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Visible-Light-Induced Selectively Photocatalytic Aerobic Oxidation of Amines into Imines on Cu/graphene

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Graphene can stabilize metallic copper nanoparticles and enable them to exhibit excellent photocatalytic activity for aerobic oxidation of various primary and secondary amines into corresponding imines. The copper nanoparticles stabilized on graphene absorb the energy of visible light via the localized surface plasmon resonance, and produce energetic hot electrons that activate the reactants adsorbed on the surface of copper nanoparticles. The formation of imines involves a selective oxygenation of amines to aldehydes and a subsequent condensation with amines to form imines.

Introduction

Imine derivatives are important building blocks for the synthesis of fine chemicals, pharmaceuticals and pesticides, and they are traditionally synthesized through condensation of an amine with a suitable carbonyl compound, aldehydes or ketones.[1] However, the wide application of this method is still limited by the low selectivity for the condensation of primary aliphatic aldehydes and amines, low reaction efficiency and harsh reaction conditions.[2] The direct oxidation of amines, which directly uses benign and readily available molecular O_2 or air as oxidant, has attracted much interest because it is hopeful to solve the above problems.[3,4] For example, Furukawa et al. found that intermetallic Pd_3Pb supported on Al_2O_3 can act as an efficient heterogeneous catalyst for the oxidation of various amines.[5] For many heterogeneous catalysts, the reactivity of dioxygen is difficult to control, the selectivity of target product is usually poor, and the substrate scope is limited.[2]

Recently, selectively photocatalytical oxidation of amines has received increased attention because it allows the oxidation reactions to occur at lower temperature and use O_2 as oxidant under renewable solar light irradiation.[6-8] For instance, Zhao et al. reported the photocatalytic oxidation of aromatic amines to corresponding imines using TiO_2 as the photocatalyst.[9] However, most of these reactions were only carried out under UV light. Therefore, the development of visible-light-driven catalysts for aerobic oxidation of amines remains a challenge. Different photocatalysts have been proposed to implement the oxidation reaction. Sadow et al. studied the photocatalytic performance of rhodium phosphine complexes for the aerobic oxidation.[10] Lin et al. found that some doped metal-organic frameworks showed photocatalytic activity for the oxidation.[11] Blechert et al. developed a metal-free, heterogeneous catalysis protocol for the oxidation using carbon nitride and visible light.[12] Tanaka et al. found various amines including primary, secondary, and cyclic amines could be photocatalytically transformed into corresponding imines in high yields by using Nb_2O_5 as photocatalyst and O_2 as oxidant under visible light.[13]

Localized surface plasmon resonance (LSPR) is the resonant photon-induced coherent oscillation of charge at the metal–dielectric interface, established when the photon frequency matches the natural frequency of metal surface electrons oscillating against the restoring force of their positive nuclei. [14-16] The conduction electrons of the nanoparticles of gold (Au), silver (Ag) and copper (Cu) can harvest visible light energy through the LSPR effect to produce "hot" electrons with high energy at the surface of metallic nanoparticles.[17] These "hot" electrons can facilitate chemical reactions and improve the yield of chemical transformations under mild conditions.[7,18,19] Studies on light-driven reactions catalyzed by Au or Ag nanoparticles have formed the basis of a new and fast-expanding field in green photocatalysis.[14] Recently, Zhu et al. found that Au-Pd alloy nanoparticles can strongly absorb visible light and efficiently catalyze the aerobic oxidation reactions of primary amines.[20] Although Cu nanoparticles exhibit strong LSPR absorption in visible light range and are catalytically active for many reactions,[21,22] few studies on the photocatalytic performance of Cu nanoparticles have been reported due to their poor chemical stability under catalytic reaction conditions. Cu nanoparticles are easily oxidized to Cu_2O or CuO in the presence of oxygen.

Recently, we found that Cu nanoparticles can be effectively stabilized by using graphene sheets as the support, and the Cu/graphene can controllably catalyze the coupling reactions of nitroaromatics to corresponding azoxy or azo compounds under visible light irradiation.[19] Because Cu based catalysts can thermally catalyze many organic reactions and they are more easily and abundantly available, herein we employ graphene supported Cu nanoparticles as the photocatalyst for aerobic oxidation of amines under visible light irradiation, and report its excellent photocatalytic performance.

Experimental

Preparation of 5wt% Cu/graphene catalyst. According to previous work,[19] Cu/graphene catalyst with a Cu loading of 5wt% has suitable LSPR absorption intensity and exhibits the best catalytic activity. Therefore, the 5wt% Cu/graphene catalyst was employed in this work for the photocatalytic aerobic oxidation reaction of benzylamine. The catalyst was prepared by liquid reduction method. Firstly, 16 mg $Cu(OAc)_2•H_2O$ and 95 mg graphene were dispersed into 30 mL oleylamine under sonication for 0.5h. After that, the suspension was slowly heated to 230°C and kept at this temperature for 6 hours. Oleylamine acted as not only solvent but also reducing agent. It can transfer electrons to Cu^{2+} and reduce them to Cu^0. The mixture was separated and put into vacuum drying chamber at 60°C for 24 h. Then, a 5wt% Cu/graphene catalyst was obtained. The crystalline phases of the catalyst were characterized by X-ray diffractometer (XRD, Rigaku D-Max/RB). The microstructures of the catalyst were investigated by high-resolution transmission electron microscope (HRTEM, JEM-2010). X-ray photoelectron spectroscopy (XPS) was measured on a Kratos XSAM800 spectrometer, using Al Ka (hk=1486.6 eV) X-ray source as the excitation source. The UV-visible absorption spectra of the catalyst were examined by a HITACHI U-3900 spectrometer with Al_2O_3 as a reference.

Photocatalytic aerobic oxidation reactions of amines. The photocatalytic aerobic oxidation reactions of amines were conducted in 1 atm O_2 atmosphere. The whole reaction system was strictly controlled at 40^{o}C during the reaction process by an oil bath. The reactant mixture consists of 10 mL absolute ethanol, 1 mmol amines and 100 mg 5wt% Cu/graphene catalyst. A 300W Xe lamp (wavelength from 400-800 nm) was employed as light source to irradiate the reaction system. The irradiation intensity was 0.5 Wcm^{-2}. The dependence of the catalytic performance on the wavelength range of light was investigated by employing various low pass optical filters to block light below specific cut-off wavelengths while keeping the light intensity the same with the reaction system without optical filter. For instance, a filter with the cut-off wavelength of 450 nm can block light with wavelengths shorter than 450 nm (the system is irradiated by light with wavelengths between 450 and 800 nm). Similarly light with wavelengths in the ranges of 520-800 and 600-800 nm were applied to the reaction system using filters with cut-off wavelengths of 520 nm and 600 nm, respectively. After reaction, 2 mL aliquots were collected, centrifuged, and then filtered through a Millipore filter (pore size 0.22 μm) to remove the catalyst particulates. The filtrates were analyzed by BRUKER SCION SQ 456 GC-MS to measure the concentration change of reactants and products. The quantitative analysis of specific analytes was detected by SIM mode in GC-MS.

Results and Discussion

Figures 1A and B show the Transmission Electron Microscopy (TEM) images of the 5wt% Cu/graphene catalyst. Spherical Cu nanoparticles with a mean diameter of 10 nm are uniformly dispersed on graphene sheets. The interplanar crystal spacing of Cu nanoparticles is 0.19 nm, corresponding to the Cu (111) crystal faces. From the X-ray diffraction patterns (XRD) (Figure 1C), the peak at $2\theta=43.3°$ is indexed to Cu (111), suggesting that the graphene sheets can effectively stabilize metallic Cu nanoparticles. The graphene used in this work is obtained from reduction of graphene oxide. In this process, the long-range ordered stacking of graphene oxide was dissociated of by random interlayer expansion and exfoliation, leading to the broad diffraction peak at 23.5^{o}. The existence of metallic Cu is also supported by the X-ray photoelectron spectroscopy (XPS) (Figure 2A). The binding energies of Cu $2p_{1/2}$ at around 951.9 eV and Cu $2p_{3/2}$ at 932.4 eV, respectively, can be attributed to the Cu^0 state, confirming that Cu exists on the graphene sheets as the metallic phase. In the UV-vis spectra (Figure 1D), the absorption peak at approximately 558 nm is due to the LSPR absorption of Cu nanoparticles. Meanwhile, the absorption intensity of Cu/graphene increases with the Cu loading increasing.

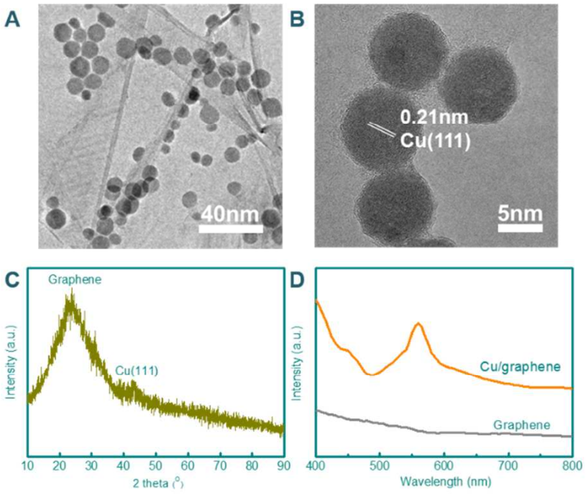


Figure 1. TEM images (A, B), XRD patterns (C), and UV-Vis absorption spectra (D) of fresh 5wt% Cu/graphene catalyst.

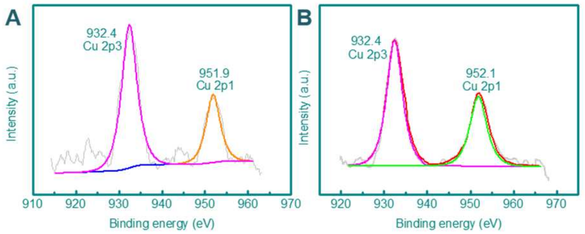


Figure 2. XPS profile of fresh 5wt% Cu/graphene (A) and used Cu/graphene after 5 rounds (B).

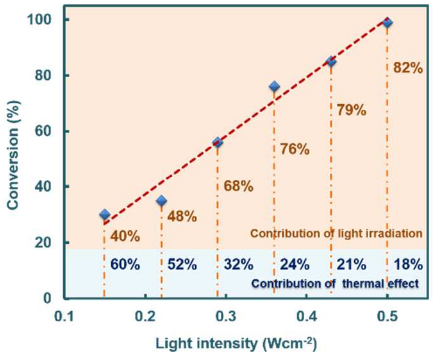


Figure 3. Dependence of the catalytic activity of 5wt% Cu/graphene for the aerobic oxidation of benzylamine into N-benzylidenebenzylamine on the irradiation intensity.

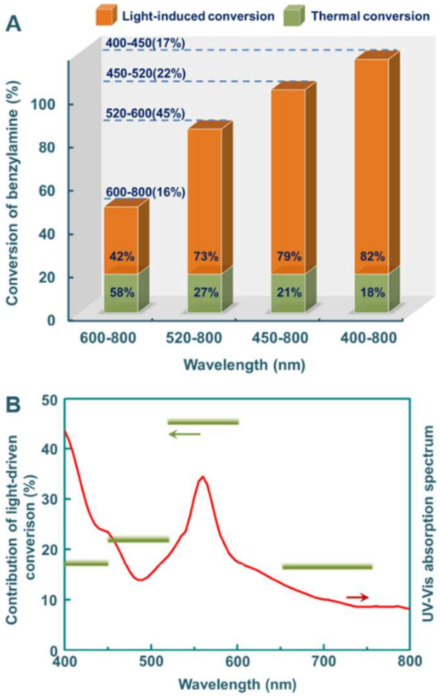
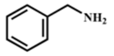
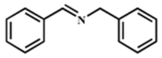
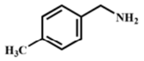
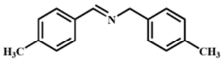
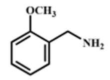
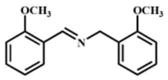
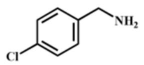
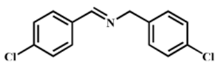
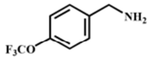
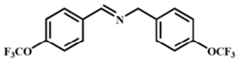
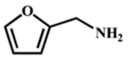
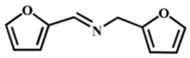
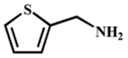
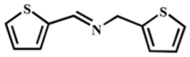
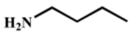
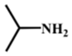


Figure 4. Dependence of benzylamine conversion on the irradiation wavelength (A), and the absorption spectrum of the photocatalytic reaction, in which the light driven conversion is plotted against the irradiation wavelength (B).

In the control experiments using only graphene as the catalyst in O_2 atmosphere or using the Cu/graphene as the catalyst in Ar, the oxidation reaction of benzylamine did not occur. However, the 5wt% Cu/graphene exhibits high photocatalytic activity and selectivity. The conversion of benzylamine is 99% and the selectivity of N-benzylidenebenzylamine is 93% (Table 1, entry 1). Control experiments reveal that the Cu/graphene catalyst in dark (without irradiation) can only achieve a benzylamine conversion of 18%, indicating that the enhanced catalytic activity results from the light irradiation. The reaction can also occur in air atomsphere with a lower conversion of benzylamine (82%) comparing with that in O_2. Under the same temperature, increasing of irradiation intensity resulted in an almost linear growth of the benzylamine conversion (Figure 3). To ensure that the thermal effect could be discounted, the reaction temperature was carefully controlled and maintained at 40°C. The contribution of light induced conversion was calculated by subtracting the conversion in the dark (thermal effect) from the total one under irradiation. The relative contributions of irradiation and thermal effect to the total conversion are shown in Figure 3. The contribution of light induced conversion increases with the light intensity. For instance, the contribution of light induced conversion was 82% ((99-18)/99×100%) at a light intensity of 0.5 Wcm^{-2} , while it is only 40% at a light intensity of 0.15 Wcm^{-2}. These results indicate the indispensable role of light irradiation.

The wavelength dependence of the catalytic activity was illustrated in Figure 4A. Without any filters, the light intensity and the reaction temperture was strictly controlled at 0.5 W/cm^2 and 40 ^{o}C, respectively. Then, a series of optical low-pass filters were employed to block light below specific cut-off wavelengths. The irradiation of the light with wavelength range from 400 to 800 nm gives a benzylamine conversion of 99%. The conversion decreases to 85%, 67% and 31% when the wavelength range of the irradiation is 450-800, 520-800, and 600-800 nm, respectively. By deducting the contribution of thermal reaction, the contribution of 400-450 nm light accounts for about 17% ((99-85)/(99-18)×100%) in the total light-induced conversion. Similarly, the light in the wavelength range of 450-520, 520-600 and 600-800 nm, respectively accounts for 22%, 45% and 16% of the light-induced conversion. These values agree well to the UV-visible absorption spectrum of the Cu/graphene catalyst (Figure 4B). Because the Cu/graphene catalyst has a strong SPR absorption at about 558 nm, the light in the wavelength range of 520-600 nm contributions the highest light-induced conversion. This further confirms that the light absorbed by Cu nanoparticles is the major driving force of this reaction. The conduction electrons of Cu nanoparticles gain the energy of incident light through the LSPR effect and yield energetic electrons at the surface of nanoparticles. The resonance of conduction electrons with the electromagnetic field of incident light results in a significant enhancement of the local electromagnetic field near the surface of Cu nanoparticles. The light-excited electrons can activate adsorbed reactant molecules on the surface of Cu nanoparticles. The enhanced local field may also promote the reaction.

Table 1. Photocatalytic aerobic oxidation of primary benzylic amines over a 5wt% Cu/graphene catalyst[a].

Entry	Substrate	Product	t(h)	Conv. (%)	Select. (%)
1			6	99	93
2			6	99	95
3			6	97	93
4			6	94	90
5			6	87	91
6			9	99	95
7			9	91	88
8		—	6	21	—
9		—	6	37	—

[a] Reaction conditions: The reaction was conducted in 1 atm O_2 at 40°C using 1mmol primary benzylic amines and 10 mL of absolute ethanol mixing with 100 mg 5wt% Cu/graphene catalyst under the irradiation of 400-800 nm light. The light intensity was 0.5 Wcm^{-2}.

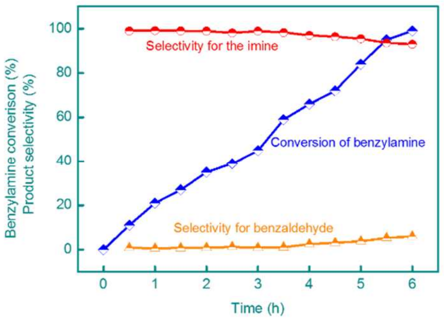
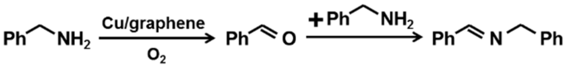


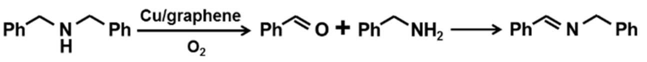
Figure 5. Reaction profiles for the oxidation of benzylamine on 5wt% Cu/graphene under visible-light irradiation. Reaction conditions: benzylamine (1 mmol), absolute ethanol (10 mL), 5wt% Cu/graphene (100 mg), Xe lamp (300 W, 400-800 nm, 0.5 Wcm^{-2}), O_2 (1 atm), 40°C, 6 h.

To demonstrate the general applicability of the catalyst, the photocatalytic oxidation of a variety of amine substrates was investigated. The results were summarized in Table 1. The oxidation of benzylamine derivatives proceeded efficiently under visible-light irradiation with high conversion of amines and high selectivity of imines (Table 1, entries 1–4). The substituents on benzene ring have only a small influence on the conversion and selectivity. This photocatalyst also has good applicability for heteroatom-containing substrates (Table 1, entries 6 and 7), whose imine products are usually difficult to be obtained by transition-metal complex catalysts due to the rapid deactivation of catalysts caused by the strong coordination of these amines with metal centers.[23] When employing aliphatic primary amines as reactants, no imines were produced and only fragmentation products were detected (Table 1, entries 8 and 9). Because the unselective autooxidation caused by the activation of multiple reactive sites can easily occur during the photocatalytic reaction,[23] the oxidation of aliphatic primary amines with dioxygen usually has a poor selectivity.

To study the mechanism of the photocatalytic oxidation, the reaction profile for the aerobic photocatalytic oxidation of benzylamine was investigated (Figure 5). In the beginning, little benzylamine converted into N-benzylidenebenzylamine with high selectivity. As the reaction time was prolonged, the conversion of benzylamine increased, but the selectivity of the imine slightly decreased step by step and small amounts of benzaldehyde could appear in the products. This is mainly because the increased consumption of benzylamine in the solution could not ensure the full condensation of nascent aldehyde and amine. Based on these results, a similar reaction mechanism to the previous reports[9] was proposed and shown in Equation (1). This represents an involvement of a selective oxygenation step to form aldehydes, which then undergo a subsequent condensation step to produce imines. The high selectivity of imines (Table 1) is mainly because highly selective formation of aldehydes from amines and easy nucleophilic attack of such nascent aldehydes by the unreacted amines to yield corresponding imines.



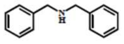
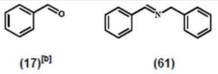
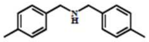
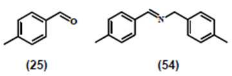
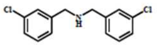
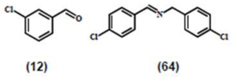
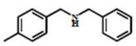
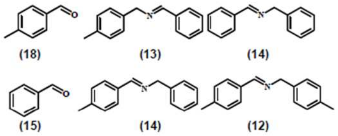
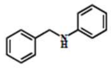
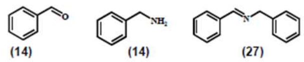
(1)



(2)

A series of aromatic secondary amines converting into dehydrogenated imines were also investigated (Table 2). Comparing with the oxidation of primary amines, both conversion and selectivity become low. Significant amounts of benzaldehyde and its derivative from oxidative cleavage of the C-N bond, were also formed as byproducts in the oxidation of secondary benzylic amines. These clearly indicate that the reaction proceeded via an oxygenation pathway. That is, a detour for aldehyde and benzylamine occurred [Equation (2)]. Because the self-coupling of in-situ generated benzylamines could also happen during the reaction, some accumulated aldehydes can be detected as the final product in addition to

Table 2. Aerobic oxidation of secondary amines on 5wt% Cu/graphene catalyst under visible light irradiation[a].

Entry	Substrate	Product (select.,%)	t(h)	Con.(%)
1		 (17)[b] (61)	12	31
2		 (25) (54)	8	34
3		 (12) (64)	12	23
4		 (18) (13) (14) (15) (14) (12)	8	49
5		 (14) (14) (27)	12	17

[a] The reaction conditions were same as Table 1. [b] Values in parentheses show the selectivity for the desired product.

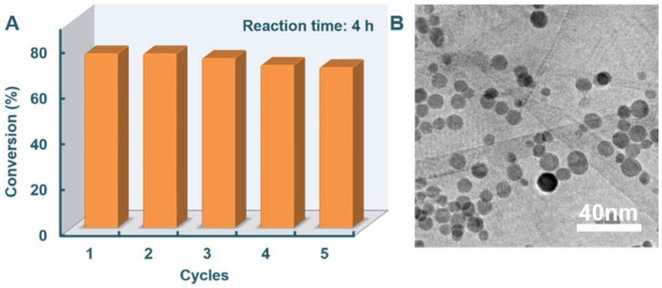


Figure 6. Recyclability of the 5wt% Cu/graphene for the aerobic oxidation of benzylamine into N-benzylidenebenzylamine in 5 rounds (A); and TEM image of the catalyst after 5-round test (B).

imines. The low conversion is mainly due to that the energy of energetic electrons is relatively low comparing with the required energy of oxidative cleavage of the C-N bond. Conducting the oxidation of dibenzylamine under the UV irradiation but keeping the other reaction conditions unchanged, a conversion of 95% of dibenzylamine was achieved. The UV absorption of Cu nanoparticles can induce the inter-band electron transition. Thus, these UV excited electrons have high energy and are capable of cracking of the C-N bond.[24,25] For asymmetric dibenzylamine derivative, because C_α-H bonds on both sides adjacent to the nitrogen atom have equal opportunities to activate and the condensation between different aldehydes and amines also have equal reaction rates, four different imines with molar ratio close to 1:1:1:1 and two accumulated aldehydes were observed (Table 2, entry 4). For the N-phenylbenzylamine (Table 2, entry 5), the difficulty of the condensation between benzaldehyde and aniline led to the low selectivity of N-benzylideneaniline.

Generally, the reaction temperature greatly affects the catalytic activity. The oxidation reaction of benzylamine was respectively conducted at room temperature (25^{o}C) and 60^{o}C under a constant light intensity of 0.5 Wcm^{-2}. The reaction can be completed in 7.5 and 5 h, respectively. Both conversions of benzylamine are 99%. The conversion is only 13% and 27% without irradiation at 25^{o}C and 60^{o}C, respectively. The conversion of dibenzylamine can increase to 69% if the oxidation of dibenzylamine was carried out at 80^{o}C for 12 h under irradiation with intensity of 0.5 Wcm^{-2}. The above results suggest that light-induced conversion can contribute the most of total yield even at higher temperture. Elevated temperature can cause a redistribution of the conduction electrons of Cu nanoparticles into higher energy levels.[26,27] Those electrons at higher levels can gain additional energy through light absorption when irradiated. This increase in energy further enhances the probability that the energetic electrons activate the reactant molecules adsorbed on the surface of nanoparticles. Moreover, the relative population of reactant molecules in excited states increases with temperature rising according to the Bose-Einstein distribution.[20] This means that the reactant molecules will require less energy to overcome the activation barrier and this energy could be easily provided by light irradiation. These results indicate that the electrons of Cu nanoparticles can effectively couple thermal and photonic energies to drive the chemical reactions.

To test the recyclability of the Cu/graphene photocatalyst in the oxidation of benzylamine, the catalyst was reused for 5 times after filtering and drying and the experiments were conducted for 4 h to ensure that the reactions did not reach equilibrium. A slow decrease in the activity was found after five reaction cycles, from 76% at the first cycle to 70% at the 5th (Figure 6A). TEM images of the used catalyst show no obvious change in morphology of the Cu nanoparticles (Figure 6B). However, the binding energy of Cu $2p_{1/2}$ (952.1 eV) in the XPS of the used Cu/graphene slightly shifts to higher value comparing with the fresh catalyst (Figure 2B). Moreover, the activity of used Cu/graphene can be recovered to its initial level after it is reduced in H_2-containing atmosphere, indicating that a slight oxidation of Cu nanoparticles occurs during the photocatalytic process.

Conclusion

The present work demonstrates a novel photocatalytic route of the aerobic oxidation of amines into imines over a Cu/graphene catalyst. The Cu/graphene shows an excellent photocatalytic activity for oxidation of benzylamine, and achieves a 99% conversion of benzylamine with a 93% selectivity of N-benzylidenebenzylamine. Meanwhile, Cu/graphene has an excellent general applicability for the aerobic oxidation of various primary and secondary amines into corresponding imines. The enhanced catalytic activity of the Cu/graphene under light irradiation results from the localized surface plasmon resonance of copper nanoparticles. The formation of imines follows an oxygenation mechanism involving a selective oxygenation step to generate the aldehydes, followed a subsequent condensation step to form the imines. Therefore, it provides an efficient and green photocatalytically and heterogeneously catalytic route for the production of imines.

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Notes and references

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1. S. I. Murahashi, *Angew. Chem. Int. Ed.* 1995, **34**, 2443-2465.
2. R. D. Patil and S. Adimurthy, *Asian J. Org. Chem.* 2013, **2**, 726-744.
3. K. Mori, K. Yamaguchi, T. Mizugaki, K. Ebitani and K. Kaneda, *Chem. Commun.* 2001, 461-462.
4. K. Yamaguchi and N. Mizuno, *Angew. Chem. Int. Ed.* 2003, **42**, 1480-1483.
5. S. Furukawa, A. Suga and T. Komatsu, *Chem. Commun.* 2014, **50**, 3277-3280.
6. M. Rueping, C. Vila, A. Szadkowska, R. M. Koenigs and J. Fronert, *J. ACS Catal.* 2012, **2**, 2810-2815.
7. Z. F. Zheng, C. Chen, A. Bo, F. S. Zavahir, E. R. Waclawik, J. Zhao, D. J. Yang and H. Y. Zhu, *ChemCatChem* 2014, **6**, 1210-1214.
8. X. J. Yang, B. Chen, X. B. Li, L. Q. Zheng, L. Z. Wu and C. H. Tung, *Chem. Commun.* 2014, **50**, 6664-6667.
9. X. J. Lang, W. H. Ma, Y. B. Zhao, C. C. Chen, H. W. Ji and J. C. Zhao, *Chem. Eur. J.* 2012, **18**, 2624-2631.
10. H. A. Ho, K. Manna and A. D. Sadow, *Angew. Chem. Int. Ed.* 2012, **51**, 8607-8610.
11. C. Wang, Z. Xie, K. E. de Krafft and W. J. Lin, *J. Am. Chem. Soc.* 2011, **133**, 13445-13454.
12. F. Su, S. C. Mathew, L. Mohlmann, M. Antonietti, X. Wang and S. Blechert, *Angew. Chem. Int. Ed.* 2011, **50**, 657-660.
13. S. Furukawa, Y. Ohno, T. Shishido, K. Teramura and T. Tanaka, *ACS Catal.* 2011, **1**, 1150-1153.
14. S. Sarina, E. R. Waclawik and H. Y. Zhu, *Green Chem.* 2013, **15**, 1814-1833.
15. A. Marimuthu, J. W. Zhang and S. Linic, *Science* 2013, **339**, 1590-1593.
16. P. Christopher, H. L. Xin and S. Linic, *Nat. Chem.* 2011, **3**, 467-472.
17. A. Bansal, J. S. Sekhon and S. S. Verma, *Plasmonic*s 2013, **9**, 143-150.
18. S. Naya, K. Kimura and H. Tada, *ACS Catal.* 2013, **3**, 10-13.
19. X. N. Guo, C. H. Hao, G. Q. Jin, H. Y. Zhu and X. Y. Guo, *Angew. Chem. Int. Ed.* 2014, **53**, 1973-1977.
20. S. Sarina, H. Y. Zhu, E. Jaatinen, Q. Xiao, H. Liu, J. Jia, C. Chen and J. Zhao, *J. Am. Chem. Soc.* 2013, **135**, 5793-5801.
21. D. B. Pedersen and S. Wang, *J. Phys. Chem. C* 2007, **111**, 17493-17499.
22. J. D. Lin, X. Q. Zhao, Y. H. Cui, H. B. Zhang and D. W. Liao, *Chem. Commun.* 2012, **48**, 1177-1179.
23. X. J. Lang, H. W. Ji, C. C. Chen, W. H. Ma and J. C. Zhao, *Angew. Chem. Int. Ed.* 2011, **50**, 3934 –3937.
24. A. Pinchuk, G. Plessen and U. Kreibig, *J. Phys. D: Appl. Phys.* 2004, **37**, 3133-3139.
25. K. Yamada, K. Miyajima and F. Mafune, *J. Phys. Chem. C.* 2007, **111**, 11246-11251.
26. S. Linic, P. Christopher and D. B. Ingram, *Nat. Mater.* 2011, **10**, 911-921.
27. P. Christopher, H. L. Xin, A. Marimuthu and S. Linic, *Nat. Mater.* 2012, **11**, 1044-1050.

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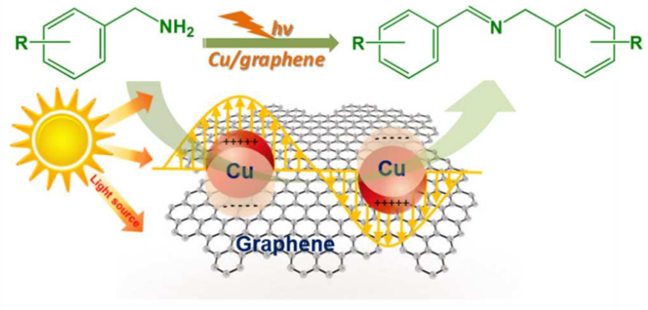

Cu/graphene can selectively photocatalyze the aerobic oxidation of amines into imines at mild conditions by harvesting visible light via the localized surface plasmon resonance of Cu nanoparticles.