

Visible Light-Driven Efficient Synthesis of Amides from Alcohols using Cu–N–TiO₂ Heterogeneous Photocatalyst

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Amides were synthesized from alcohols and amines in high yields using an in situ generated active ester of *N*-hydroxyimide with our developed $Cu-N-TiO_2$ catalyst at room temperature using oxygen as a sole oxidant under visible light. The catalyst can be easily prepared, robust, and recycled four times without a considerable change in catalytic activity. This developed

Introduction

The amide derivatives are the most important class of compounds found in natural products, pharmaceutical compounds, and synthetic polymers.^[1] More than 25% of commercial drugs contain an amide group.^[2] In general, amide bonds are synthesized by the reaction between activated forms of carboxylic acids and amines, and/or by using a coupling reagent.^[3] The synthesis of amides directly from alcohol is highly desirable, it affords a high atom and cost economical synthetic route.^[4] In 2007, Milstein and co-workers 1st reported environmentally benign direct amidation of alcohols and amines using the ruthenium PNN pincer complex as a catalyst.^[5] Since then several groups have reported the direct synthesis of amides from alcohols mainly using, homogeneous Ru,^[6] Rh,^[7] Ir,^[8] Fe,^[9] Cu,^{[10],} and other transition metal catalysts.^[11] Supported Aq,^[12] Au,^[13] and heterogeneous Mn^[14] catalyst also reported for amidation of alcohol. These methods have the advantages of environmentally benign and atom efficiency from the traditional acid chloride or coupling reagents-based amide bond synthesis. However, most of the reactions need an elevated temperature and problem associated with TM-catalyst contamination in the desired product. Towards sustainable development, visible-light-mediated organic synthesis, and energy-efficient reactions at ambient conditions are challenging tasks and highly desirable.^[15] Sunlight (visible light), prime sustainable energy resources on earth, driven reactions (photocatalysis), i.e., conversion of solar energy to chemical energy, using reusable heterogeneous photocatalyst, has been stimu-

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protocol applies to a wide substrate scope and has good functional group tolerance. The application of this amidation reaction has been successfully demonstrated for the synthesis of moclobemide, an antidepressant drug, and an analog of the itopride drug on a gram scale.

lated in recent years, as such reactions proceed smoothly at room temperature (RT).^[15-16] Recently we have reported Ndoped TiO₂ catalyst for the synthesis of *N*-hydroxyimide active ester from alcohol using two equivalent of sacrificial TBHP as an external oxidant.^[17] A similar strategy was reported by Xie and Yu groups for lodide-catalyzed amide synthesis^[18a] and Iron catalyzed esterification^[18b] via the *N*-hydroxyimide active ester route. Although the substrate scope of the reactions has wide under moderately mild conditions, the most critical disadvantage of the reaction was the use of super stoichiometric amounts of TBHP in decane and longer reaction time (24 h). This aspect has led us to the development of a new catalyst for the amidation of alcohols under mild reaction conditions and with good substrate scope. Based on the proposed mechanism, the role of TBHP is to accelerate the rate of selective oxidation of alcohol to aldehyde. We have envisioned that the loading of copper in our catalyst can do a similar job, ease the oxidation of alcohol under the aerobic condition in the presence of a photocatalyst. In continuation of our effort, herein we report our developed heterogeneous photocatalyst Cu-N-TiO₂ under very mild conditions for the synthesis of amides from alcohols and amines under 40w CFL light source using oxygen as sole oxidant and short reaction time at room temperature.

Results and Discussion

XRD pattern of the Cu–N–TiO₂ catalyst evidenced the presence of all the peaks of anatase TiO₂. In addition to all the peaks of anatase TiO₂ two additional peaks at $2\theta = 43.3^{\circ}$ and 50.6° , ascribed to the (111) and (200) planes of metallic Cu, was also observed and confirmed the successful incorporation of metallic Cu in the catalyst system (Figure 1a). The calculated crystallite size of Cu–N–TiO₂ is almost equivalent to that of bare N–TiO₂. The results imply that the structure of bare N–TiO₂ remains unaltered during Cu impregnation. A low magnified TEM image of Cu–N–TiO₂ showed the presence of 2D sheet assembled spheres, similar to that of bare N–TiO₂ (Figure S1). Magnified, indicate the presence of some foreign particles, in the size range of 1–4 nm, in the surface of the 2D sheet (Figure 1b),





Figure 1. (a) XRD pattern of synthesized bare and Cu impregnated N–TiO₂ hollow sphere; (b) TEM and (c) HR-TEM images of the synthesized Cu impregnated N–TiO₂ hollow sphere; (d) Core level Cu2p XPS; (e) UV-Vis. DRS and (f) PL spectra of synthesized bare and Cu impregnated N–TiO₂ hollow sphere.

which was absent in the bare $N-TiO_2$ (Figure S1). The foreign particles are most probably metallic Cu nanoparticles. Further through investigation of respective HRTEM images, evidenced that presence of distinct lattice fringes in sheets and parties with inter planner distance of 0.23, ascribed to (001) plane of anatase TiO₂, and can be 0.21 nm, ascribed to the (111) plane of metallic Cu, respectively (Figure 1c). HRTEM images confirmed the presence of crystalline Cu nanoparticles on the surface of the 2D N-TiO₂ sheet. N₂ adsorption-desorption isotherm of Cu–N–TiO₂ catalyst corresponds to type IV (Figure S2), typically which is similar to that of bare N-TiO2.[17] The calculated total BET surface area and average pore size of Cu-N-TiO₂ are 174 m²g⁻¹ and 6.5 nm, respectively. Although with respect to the bare N-TiO₂ no significant change in pore size distribution for Cu-N-TiO₂ took place, a reasonable enhancement of the total surface area, from 155 m^2g^{-1} to 174 m^2g^{-1} was observed, most probably due to the contribution from the metallic Cu nanoparticles on the surface of TiO₂ sheets. Wide survey XPS spectra of Cu-N-TiO₂ evidenced the presence of Ti, O, Cu, and more importantly the N (Figure S3). Corresponding, highresolution Ti2p spectra showed the presence of two peaks at 464.8 and 459.1 eV, ascribed to the Ti2p1/2 and Ti2p3/2, respectively, and confirm the presence of Ti^{4+} as TiO_2 . Deconvoluated N1s spectra demonstrated the presence of two peaks at 398.08 and 399.11 eV, corresponds to the O-Ti-N and oxidized Ti–O–N species as substitutional N of TiO₂, respectively (Figure S3).^[19] All the above-mentioned results are quite identical to that of bare N–TiO₂ and indicate that the doped nitrogen of bare N-TiO₂ remains intact even after Cu impregnation. The Cu 2p (Figure 1d) spectra evidenced the presence of peaks at 930.7 and 951.6 eV, ascribed to either Cu⁰ or Cu¹⁺, and peaks at 933.06 and 953.3 eV beside with spin splitting originated separately at around 961.11 eV, recognized as Cu²⁺. Two intense peaks in the range of 938-942 eV, identified as satellite peaks of Cu²⁺, were also identified. Here it is essential to mention that the recognized peaks at 930.7 and 951.6 eV are for only Cu⁰, as a distinct Cu-LMM peak at 568.2 eV was identified (Figure S3). Thus, XPS spectra confirmed the Cu–N–TiO₂ catalyst contains both Cu⁰ and Cu²⁺ and the existence of Cu²⁺ is due to the aerial surface oxidation of metallic Cu during catalyst collection and storage. In the UV-Vis diffuse reflectance spectra (DRS) of Cu–N–TiO₂, a reasonable improvement in the absorption of light in the visible region to that of bare N–TiO₂ (Figure 1e). Visible light absorption efficiency is increased incorporation of metallic Cu nanoparticles in the N–TiO₂ system (Cu–N–TiO₂), which can be ascribed to the Surface Plasmon Resonance peak of plasmonic Cu NPs.^[20] Pl spectra evidenced a reasonable reduction of peak intensity for Cu–N–TiO₂ to that of N–TiO₂ (Figure 1f). This is due to the migration of photo-generated electrons in CB of N–TiO₂ to Cu and restricts recombination.

Photocatalytic reactions

After successful synthesis and full characterization of the $Cu-N-TiO_2$ catalyst in hand, we next explored the catalytic activity. The reaction of 4-chlorobenzyl alcohol **1a** with 2-phenylethylamine **3a** in presence of N-hydroxyphthalimide **2a** was taken as a model substrate to optimize the reaction condition under the irradiation of light from a 40 W CFL lamp and at ambient condition (Table 1). In first consideration, we have used our synthesized 5 wt% Cu loaded TiO₂ catalyst on the amidation reaction in acetonitrile solvent, to our delight as envisioned our catalyst showed excellent reactivity, and 91% of



[a] Reaction condition: Unless otherwise specified, all the optimization reactions were carried out with 4-chlorobenzyl alcohol 1a (0.4 mmol, 1.0 equiv), *N*-hydroxyphthalimide 2a (0.48 mmol, 1.2 equiv), 2 ml solvent, 15 mg catalyst, under the irradiation of light from 40 W CFL lamp, at ambient condition for 6 h then 2-phenylethylamine 3a (0.6 mmol, 1.5 equiv.) was added and stirred for additional 15 min; b] reaction carried out under the irradiation of light from a blue LED. [c] reaction carried out under dark.



the desired 4-chloro-N-phenethylbenzamide product was observed (Table 1, entry 1). Next, we have checked the amount of copper loading on N-TiO₂, 2.5% wt% Cu-N-TiO₂ showed little diminished activity (65%, entry 2) and 10% Cu-N-TiO₂ catalyst showed similar reactivity (93%, entry 3). The amount of catalyst found to be critical, 5 mg and 10 mg catalyst have inferior results (40%, and 75%, entries 4-5 respectively), and 20 mg catalyst showed a similar result (92%, entry 6). The addition of hydrogen peroxide and DTBP as an external oxidant (2 equiv) found to be ineffective completely inhibits the reaction (entries 7-8), whereas TBHP as an oxidant gave a similar result (89%, entry 9). Simple N–TiO₂ gave a lower yield (20%, entry 10), which indicates the copper loading on TiO2 is critical. Next, a screening of solvents was carried out and found DMF, DCE, ethanol, and BTF are ineffective, no product was observed (entries 11-14), so the solvent choice is critical and acetonitrile found to be superior. When we carried out the reaction with 3 W blue LED light, a similar yield was observed (entry 15) Finally, when carried out the reaction at dark even after 16 h no product formation was observed (entry 16), indicates the necessity of light and photocatalysis pathway of the reaction. It is noteworthy that the addition of amine from the beginning gives the lower yield of the desired amide, and in an absence of NHPL, no amidation product was observed. To get a better understanding of the reaction profile, the conversion of 4chlorobenzyl alcohol (1 a) with NHPI (2 a) was monitored with time and found the formation of an active ester is completed within 6 h (Figure 2). After 6 h, upon the addition of 2-phenylethylamine, amidation was very fast, within 15 min reaction was completed to get the desired amide (5 a) product with a 91% yield.

With the optimization condition in hand (Table 1, entry 1), the scope and limitation of this tandem amidation reaction were then explored with various alcohols and amines. In general, most of the reaction proceeds well and gave the desired amide in good yields as shown in Table 2. Several benzyl alcohols with electron-donating substituted in the para



Figure 2. Reaction progress monitored by HPLC: reaction of the alcohol with NHPI to active ester.

position of phenyl ring reacts with 2-phenyl amine and gave the desired sec-amide in good to excellent yields (up to 91%, entries **5b**–**5d**), halide substituted (weak electron-withdrawing) chloro and bromo derivatives gave excellent yields (91% and 89% respectively, entries 5a, and 5e). Whereas strong electronwithdrawing groups such as fluoro, nitrile, and nitro proceeded will with slightly less yield (70-72%, entries 5f-5g). These results indicate the electronic effect is not so significant. Orthosubstituted benzyl alcohols, which might have some steric hindrance are also effective for tandem amidation (entries 5i-5 i) gave the desired sec-amide in good yields. Next, we check, other aryl and heteroaryl methyl alcohols as a substrate, naphthalene, furan, pyridine, and thiophene derivatives with 2phenylethylamine proceed well to produce the sec-amide in good yields (entries 5k-5n). Other primary amines such as benzylamine and n-butyl amines were also worked well with 2thiophene methanol and gave the desired product in very good yield (70%, 5o; 73%, 5p). To our delight, secondary amines such as pyrrolidine and diethylamine were also worked well and gave the desired *tert*-amide in very good yields (5 g, 67%; 5r, 68%, 5u, 82% and 5v, 87%). Aliphatic alcohol, 3-Phenyl-1propanol reacted with 2-Phenethylamine and gave the desired amide in moderate yield (5w, 40%), highlighting that reaction is not limited to benzylic alcohols. On a gram scale, tandem amidation of 4-chloro benzyl alcohol with morpholinoethanamine gave 76% of moclobemide (5x), a generic drug used for the treatment of depression. An analog of the itopride drug molecule was easily synthesized with good yield in gram scale 65% (5y), itopride is used in the treatment of gastrointestinal (GI) symptoms (Scheme 1).

To get some insight into the reaction mechanism, we have carried out some control experiments. First, we carried out the reaction in presence of radical scavengers like TEMPO [(2,2,6,6-Tetramethylpiperidin-1-yl)oxyl] and BHT (butylated hydroxyl toluene) which completely inhibited the reaction (Scheme 2). These results indicate the reaction might proceed through a radical mechanism i.e. SET (single electron transfer) process. To understand the role of visible light we have performed the light on-off studies, at the beginning for 30 min, the light was on after that for every 1 h we have turned off the light and subsequently turned it on and check the reaction progress by HPLC (Figure 3). It was observed that in absence of light no progress in the reaction and upon light on condition reaction again re-started, which indicates the reaction is photocatalytic.



Scheme 1. Synthetic application, gram-scale synthesis of moclobemide, and itropide in one pot.





[a] Reaction conditions: A reaction tube containing a solution of benzyl alcohol 1 (0.4 mmol), *N*-hydroxyphthalimide 2a (0.48 mmol, 1.2 equiv), 15 mg catalyst, in acetonitrile (2 mL) was stirred under the irradiation of light from 40 W CFL lamp, at ambient condition for 6 h; then amine 3 (0.6 mmol, 1.5 equiv.) was added and stirred for additional 15 min.





Scheme 2. Radical inhibition study.



Our catalyst showed very good recyclability, after completion of the reaction catalyst was filtered, washed and dried, and reused (Figure 4). Further, the hot filtration test confirmed the heterogeneity of the reaction. We monitored the reaction progress after taking out the reaction mixture *via* cannula from the solid catalyst, No further reaction was observed, in the solution part, which suggests that the active catalyst was not leached out to the solution and the reaction is heterogeneous in nature. ICP-AES analysis of the filtrate of the standard reaction also tested after completion of the reaction, a negligible amount of Cu (3 ppm and 5 ppm) leached in the filtrate for both the second and fourth cycle respectively.





Figure 4. Recyclability of the catalyst for standard amidation (5 a).

Conclusion

In conclusion, we have developed an efficient and reusable heterogeneous Cu–N–TiO₂ hollow sphere with superior visible-light absorption efficiency for the synthesis of amides starting from alcohol and amine at room temperature. The synthesized Cu–N–TiO₂ hollow sphere showed excellent photocatalytic activity. The applicability of the method is further showcased by the gram-scale synthesis of drug or drug analogs such as moclobemide and itropide. The catalyst is reused for 4 times without significant loss of reactivity. Compared with previous reports, our catalyst is effective at room temperature, no need for an inert atmosphere, good functional group tolerance, and recyclable.

Experimental Section

For the synthesis of $Cu-N-TiO_2$, the first sheet mediated $N-TiO_2$ hollow spheres were synthesized, and then the metallic Cu was impregnated on it.

Synthesis of sheet mediated N–TiO₂ hollow spheres. It was synthesized following our previously reported method. In a typical synthetic procedure, 30 mL NH₄OH (30%) solution was added to a 30 ml titanium peroxy-carbonate solution, from 3 ml titanium isopropoxide, was added under constant stirring. Then by adding deionized water, the total of the solution was made up to 90 ml. 33 ml of this solution mixture was taken in 50 ml Teflon lined stainless steel autoclave. After proper sealing, the autoclave was transferred to a pre-heated oven at 120°C for 18 h. Finally, the obtained precipitate was collected after proper washing with deionized water followed by ethanol and drying and calcined at 400°C for 2 h.

Metallic Cu impregnation on N–**TiO**₂: First the calcined N–TiO₂ was dispersed in methanol-water and to it required amount of freshly prepared methanolic Cu(OAc)₂.H₂O solution was added dropwise with stirring. To that solution, hydrazine hydrate solution was added dropwise and stirred the whole solution for an additional 2 h. Finally, the precipitate was collected by washing with deionized water followed by ethanol and dried the precipitate at 70 °C for 12 h.

Characterizations. The following instruments were used for Characterization: Miniflex-II (FD 41521) powder diffractometer (Rigaku, Japan), JEOL JEM 2100 transmission electron microscope (TEM), Shimadzu UV-2550 spectrophotometer, Raman spectrometer (NICO-

LET ALMECA XR) with a 532 nm laser beam, ESCALAB 250 XPS System with a monochromatic Al K α (150 W) source, Horiba Jobin spectrophotometer.

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Conflict of Interest

The authors declare no conflict of interest.

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- a) J. M. Humphrey, A. R. Chamberlin, *Chem. Rev.* **1997**, *97*, 2243–2266;
 b) V. R. Pattabiraman, J. W. Bode, *Nature* **2011**, *480*, 471–479; c) T. Cupido, J. Tulla-Puche, J. Spengler, F. Albericio, *Curr. Opin. Drug Discovery Dev.* **2007**, *10*, 768–783.
- [2] a) J. R. Dunetz, J. Magano, G. A. Weisenburger, Org. Process Res. Dev. 2016, 20, 140–177; b) J. S. Carey, D. Laffan, C. Thomson, M. T. Williams, Org. Biomol. Chem. 2006, 4, 2337–2347.
- [3] E. Valeur, M. Bradley, Chem. Soc. Rev. 2009, 38, 606–631.
- [4] a) C. Gunanathan, D. Milstein, *Chem. Rev.* 2014, *114*, 12024–12087;
 b) G. E. Dobereiner, R. H. Crabtree, *Chem. Rev.* 2010, *110*, 681–703; c) C. Chen, S. H. Hong, *Org. Biomol. Chem.* 2011, *9*, 20–26.
- [5] C. Gunanathan, Y. Ben-David, D. Milstein*, Science 2007, 317, 790–792.
- [6] a) L. U. Nordstrøm, H. Vogt, R. Madsen, J. Am. Chem. Soc. 2008, 130, 17672–17673; b) S. C. Ghosh, S. Muthaiah, Y. Zhang, X. Xu, S. H. Hong, Adv. Synth. Catal. 2009, 351, 2643–2649; c) A. J. A. Watson, A. C. Maxwell, J. M. J. Williams, Org. Lett. 2009, 11, 2667–2670; d) S. Muthaiah, S. C. Ghosh, J. E. Jee, C. Chen, J. Zhang, S. H. Hong, J. Org. Chem. 2010, 75, 3002–3006; e) T. Higuchi, R. Tagawa, A. limuro, S. Akiyama, H. Nagae, K. Mashima, Chem. Eur. J. 2017, 23, 12795–12804.
- [7] a) K. Fujita, Y. Takahashi, M. Owaki, K. Yamamoto, R. Yamaguchi, Org. Lett. 2004, 6, 2785–2788; b) T. T. Nguyen, K. L. Hull, ACS Catal. 2016, 6, 8214–8218.
- [8] O. Saidi, M. J. Bamford, A. J. Blacker, J. Lynch, S. P. Marsden, P. Plucinski, R. J. Watson, J. M. J. Williams, *Tetrahedron Lett.* 2010, *51*, 5804–5806.
- [9] a) M. Arefi, D. Saberi, M. Karimi, A. Heydari, ACS Comb. Sci. 2015, 17, 341–347; b) S. C. Ghosh, J. S. Y. Ngiam, A. M. Seayad, D. T. Tuan, C. W. Johannes, A. Chen, Tetrahedron Lett. 2013, 54, 4922–4925.
- [10] a) J. Gu, Z. Fang, Y. Yang, Z. Yang, L. Wan, X. Li, P. Wei, K. Guo, *RSC Adv.* 2016, *6*, 89413–89416; b) P. E. Piszel, A. Vasilopoulos, S. S. Stahl, *Angew. Chem. Int. Ed.* 2019, *58*, 12211–12215.
- [11] Y. F. Guo, T. L. Ren, B. H. Xu, Y. F. Wang, S. J. Zhang, Asian J. Org. Chem. 2016, 5, 568–574.
- [12] K. Shimizu, K. Ohshima, A. Satsuma, Chem. Eur. J. 2009, 15, 9977-9980.
- [13] a) Y. Wang, D. Zhu, L. Tang, S. Wang, Z. Wang, Angew. Chem. Int. Ed. 2011, 50, 8917–8921; b) J. F. Soulé, H. Miyamura, S. Kobayashi, J. Am. Chem. Soc. 2011, 133, 46, 18550–18553; c) L. Zhang, W. Wang, A. Wang, Y. Cui, X. Yang, Y. Huang, X. Liu, W. Liu, J. Y. Son, H. Oji, T. Zhang Green, Chem., 2013,15, 2680–2684.
- [14] K. Yamaguchi, H. Kobayashi, T. Oishi, N. Mizuno, Angew. Chem. Int. Ed. 2012, 51, 544–547.
- [15] a) X. Lang, X. Chen, J. Zhao, *Chem. Soc. Rev.* **2014**, *43*, 473–486; b) Sk. S. Shah, M. Shee, Y. Venkatesh, A. K. Singh, S. Samanta, N. D. P. Singh, *Chem. Eur. J.* **2020**, *26*, 3703–3708.
- [16] a) J. Chen, J. Cen, X. Xu, X. Li, *Catal. Sci. Technol.* **2016**, *6*, 349–362; b) J. L. White, M. F. Baruch, J. E. Pander Iii, Y. Hu, I. C. Fortmeyer, J. E. Park, T. Zhang, K. Liao, J. Gu, Y. Yan, T. W. Shaw, E. Abelev, A. B. Bocarsly,



Chem. Rev. 2015, 115, 12888–12935; c) S. K. Pahari, P. Pal, D. N. Srivastava, S. Ghosh, A. B. Panda, Chem. Commun. 2015, 51, 10322–10325; d) R. Vadakkekara, A. K. Biswas, T. Sahoo, P. Pal, B. Ganguly, S. C. Ghosh, A. B. Panda, Chem. Asian J. 2016, 11, 3084–3089; e) K. Singha, A. Mondal, S. C. Ghosh, A. B. Panda, Chem. Asian J. 2018, 13, 255–260; f) Q. Liu, L.-Z. Wu, Natl. Sci. Rev. 2017, 4, 359–380.

- [17] K. Singha, S. C. Ghosh, A. B. Panda, Chem. Asian J. 2019, 14, 3205-3212.
- [18] a) G. Wang, Q. Y. Yu, J. Wang, S. Wang, S. Y. Chen, X. Q. Yu, *RSC Adv.* 2013, 3, 21306–21310; b) X. Xu, J. Sun, Y. Lin, J. Cheng, P. Li, X. Jiang, R. Bai, Y. Xie, *Eur. J. Org. Chem.* 2017, 7160–7166.
- [19] a) S. Sun, P. Gao, Y. Yang, P. Yang, Y. Chen, Y. Wang, ACS Appl. Mater. Interfaces. 2016, 8, 18126–18131; b) Y. Cong, J. Zhang, F. Chen, M. Anpo,

D. He, J. Phys. Chem. C 2007, 111, 10618–10623; c) F. Wang, X. He, L. Sun, J. Chen, X. Wang, J. Xu, X. Han, J. Mater. Chem. A. 2018, 6, 2091–2099; d) C. Zhang, Y. Zhou, J. Bao, X. Sheng, J. Fang, S. Zhao, Y. Zhang, W. Chen, ACS Appl. Mater. Interfaces 2018, 10, 18796–18804.

[20] P. Zhang, T. Song, T. Wang, H. Zeng, RSC Adv. 2017, 7, 17873–17881.

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