Hybrid composite of CuO with g-C₃N₄ as a photoactive catalyst: an efficient approach for the oxidation of alcohols

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Abstract. An eco-friendly method for the oxidative transformation of alcohols to their corresponding carbonyl compounds by using g-C₃N₄@CuO as a photoactive heterogeneous catalyst has been developed. The catalyst was characterized by SEM-EDX, TEM, BET surface area measurements, powder XRD, FTIR, photoluminescence and UV-Vis spectroscopy. It was found to be very effective for the conversion of both primary and secondary alcohols into aldehydes and ketones with excellent yields using *tert*-butyl hydrogen peroxide (TBHP) as oxidant at room temperature in the presence of visible light in aqueous medium. The catalyst can be separated from the reaction mixture by simple centrifugation and reused up to five cycles without significant loss in activity.

Keywords. Nanocomposite; graphitic carbon nitride; alcohol oxidation; copper oxide; photocatalyst.

1. Introduction

The use of photocatalyst in the presence of visible light energy for chemical transformation is an active area of research today.^{1–3} Photocatalysis is considered to be an environmentally benign protocol with applications in hydrogen production,^{4,5} dye degradation,^{5,6} water splitting, etc. The controlled oxidation of alcohols into corresponding aldehydes or ketones is one of the most important organic syntheses with applications as intermediates in pharmaceutical industries or in bulk/fine chemical industries. Traditionally, in the oxidation of alcohols to get aldehydes and ketones, transition metals such as Cr(VI) and Mn(II)⁷ were widely used, which are toxic, corrosive as well as expensive. Several reports on both homogeneous and heterogeneous catalysis based on metals such as Ag,⁸ Fe,⁹ Pd,¹⁰ Au,¹¹ and V¹² have shown excellent catalytic activity in alcohol oxidation in the presence of molecular O₂, air, H₂O₂ or TBHP as oxidizing agents. However, in recent times, heterogeneous catalysts have gained much importance due to its easy separation, selectivity, stability and reusability.¹³ In recent times, among various photocatalysts, TiO₂ (anatase) showed excellent results¹⁴ but it has two major constraints like low quantum efficiency and limited photo absorption

range¹⁵ due to wide bandgap. However, using TiO₂ supported Au nanocomposites have shown excellent photoactivity in alcohol oxidation¹⁶ and dye degradation in the presence of visible light indicating the role of structure and properties of support material. Recently, g-C₃N₄ has been highly explored as photocatalyst due to its unique stability, low cost, low bandgap (2.7 eV), excellent heat endurance (as high as 600 °C) and high resistance to chemicals such as strong acids and strong bases.¹⁷ The presence of metal in g-C₃N₄ enhances the photocatalytic activity by narrowing the band gap and expanding photo absorption into visible range.^{18,19} Although g-C₃N₄ has a better capacity for utilization of sunlight compared to other photocatalysts due to lower bandgap, it suffers from a high recombination rate of electron–hole pairs. However, the coupling of g-C₃N₄ with appropriate semiconductors can enhance its photocatalytic activity by lowering the recombination rate. There are very few reports on the use of g-C₃N₄ as a photocatalyst in oxidative transformations. Recently researchers have demonstrated benzyl alcohol conversion to benzaldehydes using CdS/g-C₃N₄,²⁰ Ru-g-C₃N₄,²¹ MIL-125-Ag/g-C₃N₄²² and BiVO₄/g-C₃N₄²³ catalysts. In 2016, Verma and coworkers have reported the selective oxidation of alcohols²⁴ as well as alcohol esterification²⁵ by photoactive VO@g-C₃N₄. Good

mechanical stability, rich nitrogen content, wideband semiconductor and chemical inertness provide a good prospect for using carbon nitride as a catalyst support.¹⁹ However, the use of expensive, toxic metals and harsh reaction conditions demand the need for more eco-friendly catalyst systems which urged us to use cheaper, low cost, environment-friendly CuO. Moreover, it is an important p-type semiconductor which has found many diverse applications such as in gas sensors, catalysis, batteries, high-temperature superconductors, solar energy conversion and field emission emitters.²⁶ As part of our ongoing efforts to develop solidly supported transition metal photocatalysts, we report here a facile method for the synthesis of $g\text{-C}_3\text{N}_4\text{@CuO}$ and its application in the oxidation of alcohol to corresponding aldehydes and ketones. To the best of our knowledge, this is the first example of a photoactive $g\text{-C}_3\text{N}_4\text{@CuO}$ catalyst for the oxidative transformation of alcohol. As the reaction proceeds under mild conditions and the catalyst are recoverable, it provides an environmentally benign alternative to the existing protocols.

2. Experimental

2.1 Materials and methods

Urea (Merck), cupric acetate (Loba Chemie), TBHP (Merck) and all alcohols were obtained from Alfa Aesar. The chemicals were used as received without any further purification or drying. The ^1H NMR spectra of the products were recorded in CDCl_3 at 400 MHz spectrometer. X-ray diffraction pattern (XRD) of $g\text{-C}_3\text{N}_4$ and $g\text{-C}_3\text{N}_4\text{@CuO}$ were recorded on a Bruker AXS D8 Diffractometer with $\text{Cu-K}\alpha$ (1.541 Å radiation). FTIR spectra were recorded in KBr pellets on a Shimadzu IR prestige-21 FTIR spectrophotometer ($400\text{--}4000\text{ cm}^{-1}$). The solid UV-Vis spectra (200–800 nm) were recorded on JESCO750 spectrophotometer. The Photoluminescence (PL) spectra were recorded on a Fluoromax-4 spectrofluorometer with an excitation wavelength of 350 nm. The Cu loading in the catalyst were determined using inductively coupled plasma-atomic emission spectroscopy (ICP-AES) analysis on a Thermo Electron IRIS INTERPID II XSP DUO. ^1H and ^{13}C spectra were recorded in CDCl_3 using TMS as an internal standard on a BRUKER AVANCE II 400 MHz spectrometer. The SEM images were obtained with a Quanta 200 FEG Scanning electron microscope, EDX spectra were recorded on the same instrument attached to the SEM. TEM analyses were performed on Jeol/ JEM 2100 instrument equipped with a high-resolution CCD camera and an accelerating voltage of 200 KV. X-ray photoelectron spectra (XPS) were recorded on an XPS-AES Module, Model: PHI 5000 Versa Prob II. Specific surface areas were recorded following BET procedure.

2.2 Preparation of $g\text{-C}_3\text{N}_4\text{@CuO}$

Two grams of urea is taken (as it is cheap, easily available compound and an active molecular precursor under thermal treatment²⁷ in a mortar pestle and 10 mg of cupric acetate is added into it and grounded in a pestle to make it into a fine powder and kept in a muffle furnace at 400°C for 1 h. After cooling, the catalyst was grounded into fine powder.^{28,29}

2.3 Photocatalytic experiment

In a typical procedure, a mixture of alcohol (1 mmol), catalyst (3 mg), oxidant (0.3 mL) and solvent (5 mL) was added in the 50 mL round-bottomed flask surrounded by circulating water jacket for reaction to prevent thermal oxidation and the mixture was stirred for the required time in presence of visible light using 100 W LED light (400–700 nm) which is equivalent to 0.16 sun (distance of light source from reaction flask is 28 cm).¹⁶ The progress of the reactions was monitored by TLC. After completion of the reaction, the catalyst was recovered by simple filtration and the filtrate was poured into water. The organic product was extracted with ethyl acetate (3x10 mL). The combined organic fractions were dried over anhydrous sodium sulphate and concentrated. The residue was purified by column chromatography using silica gel (60–120 mesh) with ethyl acetate/hexane as eluent to obtain the desired products.

3. Results and Discussion

3.1 Characterization of the catalyst

The FTIR spectrum of $g\text{-C}_3\text{N}_4$ (Figure S1, SI) shows similarities with the previous reports.³⁰ In the IR spectrum, $g\text{-C}_3\text{N}_4$ exhibits characteristic IR bands due to

Figure 1. Solid UV-Vis spectra of (a) $g\text{-C}_3\text{N}_4$ (black) (b) $g\text{-C}_3\text{N}_4\text{@CuO}$ (blue).

$\nu_{\text{C}=\text{N}}$ at 1636 cm^{-1} and 1499 cm^{-1} and due to aromatic $\nu_{\text{C}=\text{N}}$ at 1327 and 1271 cm^{-1} . The peak at 810 cm^{-1} could be assigned to the characteristic out-of-plane bending vibrational modes of s-triazine units. The broad absorption band at 3174 cm^{-1} corresponds to $\nu_{\text{N}-\text{H}}$. After the introduction of CuO, no noticeable change in the main characteristic bands of g- C_3N_4 could be observed, indicating that there is non-covalently coupled interaction between g- C_3N_4 and CuO in the composite. The optical properties of both pure g- C_3N_4 and g- C_3N_4 @CuO were determined by solid UV-Vis

spectroscopy (Figure 1). It was seen that in g- C_3N_4 a sharp increase of light absorption occurs at wavelength 450 nm which can be assigned to its intrinsic band gap of 2.7 eV which is consistent with earlier reports.³¹ However, in the spectrum of g- C_3N_4 @CuO, it was observed that there is a stronger light absorption in both ultraviolet at 327 nm and in the visible region around 736 nm which can be attributed to the presence of CuO in the sample.

From the powder X-ray diffraction (PXRD) pattern of g- C_3N_4 (Figure 2), two broad diffraction peaks at 2θ values of 10.6° and 26.8° which are indexed to (001) and (002) planes were obtained. As in the case of VO@ g- C_3N_4 no XRD peak was obtained for VO,²⁴ in XRD of g- C_3N_4 @CuO due to the amorphous nature of g- C_3N_4 and very low loading of CuO, a signal for CuO could not be detected. However, the presence of

Figure 2. XRD patterns of (i) g- C_3N_4 and (ii) g- C_3N_4 @CuO.

Figure 3. TEM image of g- C_3N_4 @CuO with SAED pattern.

Figure 4. XPS spectra of Cu 2p and O1s level (inset).

Figure 5. PL spectra (excitation wavelength 350 nm) of (a) g- C_3N_4 and (b) g- C_3N_4 @CuO.

Table 1. Surface area and pore size distribution of the nanomaterials.

Entry	Catalyst	Surface area (m ² g ⁻¹)	Pore volume (cm ³ g ⁻¹)	Pore radius (nm)
1	g-C ₃ N ₄	12	0.013	1.668
2	g-C ₃ N ₄ @CuO	44	0.073	1.864

CuO was confirmed from SEM-EDX and XPS analyses. The TEM analysis (Figure 3) shows the sheet formation of g-C₃N₄ and SAED pattern (in the inset of Figure 3) indicates a diffused ring pattern which suggests the amorphous nature of the material and also confirms the nanosized structure of g-C₃N₄.¹⁷ The presence of copper is confirmed by SEM-EDX and ICP-AES analysis of the catalyst. The SEM images of g-C₃N₄ [Figure S3(a), Supplementary Information] and g-C₃N₄@CuO [Figure S4(b), Supplementary Information] clearly indicates the changes in the morphology of the catalyst after the introduction of metal in g-C₃N₄. The amount of metal content in g-C₃N₄@CuO catalyst is found to be 0.0029 mmol of Cu in 0.003 g of the catalyst.

X-ray photoelectron spectroscopy (XPS) is a quantitative spectroscopic method that determined the elemental composition, kinetic energy, empirical formula, chemical state, binding energy, and electronic-state of the elements that present within a material. Here XPS analysis was performed to check the oxidation state of copper in the catalyst as shown in Figure 4. The two peaks at 929.37 eV and 931.6 eV can be assigned to Cu2p_{3/2} and 949.14 eV is for Cu2p_{1/2} of CuO which is in good agreement with the previous literature reports.^{32–35} The gap between Cu2p_{3/2} and Cu2p_{1/2} is 19.8 eV which is in agreement of standard value of 20.0 eV for CuO.²⁵ Moreover, the presence of two satellite peaks at 940.8 eV and 960.5 eV also indicate the existence of CuO on g-C₃N₄ sheets.³³ Furthermore, the peak at 528.4 eV also indicates the presence of CuO.³⁴

Figure 5 shows steady-state photoluminescence (PL) spectra for g-C₃N₄ and g-C₃N₄@CuO. The g-C₃N₄ shows a strong PL emission peak at 432 nm with an excitation wavelength of 350 nm. It was seen that the intensity of PL of g-C₃N₄@CuO decreases as compared to g-C₃N₄ which is due to the decrease in the recombination rate of electron–hole (e⁻–h⁺) pair leading to better charge separation on insertion of metal in the support.^{16,17} This explains the better photocatalytic oxidation of alcohol by g-C₃N₄@CuO compared to bare g-C₃N₄. The BET analysis of g-C₃N₄ and g-C₃N₄@CuO provides key information regarding change occurring in the surface of the catalyst. The surface areas of g-C₃N₄ and g-C₃N₄@CuO were found to be 12 m² g⁻¹ and 44 m² g⁻¹ respectively (Table 1). Undoubtedly, the higher surface area of the catalyst, g-C₃N₄@CuO would

Table 2. Optimization of oxidation of 1-phenyl ethanol using g-C₃N₄@CuO^a.

Entry	Solvent	Oxidant	Catalyst(mg)	Yield (%) ^b
1	CH ₃ CN	H ₂ O ₂	5	40
2	H ₂ O	H ₂ O ₂	5	45
3	CH ₃ OH	H ₂ O ₂	5	30
4	H ₂ O	TBHP	5	60
5	H₂O	TBHP	3	60
6	H ₂ O	TBHP	2	50
7	H ₂ O	O ₂	2	35
8	–	TBHP	3	Trace
9	H ₂ O	TBHP	–	–
10 ^c	H ₂ O	TBHP	3	30
11 ^c	CH ₃ CN	TBHP	3	20
12 ^d	H ₂ O	TBHP	3	20

Bold indicates optimised condition

^aReaction Conditions: 1-phenyl ethanol (1 mmol), catalyst (2–5 mg), solvent (5 mL) Oxidant (3 mL), time 2 h, 100W LED light

^bIsolated yield, ^cg-C₃N₄ as catalyst, ^din dark condition.

be favourable for adsorbing reactant molecules on the active sites of the catalyst.³⁶ We have reported earlier the photocatalytic oxidation of the alcohol with TiO₂ supported gold¹⁶ as a heterogeneous catalyst with a band gap of 2.9 eV and TiO₂ (anatase) has a band gap of 3.2 eV. In the present work, we have used g-C₃N₄@CuO as a photocatalyst where g-C₃N₄ has a band gap of 2.8 eV and g-C₃N₄@CuO has a band gap of 2.3 eV obtained from Tauc plot (Figure S2, Supplementary Information). The lower band gap of g-C₃N₄@CuO increases the photocatalytic activity of the catalyst.

3.2 Photocatalytic activity

Initially, we have chosen 1-phenyl ethanol as the model substrate with 100 W LED as a light source to perform optimisation studies (Table 2). We have investigated the reaction with different solvents such as water, acetonitrile and methanol and the amount of catalyst on the oxidation of alcohol. On studying the effects of solvent

Table 3. CuO@g-C₃N₄ catalysed oxidation of alcohol.

$$\text{R}_1\text{-CH(OH)-R}_2 \xrightarrow[\text{visible light}]{\text{g-C}_3\text{N}_4\text{@CuO, H}_2\text{O, TBHP}} \text{R}_1\text{-C(=O)-R}_2$$

Entry	Substrate	Product	Time (h)	Yield (%) ^a	TON	TOF
1			4	96	343	86
2			4.5	95	339	75
3			4	96	343	86
4			4.5	94	336	75
5			4	90	321	80
6			5	93	332	66
7			5	91	325	65
8			4	90	321	80
9			5	85	304	61
10			4	80	286	71
11			5	70	250	50
12			4.5	88	314	70

Reaction conditions: Alcohol (1 mmol); g-C₃N₄@CuO(3 mg); TBHP (0.3 mL) H₂O (5 mL); 100W LED light, room temperature, TON= mole of product/mole of Cu, TOF=TON/time, ^aIsolated yields.

we have observed water is the most suitable solvent with 3 mg of the catalyst (0.28 mol%) gives comparatively high conversion in 2 h (Table 2, entry 5). The use of g-C₃N₄ (Table 2, entry 10 and 11) instead of g-C₃N₄@CuO decreases the yield of the product.

During the course of our photocatalytic study, we have examined the performance of various oxidants such as H₂O₂, TBHP, O₂-atmosphere. Out of these TBHP provides an effective conversion of the oxidation reaction. TBHP is considered to be a non-toxic and environmentally benign oxidant and generates *tert*-butanol as co-product which is easily separated by distillation.^{37–39} In our next move, we have examined the catalytic activity of g-C₃N₄@CuO to a wide range of primary and secondary alcohols to evaluate the scope and limitations of the current protocol. The oxidation of secondary alcohols such as 1-phenyl ethanol, its derivatives and diphenylmethanol gave the corresponding ketones in

90–96% yield (Table 3, entry 1–5). Benzyl alcohol and its derivatives were also efficiently oxidized to corresponding aldehydes with 88–93% yield (Table 3, entry 6–12). However, there is no such notable differences in product yield with electron donating (–OMe, –Cl, etc.) and an electron withdrawing groups (–NO₂, –OH, etc.) in the benzene ring (Table 3, entry 6–12). Moreover, the position of the substituent in the benzene ring did not bring any appreciable difference in product yield (Table 3, entry 9 and 12).

3.3 Reusability test

Reusability of the catalyst was checked by using 1-phenyl ethanol as the substrate. After the completion of the reaction, the catalyst was recovered by centrifugation and washed 2–3 times with distilled water and dried in an oven for 1 h and reused for next cycle. The

Scheme 1. Plausible mechanism for g-C₃N₄@CuO catalyzed oxidation of alcohols.

Table 4. Comparative study on reported conditions of Cu along with metals like V, Bi, Cd and Ag catalyzed the oxidation of alcohols to corresponding carbonyl compounds with the present protocol.

Entry	Metal catalyst	Condition	Yield/Conversion (%)	Reference
1	Cu/HT (7.3 mol%)	<i>p</i> -xylene, Ar atmosphere, time: 4–24 h, temp: 130 – 150 °C	72–99% conversion	40
2	Cu@imine-nano SiO ₂	TBHP, acetonitrile, time: 5–35 min, 50 °C	55–98% yield	41
3	Cu(bpy) ₂ +/bentonite	TBHP, time: 8 h reflux, N ₂ atmosphere	42–57% conversion	42
4	CdS/g-C ₃ N ₄	Benzotrifluoride, 300W Xe arc lamp, time: 6 h, temp: 60 °C		20
5	Ru/g-C ₃ N ₄	UV LED (390 nm), H ₂ O, r.t	73% conversion	21
6	MIL-125/Ag/g-C ₃ N ₄	ethanol, visible-light irradiation (>400 nm), O ₂ -atm; 6 h.	12–92% conversion	22
7	BiVO ₄ /g-C ₃ N ₄	methanol, time : 16 h, temp (25 – 27 °C), light source (250 W medium pressure visible Hg Lamp), oxidant (molecular O ₂)	79%	23
8	VO@ g-C ₃ N ₄	CH ₃ CN, H ₂ O ₂ 40W domestic bulb, r.t, time: 1–2.5h	85–98% yield	24
9	g-C ₃ N ₄ @CuO	H ₂ O, TBHP, r.t, time: 4–5 h, visible light	70–96% yield	Present work

Table 5. Comparative study with benzyl alcohol in terms of yield/conversion and TON.

Entry	Catalyst	Reaction conditions	Yield/conversion (%)	TON	Ref.
1	BiVO ₄ /g-C ₃ N ₄	Methanol, time: 16 (h), temp(25 – 27 °C), light source (250 W medium pressure visible Hg Lamp), oxidant (molecular O ₂)	81.3 (conv%)	9.2	23
2	Au-TiO ₂	H ₂ O : CH ₃ CN, TBHP, visible light	86	74.13	16
3	Copper(II) complex	H ₂ O, TBHP, temp:60 °C	100 (conv%)	100	43
4	g-C ₃ N ₄ @CuO	H ₂ O, TBHP, room temp time: 4–5 h, visible light	93	332	Present work

catalyst can be reused up to five consecutive cycles with no profound loss in yield of product and no apparent loss in activity (Figure S5, Supplementary Information). To investigate catalyst leaching we have carried out ICP-AES analysis of the filtrate after 5th catalytic cycle. From ICP-AES analysis of the filtrate after the fifth cycle, we have found that there is a negligible amount Cu in the filtrate (0.91 ppm) suggesting that CuO was held tightly to the g-C₃N₄ facilitating the recycling of the catalyst.

The proposed mechanism of photocatalytic oxidation of alcohol by g-C₃N₄@CuO is shown in Scheme 1. The CuO particles loaded on g-C₃N₄ could facilitate the separation of the electron–hole pair and promote the interfacial electron transfer process.⁶ The photogenerated electron of g-C₃N₄ nanosheets might help in the decomposition of TBHP which leads to the formation of a highly reactive species t-BuOO. This species seems to be responsible for the photocatalytic oxidation of alcohols to corresponding aldehydes and ketones.

3.4 Hot filtration test

The heterogeneity of g-C₃N₄@CuO catalyst was confirmed by hot filtration test. The reaction was carried out using 1-phenyl ethanol as substrate at 60 °C under similar conditions. The catalyst was filtered off by centrifugal precipitation after 20 min and half of the contents of the vessel were allowed to react for 4 h. The percentage conversion as determined by GC showed constancy at 30% even after 4 h. A parallel reaction without hot filtration of the catalyst showed 96% conversion. These results affirmed non-leaching processes during the reactions. (Figure S6, Supplementary Information).

The catalytic performance of g-C₃N₄@CuO was compared with some other reported ligand and metal systems (Table 4). The present protocol is efficient for the oxidation of alcohols in an aqueous medium at room

temperature with broad functional group tolerance. The yield and TON of our present protocol is compared with other similar catalyst (Table 5).

4. Conclusions

We have developed an eco-friendly, novel protocol for oxidation of alcohols into corresponding aldehydes and ketones using nanocomposite g-C₃N₄@CuO. The catalyst showed an excellent catalytic activity for a variety of alcohols at room temperature under visible light in the aqueous medium. The catalyst was easily recovered and reused for five cycles without losing its catalytic activity.

Supplementary Information (SI)

The preparation of g-C₃N₄ characterization of the catalyst is available at www.ias.ac.in/chemsci.

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