Synthesis of Ag/g-C₃N₄ Composite as Highly Efficient Visible-Light Photocatalyst for Oxidative Amidation of Aromatic Aldehydes

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Abstract: In this contribution, an $Ag/g-C_3N_4$ nanocomposite was synthesized and utilized as highly efficient and green photocatalyst for organic reactions under visible light irradiation. A layered, porous g- C_3N_4 was synthesized following a modified solvothermal-roasting process by using melamine and cyanuric chloride as precursor. Silver nanoparticles (NPs) were well anchored on g- C_3N_4 nanosheets, which were prepared by a facile impregnation-roasting method. The inexpensive, stable g- C_3N_4 coupled with the localized surface plasmon resonance (LSPR)

Introduction

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The use of solar radiant energy to drive organic reactions provides a sustainable pathway for green synthesis and has attracted significant interest in recent years.^[1] However, in most cases, ultraviolet (UV) light is usually required to drive photochemical reactions. The UV radiation can activate chemical bonds in many molecules and result in undesirable consequences in many cases.^[1] Thus, to develop the direct utilization of visible light in organic synthesis, which accounts for 43% of the incoming solar spectrum, might provide a more efficient and greener approach. However, since most common organic molecules cannot absorb light in the visible light region, there are many difficulties to utilize visible light.^[2] Thus, to investigate novel visible light catalysts has proved to be the key factor in the approach. Currently, only several kinds of visible light catalysts have been reported, mainly about Ru(II) or Ir(III) complexes, and usually suffered many difficulties such as high cost, poor stabilities, and worse recyclabilities.^[3]

effect of Ag NPs exhibited high photocatalytic activities toward aerobic oxidative amidation of aromatic aldehydes under visible light irradiation. Good to excellent yields were achieved for various substrates under the light of a 25 W compact fluorescent light (CFL) bulb in air. The operationally easy procedure provides an economical, green, and mild alternative for the formation of amide bonds.

Keywords: g-C₃N₄; oxidative amidation; photocatalysis; silver nanoparticles; visible light

Graphitic CN $(g-C_3N_4)$ is a novel aggregate type semiconductor material and widely reported recently in water splitting, heterogeneous organocatalysis, and environmental remediation.^[4] Because of its smallest band gap among various CN allotropes and its solidstate aromatic system which is inert against most acids and bases,^[5] the material was believed to be the basis for a new family of solar energy transducers.^[6,7] However, pure g-C₃N₄ suffers from a high recombination rate of photogenerated electron-hole pairs, low specific surface area, and low visible-light utilization efficiency, which limited its photocatalytic performance.^[8] To resolve these problems, many methods have been exploited, such as ion doping,^[9] noblemetal nanoparticle deposition,^[10] morphology or pore structure design,^[11] acid or alkali treatment,^[12] dye sensitization,^[13] conjugated polymer coupling,^[14] and heterojunction fabrication.^[4,15]

In recent years, much attention has been directed to the use of nanoparticles as catalysts in organic reactions.^[16] Because of their easy preparation and relative stabilities in air, the nanoparticles of coinage metals, such as copper, silver and gold, were widely

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reported, and there are many excellent examples of their applications as catalysts in organic reactions.^[17] Silver and gold nanoparticles were also found to exhibit strong interactions with resonant incident photons through excitation of the localized surface plasmon resonance (LSPR),^[17a,18] and were recognized as a new form of medium that is particularly efficient in harvesting light energy for chemical processes due to their strong light absorption over a wide range of the visible and UV regions of the solar spectrum.^[18,19] The combination of Ag NPs and g-C₃N₄, provides a novel strategy to enhance the photocatalytic performance of g-C₃ N_4 .^[20a,21] Recently, there have been several examples of the use of Ag NPs-loaded graphitic carbon nitride $(g-C_3N_4)$ as a green and stable photocatalyst for the degradation of pollutants.^[20] However, to the best of our knowledge, there are few examples on their application in photocatalytic organic reaction.

Herein, we have synthesized layered $g-C_3N_4$ material by a modified method with melamine and cyanuric chloride as precursors, and first demonstrated the synthesis of Ag/g-C₃N₄ hybrid material by a facile impregnation-roasting method. The materials were characterized by TEM, XRD, XPS, nitrogen sorption, UV-Vis and PL. The inexpensive, stable $g-C_3N_4$ coupled with the localized surface plasmon resonance (LSPR) effect of Ag NPs, exhibited high catalytic activity toward the aerobic oxidative amidation of aromatic aldehydes under visible light irradiation. Good to excellent yields were achieved for various substrates under the light of a 25W compact fluorescent light (CFL) bulb in air. Furthermore, the Ag/g-C₃N₄ nanocomposite catalyst could be recycled effectively.

Results and Discussion

Material Characterization

There are many ways for the preparation of $g-C_3N_4$, the most common is to heat melamine directly under an N₂ atmosphere (for comparison, $g-C_3N_4$ was also synthesized following this procedure, and named as bulk $g-C_3N_4$).^[22] A soft solution-processing method with melamine and cyanuric chloride as starting material was also reported and nanobelt $g-C_3N_4$ was obtained.^[23] In our present work, a layered, porous $g-C_3N_4$ was synthesized following a modified solvothermal-roasting processes by using melamine and cyanuric chloride as precursors. The procedure is described in Scheme 1. With the porous $g-C_3N_4$ as support, Ag/ $g-C_3N_4$ hybrid material was then prepared by a facile impregnation-roasting method.

Carbon and nitrogen stoichiometry of the samples was determined by elemental analysis (Table 1). Results show that $g-C_3N_4$ possess a C/N molar ratio approaching 0.73 (theoretical value is 0.75). Even after



porous g-C₃N₄

Scheme 1. The preparation process for porous $g-C_3N_4$.

Table 1. Physicochemical properties of as-prepared samples

Catalyst	Molar ratio C/N	Surface area [m ² g ⁻¹]	Band gap [eV]
bulk g-C ₃ N ₄	0.71	10	2.71
g-C ₃ N ₄	0.73	34	1.98
Ag/g-C ₃ N ₄	0.73	32	1.91

the impregnation-roasting procedure to introduce Ag NPs, the C/N molar ratio in $Ag/g-C_3N_4$ was not changed.

To further study the structures of the materials, the Brunauer-Emmett-Teller (BET) specific surface area and the Barrett-Joyner-Halenda (BJH) pore size distribution were measured to provide concrete evidence (Figure S1, Supporting Information). The nitrogen sorption isotherm of as-prepared samples exhibited typical V shape isotherms and H3 shape hysteresis loop, which indicated that the materials have a slit mesoporous structure (Figure S1a, Supporting Information). The specific surface area of the as-synthesized $g-C_3N_4$ sample (34 m²g⁻¹) is approximately three times higher than that of bulk g-C₃N₄, whereas the Ag/g-C₃N₄ composite exhibited a similar BET surface area $(32 \text{ m}^2 \text{g}^{-1})$. The pore size distributions of the samples are shown in the Supporting Information, Figure S1b, which revealed that the pore size of mesopores was concentrated in 2-5 nm and the material still possessed a large number of pores after introducing Ag nanoparticles.

Figure 1A shows a TEM image of the porous g-C₃N₄ employed in our studies. As can be seen, g-C₃N₄

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Figure 1. TEM images of A) g-C₃N₄, B) Ag/g-C₃N₄.

possessed a layered structure, and it presents in the form of a thin sheet with irregular morphology. Ag nanoparticles (Ag NPs) were well anchored on g- C_3N_4 nanosheets, which were prepared by a facile impregnation-roasting method; Figure 1B indicates a relatively uniform size and shape of the Ag NPs, with the particle diameter of about 15 nm, generated on the surfaces of g- C_3N_4 . On the other hand, as the reference samples, Ag NPs and Ag NPs/AC, were also synthesized. The TEM images of them showed that the Ag NPs in both of the samples had similar sizes to those depicted in Figure 1B (Figure S2a and S2b, Supporting Information).

XRD patterns of the as-prepared Ag/g-C₃N₄ composite and $g-C_3N_4$ are shown in Figure 2, the results confirmed graphitic-like layer structures in Ag/g- C_3N_4 . The diffraction peaks at 20 of $13^{\circ}[(100)]$ diffraction plane] and 28° [(002) diffraction plane] are the characteristic peaks of g-C₃N₄ (Figure 2), which can be attributed to the in-plane structural packing motif of tri-s-triazine units and the interlayer stacking of the conjugated aromatic system, respectively.^[24] However, the diffraction peaks of $g-C_3N_4$ were very weak in the XRD pattern of Ag/g-C₃N₄, this might be attributed to the fact that the XRD signals were covered by Ag NPs. The characteristic peaks are at 38°, 44°, 65°, and 77° which can be attributed to the (111), (200), (220), and (311) lattice planes of metallic Ag, respectively. Such observations indicated that the Ag NPs were successfully loaded on the $g-C_3N_4$ after the impregnation-roasting procedure.

The surface composition and chemical state of elements in the as-prepared $g-C_3N_4$ and $Ag/g-C_3N_4$ nanocomposite were further investigated by XPS spectra, as shown in Figure 3 and Figure S3 (Supporting Information).

Figure 3A shows the XPS survey spectra of the g- C_3N_4 and Ag/g- C_3N_4 nanocomposite. Comparing these

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spectra, new Ag peaks were observed, and the decoration of Ag nanoparticles on the $g-C_3N_4$ surface was further confirmed, which is in good agreement with the TEM and XRD results. The XPS Ag 3*d* spectrum of Ag/g-C₃N₄ and Ag NPs is shown in Figure 3B, in which the peaks at 367.8 and 373.9 eV are ascribed to Ag 3*d*_{3/2} [Ag(0)] and Ag 3*d*_{5/2} [Ag(0)] and the result is in accordance with previous reports.^[25] Moreover, the binding energy values of Ag 3*d* in Ag/g-C₃N₄ are slightly lower than those of Ag NPs. The shift might result from the strong interaction between Ag NPs and g-C₃N₄.

Figure 3C and D show the high resolution C1s and N1s spectra of the $Ag/g-C_3N_4$, which can be divided



Figure 2. XRD patterns of the as-prepared Ag/g-C₃N₄.





Figure 3. A) XPS survey spectra of the g- C_3N_4 and Ag/g- C_3N_4 , high resolution XPS spectra Ag 3*d*. B) Of as-prepared Ag/g- C_3N_4 and Ag NPS, high resolution XPS spectra C1s (C) and N1s (D) of Ag/g- C_3N_4 .

into three peaks, respectively. C1s at 286.3 eV and N1s at 397.4 eV are assigned to the sp^2 C=N bond in the s-triazine ring. The peaks at 286.9 eV and 283.5 eV in the C1s zone are attributed to electrons originating from an sp^2 C atom attached to an NH₂ group and to an aromatic carbon atom.^[23,26] The N1s peaks centered at 399.2 eV and 403.2 eV are ascribed to N atoms bonded to three C atoms [N-(C)₃] and the N atoms located in the heptazine ring and as bridging atom, respectively.^[23,26] The high resolution C1s and N1s spectra of the Ag/g-C₃N₄ are in agreement with those of g-C₃N₄ (Figure S3a and b, Supporting Information), which indicated that after loading Ag nanoparticles, there were no significant changes to the graphitic C–N network.

Since the spectral absorption property of a photocatalyst is very important, UV-vis diffuse reflectance spectra (DRS) was used to examine the optical absorption properties of the photocatalysts. The UV-vis DRS of Ag NPs, $Ag/g-C_3N_4$, $g-C_3N_4$ and bulk $g-C_3N_4$ samples are demonstrated in Figure 4.



Figure 4. UV-vis diffuse reflectance spectra of $g-C_3N_4$, bulk $g-C_3N_4$, Ag NPs, and Ag/g- C_3N_4 nanocomposites.

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The absorption edge of the porous g-C₃N₄ nanosheets indicated a bathochromic shift from approximately 454 to 626 nm as compared with the bulk g-C₃N₄. After loading Ag nanoparticles on the surface of g-C₃N₄, the absorption intensities of Ag/g-C₃N₄ composite became stronger in the whole spectrum window of interest, especially in the visible-light region, which might be due to the strong LSPR absorption of Ag nanocrystals and further confirmed the formation of Ag NPs.^[27] In addition, the absorption spectra were largely red-shifted, and a broad absorption ranging from ~465 to ~660 nm was detected. As for the as-prepared Ag NPs sample, it clearly exhibits a wide light absorption in the whole UV-vis range of 200-800 nm. The results of UV-vis DRS show that the fabrication of the $Ag/g-C_3N_4$ composite can greatly improve the optical absorption property and increase the utilized efficiency of visible light, which is favorable for the enhancement of the photocatalytic activity.

The recombination process of electron-hole pairs of semiconductors can release energy, which can be detected by PL emission. A lower photoluminescence intensity is a general indication of a lower recombination rate of electron-hole pairs, and usually results in higher photocatalytic activity.^[28]

Figure 5 shows the PL spectra of bulk g-C₃N₄, g-C₃N₄ and Ag/g-C₃N₄ samples excited at 320 nm. The PL spectra of bulk g-C₃N₄ have a strong emission peak at around 454 nm, which is assigned to the recombination of the photoinduced electron-hole pairs of bulk g-C₃N₄. As can be seen from the figure, there is an obvious decrease in the PL intensity of g-C₃N₄ and Ag/g-C₃N₄ compared with that of bulk g-C₃N₄. Notably, the much lower photoluminescence intensity



Figure 5. Photoluminescence (PL) spectra of bulk g-C₃N₄, g-C₃N₄ Ag/g-C₃N₄ samples (excitation wavelength: $\lambda = 320 \text{ nm}$)

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of the Ag/g-C₃N₄ indicated that the separation of photogenerated electron-hole pairs in Ag/g-C₃N₄ was more efficient, because the excited electron could be transferred directly between the Ag NPs and g-C₃N₄ through their mutual interface.^[29] It might indicate that the Ag/g-C₃N₄ composite possessed higher photocatalytic activity under visible light irradiation than g-C₃N₄ or Ag Nps.

Oxidative Amidation of Aldehydes

Amides are functional groups of great importance in polymers, natural products, and pharmaceuticals.^[30] Recently, the oxidative transformation of aldehydes to amides has received much attention. In 2006, Li's groups reported an excellent example with Cu(I) as catalyst and AgIO₃ as oxidant.^[31] Subsequently, Marks and co-workers described the catalytic amidation of aldehydes and amines by a lanthanide catalyst.^[32] Yamaguchi et al. also developed a CuI/2-pyridonate catalytic system.^[33] Other catalyst-free methods using stoichiometric oxidants, such as TBHP,^[34] Oxone^[35] and hydrogen peroxide^[36] were also reported. However, most of these methods still have some limitations, such as the need for expensive noble transition metals, stoichiometric oxidants, and poor substrate scope as well as low atom efficiency. Thus, the visible light-promoted oxidative amidation of aldehydes might provide a sustainable approach. Until now, there are only a few examples on the transformation reported. Au@SiO₂ was reported as a highly efficient photocatalyst for the amidation of benzaldehyde and morpholine under green laser irradiation with H₂O₂ as oxidant.^[37] Recently, Leow also presented an elegant approach to the reaction by using phenazine ethosulfate as visible light photocatalyst in air via an in situ generation of H_2O_2 .^[38] However, the photocatalyst seemed easy to be decomposed and could not be recovered.

In our present work, the as-prepared $Ag/g-C_3N_4$ was utilized as visible light photocatalyst, to explore the oxidative amidation of aldehydes. Our initial research focused on the model reaction of 4-bromobenzaldehyde (**1b**) with pyrrolidine (**2a**) at ambient temperature (Table 2).

At beginning, the model reaction was performed with 5 mol% of $Ag/g-C_3N_4$ as catalyst under air atmosphere and a 25 W CFL was used as the source of visible light. Several kinds of solvents were scanned at first. It can be seen from Table 2 that toluene, CH₃CN, DMF, DCM were not suitable for the reaction and a 92% of yield was achieved in THF solution (entries 1–4 vs. entry 5, Table 2). Subsequently, to further investigate the photocatalytic property of $Ag/g-C_3N_4$, a series of control experiments were carried out: g-C₃N₄, Ag NPs and even AgNO₃ were used as asc.wiley-vch.de



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Entry	Light	Photocat. (mol%)	Solvent	Yield [%] ^[b]
1	+	$Ag/g-C_{3}N_{4}(5)$	toluene	n.r.
2	+	$Ag/g-C_{3}N_{4}(5)$	CH ₃ CN	10
3	+	$Ag/g-C_{3}N_{4}(5)$	DMF	trace
4	+	$Ag/g-C_{3}N_{4}(5)$	DCM	trace
5	+	$Ag/g-C_{3}N_{4}(5)$	THF	92
6 ^[c]	+	$g-C_3N_4$	THF	35
7	+	Ag NPs (10)	THF	28
8	+	$AgNO_3$ (10)	THF	29
9	+	Ag NPs/AC (10)	THF	trace
10	+	Ag NPs-TiO ₂ (10)	THF	trace
11	_	$Ag/g-C_{3}N_{4}(5)$	THF	10
12	+	none	THF	n.r.
13	+	$Ag/g-C_{3}N_{4}$ (10)	THF	89
14	+	$Ag/g-C_3N_4$ (20)	THF	85
15 ^[d]	+	$Ag/g-C_{3}N_{4}(5)$	THF	98
16	+	$Cu/\sigma - C N$ (10)	THE	45

Table 2. Optimization of the reaction conditions.^[a]

^[a] Reaction conditions, unless otherwise noted: aldehyde 1b (0.10 mmol), amine 2a (2.0 equiv.), solvent (1.0 mL), photocatalyst, 25 W CFL at ambient temperature in air for 30 h.

^[b] Yield of isolated product.

^[c] $g-C_3N_4$ (5 mg).

^[d] O_2 (with balloon). Abbreviations: CFL=compact fluorescent lamp, THF=tetrahydrofuran, DMF=*N*,*N*-dimethylformamide, DCM=dichloromethane, n.r.=no reaction.

photocatalyst in the oxidative amidation, respectively. However, only poor yields were observed in these reactions (entries 6–8). Considering the possible support effect on Ag Nps, Ag NPs/AC and Ag Nps/TiO₂ were also tested. However, only trace reaction occurred (entries 9 and 10). Furthermore, even after 48 h reaction, only 10% yield was obtained in the dark (entry 11). Moreover, a blanket reaction was also set up under visible light, and no reaction was observed in the absence of a photocatalyst (entry 12). These results above indicated that the combination of Ag NPs and g-C₃N₄ did enhance the photocatalytic performance of g-C₃N₄.

On the other hand, the loadings of the catalyst were also examined. It can be seen that 5 mol% loading is the best choice (entries 13 and 14 vs. entry 5). The reaction was also carried out under an oxygen atmosphere instead of air, a 98% of yield was achieved after 15 h (entry 15). Considering more convenient handling, we still selected to carry out the reaction in air. Specifically, we also prepared Cu/g-C₃N₄ as catalyst in the reaction. Obviously, the introduction of

copper gave much worse photocatalytic activity than that of silver (entry 16).

Having identified our optimized reaction conditions, the $Ag/g-C_3N_4$ catalyzed oxidative amidation of aldehydes under visible light irradiation was extended to various substrates successfully and good functionalgroup tolerance was observed. All of the results are summarized in Scheme 2.

As can be seen, benzaldehydes bearing Br, Cl, F, NO₂, CF₃, MeO, and Me groups at *para*-positions reacted with pyrrolidine (**2a**) to afford the products **3b**-**3h** in 65–95% yields. The results indicated that benzaldehydes with electron-withdrawing groups on the benzene rings seemed to react more efficiently than those with electron-donating groups (**3b–3f** *vs.* **3g** and



[a] Reaction conditions: aldehyde 1 (0.1 mmol), amine 2 (2.0 equiv.), photocatalyst (5 mol%), THF (1.0 mL), 25 W CFL irradiation at ambient temperature for 30 h. Isolated yields.

Scheme 2. Ag/g-C₃N₄-catalyzed aerobic oxidative amidation of aromatic aldehydes and amines.

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3h). Treatment of substrates bearing different substitution positions also furnished the desired products in good to excellent yields (**3i–3l**). Disubstituted aromatic aldehyde **3m** also gave the targeted product in 93% yield. Both β - and α -naphthaldehydes were also tested in the reaction, providing **3n** and **3o** in 77% and 90% yields, respectively.

Reactions of morpholine (2b) with a series of *para*and *meta*-substituted benzaldehydes were well-tolerated, and provided the corresponding products **3q-3u** in 60–90% yields. Piperidine (2c) was also utilized in the photocatalytic reaction. The transformation still proceeded very well and the desired products **3v-3z** were obtained in good to excellent yields.

On the other hand, it is worthy to note that dibutylamine was also examined instead of cyclic amines in the oxidative amidation, but there was no desired product observed.

Some heteroaromatic aldehydes were then investigated in the reaction (Scheme 3). Generally, the Ag/g- C_3N_4 catalyzed oxidative amidation of heteroaromatic aldehydes and pyrrolidine afforded the desired amides **4a**–**e** in moderate to good yields under visible light irradiation. It should be noted that picolinaldehyde reacted with **2a** to afford the corresponding product **4c** in 42% yield under the present conditions.

Under standard conditions but with sunlight irradiation instead of CFL, aldehyde **1b** reacted with pyrrolidine **2a** smoothly to give **3b** in moderate yield in sunlight (about 10 h) (Scheme 4A). Moreover, in order to prove the scalability and practicality of the novel photocatalytic system, a 1-mmol scale reaction was performed under the standard conditions: an excellent yield was achieved after 40 h (Scheme 4B).



[a] Reaction conditions: aldehyde 1 (0.1 mmol), pyrrolidine 2a (2.0 equiv.), photocatalyst (5 mol%), THF (1.0 mL), 25W CFL irradiation at ambient temperature for 30 h. Isolated yields.

Scheme 3. Ag/g-C₃N₄-catalyzed aerobic oxidative amidation of heteroaromatic aldehydes and pyrrolidine.

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Scheme 4. A) Oxidative amidation of 4-bromobenzaldehyde in sunlight. B) Expanding the reaction of 4-bromobenzaldehyde under standard conditions.

One of the advantages of heterogeneous catalysts is their easy separation from the reaction mixture. The Ag/g-C₃N₄ catalyst could be separated and recovered conveniently by centrifugation from the reaction mixture, and then, fresh substrates and solvent were added to set up a new reaction. Following this procedure, the catalyst was recycled effectively, and the results are summarized in Scheme 5. We found that the yields of the second and third runs are lower but very close. It might be due to some silver nanoparticles falling off from the Ag/g-C₃N₄ composite in the first washing process, and then, the content of silver in the catalyst tended to remain stable.^[39]



Scheme 5. The recyclability of $Ag/g-C_3N_4$ photocatalyst.

To investigate the mechanism of the reaction, several control reactions were carried out (Scheme 6). The freshly distilled THF solvent (refluxed and distilled from sodium) was stirred with the Ag NPs/C₃N₄ catalyst under an oxygen atmosphere and visible light for 1 day, and *ca.* 10% peroxide of THF (5) was observed from ¹H NMR (Figure S5 and S6, Supporting Information); and then, **1b** and **2a** were added and the



Scheme 6. Control reactions for mechanism investigation.



mixture was stirred and monitored by TLC. The reaction was finished in 3 h, and 98% of **3b** was obtained.

In the classical mechanism for the photo-promoted auto-oxidation of THF,^[40] the formation and the excitation of the charge-transfer complex by the light, followed by the dissociation of the excited-state complex, were believed to be the key steps for the auto-oxidation of THF to give the hydroperoxide product **5** (Scheme 7A). Thus, referring to the mechanism for the Ag/g-C₃N₄-catalyzed oxidative decomposition of organic compounds,^[20a] we propose that the charge-transfer between oxygen and THF would occur in two separate steps on the surface of Ag/g-C₃N₄ under visible light. The detailed description is shown in Scheme 7B).



Scheme 7. A) The key steps for the classical mechanism of photo-oxidation of THF. B) The electron-transfer approach on $Ag/g-C_3N_4$ surface under visible light irradiation.

Under visible light irradiation, $g-C_3N_4$ can be excited to generate conduction band electrons (e⁻) and valence band holes (h⁺).^[20a,8] Furthermore, with the introduction of Ag NPs, the recombination of photogenerated electron-hole pairs was inhibited efficiently, because the excited electron could be transferred directly between the Ag NPs and $g-C_3N_4$ through their mutual interface (refer to the PL spectra in Figure 5). Thus, the photogenerated electron acceptor O₂ to super-oxide radical anion. On the other hand, THF released an electron on the valence band holes to give a THF cation. Following the approach above, the rate for the auto-oxidation of THF to **5** was improved efficiently.

On the other hand, in order to learn more details for the reaction, a standard reaction of **1b** and **2a** was also carried out in THF- d_8 . From the crude ¹H NMR spectra (Figure S7, Supporting Information), an increased water peak was observed.^[41] Thus, a plausible mechanism for the visible light-promoted oxidative amidation was proposed as the following: at first, Ag NPs/C₃N₄ catalyzed the oxidation of THF with the promotion of light; and then, the THF hydroperoxide (**5**) formed *in situ* worked as a highly efficient oxidant reacting with the enamine intermediate (**3**') to give target molecule (Scheme 8).



Scheme 8. Plausible mechanism of the $Ag/g-C_3N_4$ -catalyzed oxidative amidation of aldehydes and amines in THF under visible light irradiation.

Conclusions

In conclusion, we have synthesized a layered porous $g-C_3N_4$ via a solution-process and roasting approach, and then, Ag NPs were successfully anchored on the surface of $g-C_3N_4$ by a facile impregnation-roasting method. An Ag/g-C₃N₄-catalyzed aerobic oxidative amidation of aldehydes under visible light irradiation has been developed. Mainly because of the synergetic effects between $g-C_3N_4$ and Ag NPs, the photocatalytic system can realize an excellent catalytic performance to generate benzamide bonds. This study might provide a new perspective for photocatalytic organic synthesis and environment-friendly transformations. Further studies to gain more mechanistic details of this reaction and apply this strategy to other organic transformations are ongoing in our laboratory.

Experimental Section

All chemicals and solvents as reference were procured from Aladdin (Shanghai, China), Alfa Aesar (Shanghai, China), TCI (Japan) and used as received.

Characterization

The morphology of the photocatalysts was observed by transmission electron microscopy (TEM, JEOL JEM-2100F). The crystal structures of the samples were determined using an X-ray diffractometer (XRD, Bruker D8 AD-VANCE) with a 2 scope of 5–90°at 40 kV and 40 mA using Cu-K α as the irradiation source (λ = 1.54 Å). X-ray photo-

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electron spectroscopy (XPS: PHI Quantera II, Japan) was used to examine the surface properties of the catalysts. The Brunauer-Emmett-Teller (BET) method was used to calculate the specific surface areas of the samples. The N₂ adsorption-desorption isotherms at 77 K were measured using an adsorption instrument (ASAP 2020, Micromeritics Company, USA) to evaluate their pore structures. The UV-vis diffuse reflectance spectra (UV-vis DRS) of the samples were recorded on a UV-vis spectrometer (Shimadzu UV-3600) with an integrating sphere. BaSO₄ was used as a reference sample. The photoluminescence (PL) spectra were recorded on a Varian Cary-Eclipse 500. NMR spectra were recorded on a Bruker AVANCE III-400 (400 MHz for ¹H, 101 MHz for ¹³C) instrument in the indicated solvent. Chemical shifts are reported in units of parts per million (ppm) relative to the signal for internal tetramethylsilane (0 ppm for ¹H) for solutions in CDCl₃. Multiplicities are reported by using the following abbreviations: s, singlet; d, doublet; dd, doublet of doublets; t, triplet; m, multiplet; br, broad singlet; and, J, coupling constants in Hertz. High resolution mass spectroscopy data of the product were collected on an Agilent Technologies 6540 UHD Accurate-Mass Q-TOF LC/MS (ESI).

Synthesis of Bulk g-C₃N₄ and Porous g-C₃N₄

Bulk g-C₃N₄ was prepared by heating melamine (5.0 g) to 550 °C for 4 h with a ramping rate of 2.5 °C min⁻¹ under N₂ atmosphere.^[22]

The porous $g-C_3N_4$ was obtained by a solution-process and then roasting processes. Typically, 10 mmol 1,3,5-trichlorotriazine and 5 mmol melamine powders were put into a 100-mL Teflon-lined autoclave, which was then filled with acetonitrile up to 60% of the total volume. The mixture was stirred at 180 °C for 48 h, and then the resulting sample was sequentially washed with acetonitrile, distilled water and absolute ethanol several times and dried under 60 °C for 12 h to get the orange power.^[23] Then, the power was added to a porcelain cup and calcined under N₂ flow at 500 °C for 2 h with the heating rate being 2 °C min⁻¹, the as-prepared samples were collected and ground carefully to get the final products.

Synthesis of Ag/g-C₃N₄ Nanocomposite

In a typical procedure, porous $g-C_3N_4$ (400 mg) was dispersed in a mixed solution of 50 mL of distilled water and 32 mg of AgNO₃, ultrasonicated for half an hour, then in the dark this solution was stirred vigorously at 60 °C to evaporate the water. The obtained sample was dried at 60 °C for 12 h, and then the sample was heated to 500 °C for 2 h at a rate of 2 °Cmin⁻¹ under N₂ atmosphere to obtain the final Ag/g-C₃N₄ composite. For comparison, two control samples were also prepared. The Ag/C preparation also followed the above impregnation–roasting method, which used glucan as carbon source and the same silver loading with Ag/g-C₃N₄. The Ag NPs was prepared by a classical liquid phase reduction approach.

Oxidative Amidation of Aldehydes and Amines

A 25W compact fluorescent light (CFL) bulb (Panasonic 25W cool daylight, 6500 K color temperature) and 40 mL sealed tubes was used.

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Typical Procedure for Ag/g-C₃N₄-Catalyzed Oxidative Amidation of Aromatic Aldehydes under Visible-Light Irradiation



A 40-mL oven-dried sealed tube equipped with a magnetic stir bar was charged with aldehyde **1** (0.1 mmol), amine **2** (0.20 mmol, 2 equiv.), $Ag/g-C_3N_4$ (5 mol%), and freshly distilled THF (1.0 mL) in air. The tube was capped and exposed to a 25 W CFL bulb placed approximately 10 cm from the tube at ambient temperature, the reaction time was 30 h unless otherwise specified. After completion of the reaction, the mixture was concentrated to yield the crude product, which was further purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 10:1) to give the desired product **3**; yield: 60–95%.

The detailed characterization data for 3a-3z are provided in the Supporting Information.

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FULL PAPERS

12 Synthesis of Ag/g-C₃N₄ Composite as Highly Efficient Visible-Light Photocatalyst for Oxidative Amidation of Aromatic Aldehydes

Adv. Synth. Catal. 2016, 358, 1-12

Lingling Wang, Min Yu, Chaolong Wu, Nan Deng, Chao Wang, Xiaoquan Yao*

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$$R^{1} \stackrel{O}{\underset{l}{\amalg}} H + HN_{R^{3}}^{R^{2}} \xrightarrow{Ag/g-C_{3}N_{4}, THF}_{air, 25 W CFL} R^{1} \stackrel{O}{\underset{l}{\amalg}} N_{R^{3}}^{-R^{2}}$$