

Copper Nanoparticles Immobilized on Nanocellulose: A Novel and Efficient Heterogeneous Catalyst for Controlled and Selective Oxidation of Sulfides and Alcohols

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Abstract

In this work, we have described the versatility of low metal loading copper nanoparticles immobilized on nanocellulose for the controlled and selective oxidation of sulfides to sulfoxides and primary alcohols to aldehydes using green oxidant at room temperature. Aromatic, aliphatic and heterocyclic sulfides were oxidized to their corresponding sulfoxides with high yields without formation of over oxidized sulfones. Similarly, benzylic, allylic and aliphatic alcohols were selectively oxidized to aldehydes without traces of carboxylic acids in good to excellent yields.

Graphical Abstract



Keywords Oxidation · Nanoparticles · Heterogeneous · Low metal loading · Recyclability

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1 Introduction

In organic syntheses, controlled and selective oxidation is an important transformations as the resultant products are valuable intermediates for copious numbers of drugs, vitamins and biologically active compounds [1, 2]. In particular, sulfoxides are widespread functional group found in a large number of pharmaceutically and biologically active compounds [3, 4]. Therefore, sulfoxidation is significantly an essential reaction across the chemical industries and academic research. Similarly, the selective oxidation of alcohols to their corresponding aldehydes or ketones has been exclusively examined in last few decades



Fig. 1 FESEM image (upper left), TEM images with SAED pattern (lower left), TEM-EDX spectra (upper right) and Particle size distribution histogram (lower right) of the prepared CuNPs/NC catalyst

since carbonyls can find their importance in dye industries and pharmaceuticals as well as in total synthesis of natural products [5–7].

Although for sulfides oxidation a plethora of methodologies has already been established by different research groups but the majority of the systems use homogeneous catalysts which are difficult to recycle and reuse. Traditionally sulfoxides are obtained in good yields using different catalytic systems based on different transition metals including copper [8–17], however most of the metals used in these systems are costly and metal loading is high in case of heterogeneous systems. In modern era, from green chemistry stand point, low metal loading, use of biodegradable support materials and green oxidants are very important in organic transformation.

Likewise, many traditional methods are already available for alcohols oxidation via toxic and environmentally harmful stoichiometric oxidants such as hypochlorite, permanganates, chromium oxides and others [18–20]. Considering environmental issues, non-waste producing oxidants such as air, O_2 or H_2O_2 offer a support for environmentally benign and moderately cheap systems but catalysts are crucial for activation of these oxidants [21, 22]. Significantly, the use of TEMPO (2,2,6,6-tetramethylpiperidinyl-1-oxyl) as stable nitroxyl radicals in alcohol oxidation seems to offer a noteworthy fortification for plenteous catalytic systems with transition metal complexes using air as oxidant with water as only by-product [5, 23–27]. However, additional bases or ligands, high metal loading, organic solvent and high temperature are usually coupled with this process whereas there have been several recent reports avoiding these undesirable conditions [28–30]. Therefore, there is great deal of attention in the development of low metal loading, ligand- or base-free catalytic system using green solvent media at room temperature.

Cellulose is one of the most abundant biopolymer in the world, which is found in highly crystalline form and the study of this property has been the subject of intense research, particularly to make out monocrystallites range within cellulose [31-36]. Recently, applications of



Fig. 2 DLS analysis for size distribution in solution (upper left), XRD pattern (upper right), XPS spectra of Cu $2p_{3/2}$ and $2p_{1/2}$ (lower left) and TGA and DTG curves (lower right) of the prepared CuNPs/NC catalyst

nanocellulose as a support material for metal nanoparticles (NPs) have gain more importance and they are of attractive choices to common organic or inorganic catalytic system as they comprise unique properties of high crystalline order, well defined size and morphology, a controlled surface area and higher mechanical strength [37]. Thus, for developing new and sustainable materials from renewable resources cellulose is a clean starting material.

In this work, we have described the versatility of low metal loading copper nanoparticles (<1 mol %) immobilized on nanocellulose for the controlled and selective oxidation of sulfides and primary alcohols using green oxidant at room temperature.

2 Experimental

2.1 Preparation of CuNPs/NC nanocatalyst

The preparation of CuNPs/NC is depicted in (Fig. 1, SI), which consists of two steps. In the first step, we have synthesized nanocellulose (NC) by acid hydrolysis of

microcrystalline cellulose according to previous reported methods [38, 39].

To prepare CuNPs/NC, NC suspension (2 g) was dispersed with $CuSO_4$ ·5H₂O (0.249 g) in water (500 mL) at room temperature for 0.5 h. Then, hydrazine hydrate (50%, 10 mL) was added drop wise for another 0.5 h and then reaction mixture was stirred for 2 h at room temperature. The obtained solid was centrifuged and washed with distilled water and acetone, to remove un-reacted reagents. Then the product was dried at 100 °C for 10 h and stored in desiccators. The resultant catalyst (CuNPs/NC) was fully characterized by SEM, TEM, TEM-EDX, XRD, XPS, ICP-AES and TGA analysis.

2.2 Characterization of the prepared catalyst

The structure and morphology of the synthesized nanoparticles are shown in the Fig. 1. From the Scanning electron microscopy (SEM) the structure and morphology of the nanoparticles are not clearly understood which was further determined by transmission electron microscopy Table 1 The oxidation of thioanisole with different catalysts using aqueous H_2O_2



Entry	Catalyst	Solvent	H ₂ O ₂ (mmol)	Catalyst loading	Time (h)	Yield ^a (%)
1	_	EtOH	1	_	24	20
2	CuSO ₄ ·5H ₂ O	EtOAc	1	2 mol%	5	10
3	CuI	EtOAc	1	2 mol%	5	40
4	Cu(OAc) ₂ ·2H ₂ O	EtOAc	1	2 mol%	5	15
5	CuO	CH ₃ CN	1	2 mol%	5	20
6	CuNPs/NC	EtOH	1	20 mg	6	70
7	Cu ₂ O NPs	CH ₃ CN	1	20 mg	5	_
8	CuNPs/NC	AcOEt	1	20 mg	5	40
9	CuNPs/NC	H ₂ O	1	20 mg	6	20
10	CuNPs/NC	CH ₃ CN	1	20 mg	2	40 ^b
11	CuNPs/NC	MeOH	1	20 mg	5	50
12	CuNPs/NC	EG	1	20 mg	5	40
13	CuNPs/NC	PEG	1	20 mg	5	10
14	CuNPs/NC	THF	1	20 mg	5	_
15	CuNPs/NC	Glycerol	1	20 mg	6	20
16	CuNPs/NC	DMSO	1	20 mg	5	_
17	CuNPs/NC	DMF	1	20 mg	5	_
18	CuNPs/NC	Acetone	1	20 mg	3	30 ^b
19	CuNPs/NC	EtOH	2.5	20 mg	14	85
20	CuNPs/NC	EtOH	4	20 mg	2	99
21	CuNPs/NC	EtOH	5	20 mg	2	99
22	CuNPs/NC	EtOH	2	20 mg	17	89
23	CuNPs/NC	EtOH	4	4 mg	2	65
24	CuNPs/NC	EtOH	4	10 mg	2	85
25	CuNPs/NC	EtOH	4	30 mg	2	99

Best results are hightlighted in bold

Reaction conditions: sulfide (1 mmol), H₂O₂ (n₁ mmol), CuNPs/NC (n₂ mg) was stirred at room temperature

^aIsolated yield

^bTrace amounts of sulfone are obtained

(TEM) images and revealed the presence of well-dispersed NPs with almost spherical shape and amorphous in nature which is confirmed by SAED pattern. From TEM histogram, the average size of the nanoparticles was found to be 12.079 nm. The characteristic peaks of carbon, oxygen and copper in TEM-EDX pattern confirmed the purity of the prepared catalyst. The copper content in the prepared catalyst was estimated by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) and it was found to be 2.40 wt%. Dynamic light scattering (DLS) measurements were performed at 298.15 K by using a NaBiTec Spectro-Size 300 light scattering apparatus (NaBiTec, Germany) with a He–Ne laser (633 nm, 4 mW). From DLS, the average size distribution of copper NPs combined with nanocellulose support dispersed in a liquid was found to be 210 nm showed in Fig. 2 (and Fig. 2, SI).

The prepared CuNPs/NC was well characterized by powder XRD-diffraction pattern (Fig. 2). The four peaks at $2\theta = 36.6^{\circ}$, 42.5° , 61.9° and 74.2° corresponding to the Bragg's planes (111), (200), (220) and (311) indicate Cu₂O formation and another two distinguished peaks at $2\theta = 43.5^{\circ}$ and 50.6° corresponding to (111) and (200) planes represent Cu(0) formation. The first four peaks at $2\theta = 14.7^{\circ}$, 16.7° , 22.9° and 34.7° corresponding to the

	$ \begin{array}{c} R_{1} & S_{2} \\ 1 & (a-m) \end{array} $	30% H ₂ O ₂ CuNPs/NC EtOH, r.t	$ \begin{array}{c} O\\ R_2 \\ \overset{"}{S} \\ R_2\\ 2 (a-m) \end{array} $	
Entry	Substrates	Products	Time (h)	Yield ^a (%)
1	S_	O S S	2	99
2	S~	S O	2	99
3	C s	S O	5	99
4	S-	S O	5	95
5	Br	Br S O	5	75
6	O ₂ N		12	73
7	O-S	o- s	3	99
8	SOH	о ^В он	2.5	98
9	C ^S C	O Š Š	12	65
10	C ^s C	S 0	7	98
11	$\bigtriangledown^{\rm S}$	∠,s´ ^O	2	96
12	~~~s~~~	0 S S	2.5	95
13	∕S∖	O S	3	92

Reaction conditions: sulfide (1 mmol), H_2O_2 (4 mmol), CuNPs/NC (20 mg, 0.756 mol %) stirred at room temperature in ethanol ^aIsolated Yield



Fig. 3 TEM images with particle size distribution histogram (above) and bar diagram of reusability (below) of reused CuNPs/NC catalyst in sulfide oxidation

(101), (101'), (002) and (040) planes appear in the XRD pattern due to the presence of nanocellulose support. Further, investigation was carried out to get the exact oxidation state of copper by X-ray photoelectron spectroscopy (XPS) analysis. XPS experiments were carried out on PHI 5000 Versa Prob II, X-Ray photoelectron spectrometer and binding energies $(\pm 0.1 \text{ eV})$ were determined with respect to the position C 1s peak at 284.71 eV. Calibration of the binding energy (BE) scale was done by using the C 1s (BE = 284.8 eV) signal. The binding energy of Cu $2p_{3/2}$ and $2p_{1/2}$ at 931.64 eV and 951.64 eV respectively in XPS spectrum along with a very weak satellite peak at binding energy 942.46 eV indicating the presence of Cu(I) oxide in the prepared catalyst (Fig. 2) [40-42]. To examine the thermal stability of the catalyst Thermo Gravimetric Analysis (TGA) was performed from 30 to 800 °C at ramp rate or scanning rate of 10 °C/min with TGA/SDTA851 Mettler Toledo instrument under nitrogen atmosphere (N2 gas flow rate: 50 mL min⁻¹⁰) taking empty alumina as reference. The TGA curve (Fig. 2) of the catalyst demonstrated the superior thermal stability of the catalyst up to 307 °C, indicating wide temperature range usefulness of prepared catalyst for any chemical reaction.

3 Results and Discussion

3.1 Oxidation of Sulfides

We initialized our studies with oxidation of thioanisole as a probe reaction with 30% H₂O₂ as oxidant using prepared CuNPs/NC nanocatalyst in different solvents under standard conditions. Different types of copper sources were also investigated and observed that prepared catalyst showed better results than the other copper sources. To improve the yields of the reaction, initially different types of solvents were screened and it was observed that higher yields occurred in polar solvents such as AcOEt (Table 1, entry 8), methanol (Table 1, entry 11) or ethanol (Table 1, entry 6). On the other hand, no reaction proceeds when THF (Table 1, entry 14), DMSO (Table 1, entry 16) and DMF (Table 1, entry 17) were employed. Among the polar solvents used, ethanol (Table 1, entry 6) was proven to be the most effective solvent in terms of yield of the oxidized product. Furthermore, the effect of oxidant was also studied and observed that 4 mmol 30% H₂O₂ was suitable for excellent yield of oxidation products. Finally, the catalyst loading for the reaction was investigated and interestingly found that use of 20 mg (0.756 mol %, 0.00756 mmol) catalyst resulted in completion of the reaction within 2 h. However, upon lowering the catalyst concentration from 20 to 10 mg or 4 mg the reaction still proceeded but afforded lower yield of sulfoxide.

With the optimized reaction conditions, we examined the scope of the various sulfides in order to establish the broad substrate scope of the protocol. Thioanisole (Table 2, entry 1) and substituted thioanisoles (Table 2, entries 4–7) undergo smooth oxidation with a small decrease in rate due to the presence of electron-withdrawing groups (Table 2, entries 5,6). On the other hand, electron-rich sulfides were oxidized faster than their electron-deficient counterparts. Similarly, allyl phenyl sulfides, diallyl sulfide and heterocylic sulfides were oxidized smoothly to their corresponding sulfoxides; neither sulfones nor epoxides (Table 2, entry 3) were detected in these reactions. The sulfide containing aliphatic alcohol (Table 2, entry 8) group was oxidized to its corresponding sulfoxide without affecting the alcoholic group.

In order to study the reusability, the catalyst was recovered at the completion of the reaction by simple filtration, washed with distilled water and acetone for several times and then employed in the next run after further addition of substrates in appropriate amount and results are reported in Fig. 3. To check the agglomeration of particles during the reaction TEM images of the CuNPs/NC were taken after fifth run and the results were compared with those of freshly prepared catalyst and the results are shown in Fig. 3. From the TEM histogram of reused catalyst, the average size of the nanoparticles was found to be 14.65 nm which is almost equal to the fresh catalyst. In order to rule out the leaching of copper metal for the sulfides oxidation, a leaching test of copper species in the reused catalyst (after 5th cycle) was done by ICP-OES analysis, but no significant leaching of copper from the catalyst was observed.

3.2 Selective Oxidation of Alcohols

To expand the versatility of the catalyst, alcohols oxidation was performed using prepared CuNPs/NC with TEMPO as nitroxyl radical at room temperature under aerobic conditions. 4-Chlorobenzyl alcohol was taken as the model substrate in acetonitrile which afforded corresponding aldehyde in good yields with relatively longer period of time. To improve the results, at first different types of solvents were screened and it was observed that for higher yields of aldehyde in short reaction time combination of water and ethylene glycol in 1:1 ratio was the best reaction media among the other. After getting the best reaction media, the catalyst loading as well as amounts of TEMPO were also varied and observed that 20 mg of CuNPs/NC and 10 mol% of TEMPO (Table 3, entry 8) are sufficient for complete conversion within 3 h. Three set of reactions were also carried
 Table 3
 The oxidation of 4-chlorobenzyl alcohol with CuNPs/NC and TEMPO in different solvent in open air



Entry	Solvent	CuNPs/ NC (mg)	TEMPO (mol %)	Time (h)	Yield ^a (%)
1	CH ₃ CN	20	50	6	90
2	H ₂ O/CH ₃ CN (1:3)	20	50	6	90
3	EtOH	20	50	5	99
4	EG	20	50	3	99
5	H ₂ O	20	50	3.5	99
6	H ₂ O/EG (1:1)	20	50	2	99
7	H ₂ O/EG (1:1)	20	15	3	98
8	H ₂ O/EG (1:1)	20	10	3	99
9	H ₂ O/EG (1:1)	20	5	3	83
10	H ₂ O/EG (1:1)	20	3	3	70
11	H ₂ O/EG (1:1)	20	1	3	50
12	H ₂ O/EG (1:1)	10	10	3	75
13	H ₂ O/EG (1:1)	30	10	3	99
14	H ₂ O/EG (1:1)	20	-	18	00
15	H ₂ O/EG (1:1)	_	5	3	00
16	H ₂ O/EG (1:1)	-	-	3	00

Best results are hightlighted in bold

Reaction conditions: alcohol (1 mmol), TEMPO ($n_3 \text{ mol}\%$), CuNPs/ NC ($n_4 \text{ mg}$) was stirred at room temperature with air as the oxidant ^aIsolated yield

out one without CuNPs/NC, one without TEMPO and the last one in absence of both TEMPO and copper catalyst and observed that no reaction takes place in these three reaction conditions. From these three set of reactions it is confirmed that CuNPs/NC and TEMPO both are necessary for these transformations.

After obtaining the best reaction conditions, all further reactions were carried out using this optimal condition to confirm the generality and efficiency of our methodology and the results are summarized in Table 4. Various primary and secondary benzylic, allylic and aliphatic alcohols were investigated under this catalytic condition. It was surprisingly observed that only primary alcohols were oxidized in this catalytic system in good to excellent yields without the formation of trace amounts of carboxylic acid. Further, to confirm the selectivity a reaction was carried out by taking a mixture of 4-chlorobenzyl alcohol (1°-alcohol) and 1-phenyl ethanol (2°-alcohol) with the optimized conditions. Interestingly, it was observed that only 4-chlorobenzyl alcohol was oxidized to 4-chlorobenzyldehyde and 1-phenyl

		CuNPs/NC, TEMPO		
		H ₂ O/EG		
		All 1. t		
Entry	Substrates	Products	Time (h)	Yield ^a (%)
1	ClOH	Cl	3	99
2	ОН		3	99
3	O ₂ N OH	O ₂ N	10	82
4	но	HO	6	94
5	ОН		6	95
6	,O ,O ,OH		5	95
7		$\mathbb{N}^{\mathrm{NH}_2}$	7	85
8	Br	Br	6	98
9			4	95
10			12	80
11	ОН		17.5	62
12	ОН		12	88
13	ОН		24	45
14	~~~~ ⁰ Н	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	17	50
15	ОН	0 0	17	45
16	\bigcirc		24	-
17	ОН		24	-
18	HO	o	24	-

Reaction conditions: alcohol (1 mmol), TEMPO (10 mol%), CuNPs/NC (20 mg, 0.756 mol%) stirred at room temperature in H₂O/EG (1:1) media with air as the oxidant ^aIsolated yield

Table 4Aerobic oxidation ofvarious alcohols catalyzed byCu-TEMPO system

ethanol remained intact in the reaction mixture (confirmed by GC-MS).

To evaluate the reusability, the catalyst was separated by simple filtration, washed with water and acetone for several times and then used for next runs after further addition of substrates in appropriate amount under identical conditions and results are reported in (Fig. 3, SI). In order to rule out the leaching of copper metal to the reaction media, hot filtration test was performed for the model reaction. The reaction was stopped after 1 h to obtain a conversion of 60% (analyzed by GC–MS) and the solid catalyst was then hot-filtered off. The filtrate part was then allowed to continue to react for another 5 h. The product concentration in the filtrate was found to be almost constant indicating that no Cu species had leached to the reaction mixture.

4 Conclusions

In summary, we have developed a low metal loading CuNPs/NC as efficient and versatile catalyst for eco-friendly oxidation of various sulfides to sulfoxides using 30% H₂O₂ at room temperature and selective oxidation of primary alcohols to aldehydes using TEMPO as nitroxyl radical in H₂O/EG media at room temperature. Use of biodegradable support material, low metal loading (< 1 mol%), high yield of oxidized products, short reaction time and room temperature reaction conditions make this sulfides oxidation protocol more advantageous than the existing protocols. On the other hand, low metal loading, green solvent media, ligand- and base-free conditions are the major advantages of our catalyst system in alcohol oxidation reactions. The benzylic and allylic alcohols were oxidized with excellent yields, whereas aliphatic alcohols were less reactive and required long reaction time. Both the oxidation systems are simple and mild and the copper catalyst can be recycled and reused up to 5th cycle without significant loss of catalytic activity. This work can be considered as a very good step towards the promising trend of heterogeneous and environmental friendly transformations of organic compounds.

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