, 1:1). As shown in Fig. 7(a), the isotherms of pure $g-C_3N_4$ and the four catalysts loading a single metal or the bimetal are type IV, and the hysteresis loops are all H3 type, indicating that all four substances exhibit mesoporous structures. The H3 type hysteresis loop indicates that the pore shape is formed by the gap between two plates, which is consistent with the layered structure of g-C₃N₄ [23]. The total amount of loading is 2 wt% in Fig. 7(b), which shows the surface area vs the conversion for the catalysts with different mass ratios of Ag and Pd. The specific surface area of the supported bimetallic catalyst is significantly larger than that of the supported single metal. When the mass ratio of the Ag and Pd loading is 2.5:1.5, the specific surface area is the largest. However, when the loading is 1:1, the specific surface area is not substantially different from that obtained with 2.5:1.5. In combination with the conversion and economic effect, we chose the loading ratio of 1:1 as the optimal loading ratio. Fig. 7(c) is a graph showing the relationship between the specific surface area and conversion of catalysts with an Ag and Pd mass ratio of 1:1 but different total loadings. With the increase in the loading of Ag and Pd, the specific surface of the catalyst increases and then decreases in Fig. 7(c). The conversion is also the largest for 2 wt% loading. In summary, the catalyst possesses a pore structure, and the structure of g-C₃N₄ remains unchanged after loading the noble metal. When the total loading is 2 wt%, the mass ratio of Ag and Pd is 1:1, the specific surface area of the catalyst is large, and the conversion is the largest. The specific surface area is a factor that affects the reaction.

3.8. Catalyst activity test



The activity test for the amination reaction of an alcohol and amine

Fig. 4. UV-vis DRS of the different catalysts.



Fig. 5. (a)Ag-Pd/g-C₃N₄ (2wt%,1:1) full spectrum; (b) The XPS C 1s spectrum of Ag-Pd/g-C₃N₄ (2wt%,1:1); (c)The XPS N 1s spectrum of Ag-Pd/g-C₃N₄ (2 wt%, 1:1); (d) The XPS Ag 3d spectrum of Ag-Pd/g-C₃N₄ (2 wt%,1:1); (e) The XPS Pd 3d spectrum of Ag-Pd/g-C₃N₄ (2 wt%,1:1).



Fig. 6. PL spectra of the different catalysts.

with Ag-Pd/g-C₃N₄ photocatalyst was performed.

3.8.1. Effect of different solvents on the reaction

In this experiment, the reaction substrate was selected as 1 mmol of benzyl alcohol, 1 mmol of aniline, 1 mmol of the weak base Cs_2CO_3 , 50 mg of the Ag-Pd/g- C_3N_4 (4 wt%, 1:1) catalyst, and 6 ml of solvent in a round bottom flask. The results are shown in Table 1.

The conversion of the reactant is related to the polarity of the solvent under visible light irradiation as revealed in Table 1. The smaller the polarity index of the solvent is, the greater the conversion is. The higher the polarity index of the solvent is, the larger the interaction with the reaction substrate is, which weakens the interaction between the reaction substrate and the catalyst, and further weakens their reactivity. Therefore, the conversion of the reactant in the solvent nhexane is the highest. Additionally, the conversions of all photoreactions are significantly greater than those of the dark reactions. The solvents methanol, DMSO and isopropanol normally quenches the



Fig. 7. (a) N₂ adsorption isotherms of the different catalysts; (b)The correlation between the BET surface area and the conversion for different mass ratios of Ag and Pd in the catalyst; (c) The correlation between the BET surface area and the conversion for different loading amounts of the bimetal catalyst.

8

Blank

Table 1					
Effect of the different	solvents on	the reaction	of benzyl	alcohol and	aniline.

No.	Solvent	Polar index	Light irradiation		In dark	
			Conv. (%)	Sel. (%)	Conv. (%)	Sel. (%)
1	DMSO	7.2	0	> 0	0	> 0
2	DMF	6.4	0	> 0	0	> 0
3	Methanol	6.6	2.2	78.1	0	> 0
4	1,4-Dioxane	4.8	0	> 0	0	> 0
5	Isopropanol	4.3	4.5	66.7	2.9	67.2
6	Toluene	2.4	26.5	> 99	2	> 99
7	Mesitylene	1.9	18.9	> 99	1.3	> 99
8	Petroleum ether	0.01	41.2	> 99	12.9	> 99
9	n-Hexane	0.06	43.5	> 99	14.1	> 99
10	Cyclohexane	0.1	42.0	> 99	9.0	> 99

photogenerated holes directly/indirectly (serving as sacrificial electron donors) and therefore conversion efficiency is lowered with these systems. The conversions of isopropanol and methanol are slightly higher than that of 1,4-dioxane. In summary, the coupling reaction of benzyl alcohol with aniline presents the highest conversion in n-hexane solvent, which is 43.5%. Furthermore, light is a necessary condition for catalyzing this reaction.

3.8.2. Effect of different bases on the reaction

Using the above-selected 6 ml of n-hexane as the optimal solvent, the effect of the type of base on the coupling reaction of an alcohol and amine was investigated under the above conditions. The results are shown in Table 2.

We chose 7 kinds of strong bases, weak bases and organic bases to

7

Effect of No.	f the different Base	bases on the re	action of ben	zyl alcohol and In dark	aniline.
		Conv. (%)	Sel. (%)	Conv. (%)	Sel. (%)
1	NaOH	20.6	> 99	11.9	> 99
2	KOH	13.1	> 99	0.4	> 99
3	LiOH	2.2	> 99	0.6	> 99
4	Na ₂ CO ₃	21.2	> 0	0	> 0
5	K ₂ CO ₃	13.8	> 99	0	> 0
6	CH ₃ ONa	1.9	> 99	4.0	> 0
7	Cs_2CO_3	43.5	> 99	14.1	> 99

explore the effect of alkali type on the experiment. According to Table 2, a weak base is more favorable for the coupling reaction of an alcohol and amine, with the conversion of aniline being 43.5%, and the value is the highest using Cs_2CO_3 . Additionally, it is known from the blank experiment that the alkali is necessary.

> 0

0

> 0

3.8.3. Effect of different catalysts on the reaction

0.3

The optimum base was 1 mmol of Cs_2CO_3 , and the other conditions were unchanged. The effect of different catalysts on the coupling reaction of an alcohol and amine was investigated. The results are shown in Table 3.

It can be seen from the experimental data 1–8 of Table 3 that when $g-C_3N_4$ or a single metal catalyst is used, the reaction is far less effective than that using the catalyst supporting the bimetal, indicating that the synergistic effect between Ag and Pd plays a significant catalytic role. It

Table 3

Effect of the different catalysts on the reaction of benzyl alcohol and aniline.

No.	Catalysts	Light irradiation		In dark	
		Conv. (%)	Sel. (%)	Conv. (%)	Sel. (%)
1	g-C ₃ N ₄	5.7	> 99	0.6	> 99
2	Ag/g-C ₃ N ₄ (1 wt%)	12.3	> 99	7.2	> 99
3	Pd/g-C ₃ N ₄ (1 wt%)	31.7	> 99	18.5	> 99
4	Ag-Pd/g-C ₃ N ₄ (1 wt%)	31.4	> 99	11.3	> 99
5	Ag-Pd/g-C ₃ N ₄ (2 wt%)	58.9	> 99	23.7	> 99
6	Ag-Pd/g-C ₃ N ₄ (3 wt%)	25.6	> 99	14.9	> 99
7	Ag-Pd/g-C ₃ N ₄ (4 wt%)	43.5	> 99	14.1	> 99
8	Ag-Pd/g-C ₃ N ₄ (5 wt%)	32.8	> 99	9.7	> 99
9	$Ag-Pd/g-C_3N_4$ (Ag:Pd = 3:1)	22.5	> 99	5.4	> 99
10	Ag-Pd/g-C ₃ N ₄	49.2	> 99	13.6	> 99
	(Ag:Pd = 2.5:1.5)				
11	Ag-Pd/g-C ₃ N ₄	54.0	> 99	16.1	> 99
	(Ag:Pd = 1.5:2.5)				
12	$Ag-Pd/g-C_3N4_4$ ($Ag:Pd = 1:3$)	32.9	> 99	13.7	> 99
13	Blank	2.3	> 99	0.5	> 99

Note: 4-8 catalyst: the Ag and Pd mass ratio is 1:1; 9-12 catalyst: the total loading is 2 wt%.

can be seen from the comparison of data 9–12 and 5 that when the Ag:Pd ratio is 1:1, the total loading of Ag and Pd is 2 wt%, and the catalytic effect is the best, which may be related to the morphology and the interaction between the bimetal. These results are consistent with the previous N₂ adsorption-desorption data and the specific surface area characterization, which may be due to the increased loading, the agglomeration of the supported Ag and Pd nanoparticles, and the blockage of g-C₃N₄ due to the increased loading (Therefore, the surface area is smaller). Through the blank experiment, the catalyst has a clear catalytic effect on the reaction. In this experiment, 50 mg of Ag-Pd/g-C₃N₄ (2 wt%, 1:1) was selected as the catalyst for the coupling reaction of an alcohol and amine, and its conversion is 58.9%.

3.8.4. Effect of the amount of alkali on the reaction

Through the above qualitative analysis, the best selected solvent is 6 ml of n-hexane, the best base is 1 mmol of Cs_2CO_3 , the best catalyst is 50 mg of Ag-Pd/g- C_3N_4 (2 wt%, 1:1), and the other reaction conditions remain unchanged. The effect of the amount of base on the coupling reaction of the alcohol with the amine is shown in Table 4.

When Cs_2CO_3 is gradually increased from 0.4 mmol to 1.6 mmol under light illumination, the conversion of the reactant is also gradually increased; however, when Cs_2CO_3 is continuously increased from 1.6 mmol to 1.8 mmol, the conversion of the reactant declines slightly. Under black conditions, when Cs_2CO_3 is gradually increased from 0.4 mmol to 1.8 mmol, the conversion of the reactant increases continuously. As the amount of alkali increases, the base plays an increasingly important catalytic role. However, the conversion of the reactant under visible light irradiation is substantially larger than that in the dark. When the amount of Cs_2CO_3 is 1.6 mmol, the conversion of

Table 4

Effect of the different amounts of base on the reaction of benzyl alcohol and aniline.

编号 No.	Base amount (mmol)	Light irradiation		In dark		
		Conv. (%)	Sel. (%)	Conv. (%)	Sel. (%)	
1	0.4	15.6	> 99	6.4	> 99	
2	0.6	25.8	> 99	11.4	> 99	
3	0.8	37.4	> 99	16.7	> 99	
4	1.0	58.9	> 99	23.7	> 99	
5	1.2	67.3	> 99	27.5	> 99	
6	1.4	76.8	> 99	32.4	> 99	
7	1.6	78.1	> 99	32.0	> 99	
8	1.8	69.5	> 99	33.5	> 99	

Table 5	
Effect of the amounts of reactant on the reaction of benzyl alcohol and a	niline

No.	Benzyl alcohol	Aniline (mmol)	Light irradiation		In dark		
	(IIIIIOI)	(minor)	Conv.(%)	Sel.(%)	Conv.(%)	Sel.(%)	
1	4.0	1.0	62.5	> 99	7.3	> 99	
2	3.0	1.0	77.4	> 99	28.4	> 99	
3	2.0	1.0	86.7	> 99	30.2	> 99	
4	1.0	1.0	76.8	> 99	32.4	> 99	
5	1.0	2.0	69.5	> 99	22.9	> 99	
6	1.0	3.0	54.9	> 99	23.2	> 99	
7	1.0	4.0	54.7	> 99	21.3	> 99	

the reactant reaches the maximum, but compared with the conversion of 1.4 mmol, it does not increase significantly. Therefore, 1.4 mmol is used as the optimum alkali amount. When the amount of Cs_2CO_3 is continuously increased, the conversion of the reactant decreases, which may be because the Cs_2CO_3 molecule and the benzyl alcohol preempt the active site of the catalyst. In summary, 1.4 mmol is the optimum alkali amount for the reaction, and the conversion rate is 76.8%.

3.8.5. Effect of the reactant amounts on the reaction

Taking 6 ml of n-heptane, 1.4 mmol of Cs_2CO_3 , 50 mg of the Ag-Pd/ g- C_3N_4 (2 wt%, 1:1) catalyst in a round bottom flask, and the other reaction conditions remain unchanged. We then explore the effect of the reactant amounts on the reaction of a benzyl alcohol and aniline, and the results are shown in Table 5.

When the amount of aniline is fixed at 1 mmol, and the amount of benzyl alcohol is gradually increased, the conversion of the reactants increases at first and then decreases under illumination (Table 5); while with the amount of benzyl alcohol is fixed at 1 mmol, and with gradual increase in aniline, the conversion of the reactants is gradually reduced. This result may be because that the reaction is carried out in two steps in this amination process. First, benzyl alcohol is easily oxidized into benzaldehyde under the photocatalytic action of Ag-Pd/g-C₃N₄ (2 wt%, 1:1), and then, the aldehyde group in the benzaldehyde is affinitysubstituted with the amine group in the aniline. When the aniline molecules are increased in the reaction, the active sites on the catalyst will adsorb more aniline, and because the surface of the catalyst adsorbs too little benzyl alcohol, the first step of amination will be inhibited, that is, the formation of the intermediate benzaldehyde is less, which is not conducive to the amination reaction; the excess of benzyl alcohol will also reduce the adsorption of aniline on the surface of the catalyst, and the second part of the amination reaction will then be inhibited, which is not conducive to this reaction. In summary, when the amount of benzyl alcohol is 2 mmol, and the amount of aniline is 1 mmol, the conversion is maximized, and the maximum conversion is 86.7%.

3.8.6. Effect of alcohol derivatives on the reaction

After the above experiment, the optimal conditions of the reaction were finally determined, namely 6 ml of n-hexane as the solvent, 50 mg of Ag-Pd/g-C₃N₄ (2 wt%, 1:1) as the catalyst, 1.4 mmol of Cs₂CO₃, 1 mmol of aniline, and 2 mmol of various alcohols as the reactants. The effect of different alcohol derivatives on the reaction was investigated, and the experimental results are given in Table 6.

According to datum 4 in Table 6, the catalyst exhibits a poor catalytic performance for the alcohol having an electron-donating group in the para position; as seen from data 5, 6, 11, 12, and 13, the catalyst with an electron-withdrawing group in the para position, or an alcohol that easily forms a large conjugated π bond, presents a good catalytic effect. This result may be because the reaction depends on the benzaldehyde formed, and the electron donating group causes the H on the hydroxyl group to fall off with difficultly, so that benzaldehyde is not easily formed; instead, when using a catalyst with an electron-withdrawing group or a large conjugated π bond, benzaldehyde is easily

 Table 6

 Effect of the alcohol derivative on the reaction of alcohol and aniline.

No.	ROH	Light irradia	tion	In dark	
		Conv. (%)	Sel. (%)	Conv. (%)	Sel. (%)
1	ОН	86.7	> 99	30.2	> 99
2	ОН	3.8	78.7	> 0	> 0
3	ОН	21.9	91.3	3.7	97.5
4	ОН	48.6	97.1	17.9	94.7
5	Н3С ОН	98.3	> 99	30.4	> 99
6	О2N ОН	89.1	> 99	35.7	> 99
7	он	6.7	> 99	0.3	> 99
8	·∕∕ _{OH}	23.5	> 99	1.9	> 99
9		3.9	> 99	> 0	> 0
10		2.6	75.8	> 0	> 0
11	Л	62.4	> 99	10.9	> 99
12	OH	87.3	> 99	23.7	> 99
13	ОН	70.9	> 99	21.3	> 99

formed. The H on the hydroxyl group of the alcohol easily falls off so

that benzaldehyde is easily formed. Therefore, this catalyst is suitable for alcohols that have electron-withdrawing groups.

The catalyst is not conducive to the reaction of a secondary alcohol and aniline, as given from data 2, 7, and 10. The steric hindrance presented to aniline in attacking the secondary alcohol is relatively large, and the secondary alcohol is oxidized to a ketone; ketones are more stable than aldehydes, so they do not readily react with aniline.

It can be seen from data 3, 8, and 9 that the catalytic effects of the fatty alcohol and the branched C-chain aromatic alcohol are not apparent, because such alcohols do not easily drop H to form an aldehyde.

In summary, the prepared Ag-Pd/g- C_3N_4 (2 wt%, 1:1) catalyst has a particularly clear catalytic effect on alcohols having an electron-with-drawing group or capable of forming conjugated bonds.

3.8.7. Effect of amine derivatives on the imine reaction

In this experiment, 1 mmol of different kinds of amines were selected, the other experimental conditions were the same as above, and the reaction was carried out. The effect of amine derivatives on the reaction is shown in Table 7.

It can be seen from data 4, 5, and 6 in Table 7 that the catalytic performance of the catalyst for the electron-donating group in the para position is better than that for the electron-withdrawing group, which may be due to the electron-donating group being capable of forming an amine group on the aniline. The catalyst with an electron cloud of a high density easily carries out nucleophilic reactions.

From datum 3, the conversion using the catalyst with the metasubstituent is low, which may be due to steric hindrance. From data 2 and 7, the effects of the catalyst on the aliphatic amine and the branched C-chain aromatic amine are not apparent, because the amine is not strong in nucleophilicity. It can be seen from data 8 and 9 that the effect of the catalyst on the secondary aliphatic amine is not clear, and that the secondary aromatic amine can be catalyzed.

In summary, the Ag-Pd/g- C_3N_4 (2 wt%, 1:1) catalyst has poor catalytic activity for meta-substituted anilines, while for secondary fatty amines, and branched carbon-containing amines, the catalytic activity is slight. However, the catalyst is suitable for amines with electrondonating groups and secondary aromatic amines.

Molecular Catalysis 476 (2019) 110533

Table 7							
Effect of the	amine (derivative o	ı the	reaction	of alcohe	ol and	aniline

编编号 号	NH ₂ R	Light irradiation		In dark	
		Conv.(%)	Sel.(%)	Conv.(%)	Sel.(%)
1	NH ₂	86.7	> 99	30.2	> 99
2	NH ₂	58.7	> 99	12.8	> 99
3	NH ₂	65.5	> 99	22.3	> 99
4	NH ₂	89.2	> 99	33.3	> 99
5	NH ₂	81.2	> 99	11.5	> 99
6	CIP V NH2	95.4	> 99	37.7	> 99
7		29.6	> 99	1.5	> 99
8		< 0.1	< 0.1	< 0.1	< 0.1
9		95.0	> 99	3.3	> 99

3.9. Effect of light intensity on the reaction

To explore the influence of different light intensities on the reaction, five different sets of light intensities were selected for the reaction under the above optimized conditions. The effect of different light intensities on the reaction of a benzyl alcohol and aniline to synthesize an imine is shown in Fig. 8.

It can be seen from Fig. 8 that under the illumination, as the light intensity increases, the conversion of the reactant also increases, and the contribution of light to the whole reaction is large, which indicates that the reaction is excited by light. The above-mentioned possible causes are that the light intensity is increased, then more photogenerated electrons and holes are excited on the Ag nanoparticles and $g-C_3N_4$, and the transfer of photogenerated carriers is accelerated.

3.10. Effect of wavelength on the reaction

To investigate the effect of different wavelengths on the selective synthesis of imines, this experiment selected filters of different wavelength ranges for use under the above optimized conditions.

As shown in Fig. 9, the conversion to the target product decreases as the wavelength is gradually reduced from 400 to 800 nm to 650-800 nm. It can be found that the conversion with light possessing a



Fig. 8. Effect of different light intensities on the reaction of benzyl alcohol and aniline.





Fig. 9. Effect of different wavelengths on the reaction of benzyl alcohol and aniline.



Fig. 10. The recycle ability test of Ag-Pd/g-C₃N₄(2 wt%,1:1) in the reaction of benzyl alcohol and aniline.



Fig. 11. Effects of scavengers on the reaction of benzyl alcohol and aniline.

wavelength within 400–550 nm is the largest, and the Ag-Pd/g-C₃N₄ (2 wt%, 1:1) catalyst is mainly responsive within 400–550 nm and the result is consistent with that of the UV–vis diffuse reflectance measurements. These experimental results show that under visible light illumination, the light intensity and wavelength range play an important role in the catalytic reaction.

3.11. Cycle capability test of the catalyst

The catalyst was subjected to a cycle ability test using the above reaction conditions, and the results are shown in Fig. 10.

As shown in Fig. 10, after the Ag-Pd/g- C_3N_4 (2 wt%, 1:1) catalyst was recycled 5 times, it still maintains a good selectivity, but the conversion began to decrease after the third cycle. According to the previous XRD (Fig. 3(b)) and TEM characterization (Fig. 2(f)), the structure of g- C_3N_4 is not destroyed during the cycling, but the Ag and Pd nanoparticles partially fell off, which reduces the conversion. In general, the catalyst has a good catalytic stability.

3.12. Effect of reactive groups on the mechanism

To study the role of superoxide radicals (O_2^-), photogenerated holes (h⁺) and photogenerated electrons (e⁻) in the catalytic reaction, the corresponding trapping agents benzoquinone (BQ), ethylenediaminetetraacetic acid (EDTA), and CCl₄ were added to the reaction under the above optimal conditions, and the effect of the reactive groups on the mechanism was explored. The results are shown in Fig. 11.

It can be seen from Fig. 11 that after the addition of EDTA, the reduction of the reactant conversion indicates that the photogenerated hole (h⁺) is a substance directly involved in the reaction, and the conversion is decreased after the addition of CCl₄ and BQ, indicating that the photogenerated electron and O_2^- directly participates in the reaction. However, O_2 can be converted into O_2^- , and then O_2^- is involved in the coupling reaction between the benzyl alcohol and aniline. The results show that the reaction is mainly achieved by the synergy between h⁺, e⁻ and O_2^- .

4. Conclusion

Ag-Pd/g- C_3N_4 was successfully prepared. The catalyst possesses a remarkable enhanced visible light absorption and good electron-hole separation efficiency and it can conduct the coupling reaction of alcohols and amines to imines. Compared with the g- C_3N_4 , Ag/g- C_3N_4 , Pd/g- C_3N_4 and Ag-Pd/g- C_3N_4 systems, the Ag-Pd/g- $C_3N_4(2 \text{ wt}\%, 1:1)$ system exhibits optimal photocatalytic activities, which consist of a fast electron and hole separation and a slow charge recombination. The optimal reaction conditions are 6 ml of n-hexane, 1.4 mmol of Cs₂CO₃, 50 mg of the Ag-Pd/g- $C_3N_4(2 \text{ wt}\%, 1:1)$, and 2:1 mol ratio of benzyl alcohol and aniline. The catalyst's recycling ability shows that it is relatively stable. The effect of reactive groups on the reaction shows that it is mainly controlled by the synergy between h⁺, e⁻ and O_2^{-} .

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.mcat.2019.110533.

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