Fabrication of CuO nps@ modified activated carbon (CuO nps@ modified AC) using sol-gel technique, its characterization and application to selective oxidation of benzylic alcohols avoiding usage of TEMPO as co-oxidant

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Abstract
Copper (II) oxide nanoparticles synthesized by sol-gel method were supported on carboxyl modified activated carbon (CuO nps@ modified AC) and it was studied to catalyze the selective oxidation of benzylic alcohols avoiding the use of usual TEMPO as co-oxidant and oxygen used as oxidant to yield aldehydes in comparatively lesser time than known methods. Also the catalyst has been characterized using SEM, TEM, XRD, UV, FTIR, TGA, VSM and ICP techniques. In addition the catalyst was quite recyclable upto five runs.

Key Words
CuO nps@ modified AC, TEMPO, benzyl alcohol, catalyst

I. Introduction
The selective oxidation of benzyl alcohols to corresponding aromatic aldehydes is a decisive functional group conversion in modern organic synthesis as the aromatic aldehydes are important key intermediates in numerous reactions. These aromatic aldehydes also possess industrial importance for these can be utilized as or in the synthesis of plastic additives,[1] in pharmaceuticals, in perfumes, in flame retardants,[2] in agrochemicals[3] and in textile industry.[1] The oxidation of benzyl alcohols have been previously seen with $KMnO_4$,[4] Pd-catalysts, [5,6] Co-catalysts,[7,8] and graphene oxide/ N-doped grapheme oxide[9] as catalysts. It has been seen that TEMPO has been used as a co-oxidant in all the oxidations catalyzed by Cu (II) catalysts.[1,10,11, 19, 20] In the present work, we present Cu (II) oxide nanoparticles supported on a modified activated carbon support which catalyses the selective oxidation of benzylic alcohols to corresponding aldehydes in lesser time under green conditions without use of TEMPO.
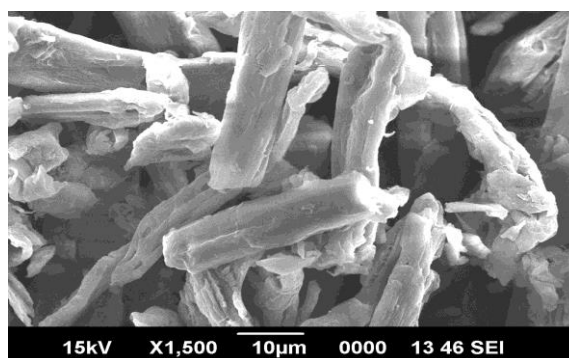
II. Result and Discussion
Characterization of CuO nps@ modified activated charcoal (CuO nps@ modified AC)
SEM Analysis
SEM analysis of the catalyst was studied on JEOL Model JSM - 6390LV. The surface morphology of CuO nps@ modified AC appears as small wooden twigs and no copper oxide nanoparticles as separate structures were observed (**Fig. 2a, 2b**).
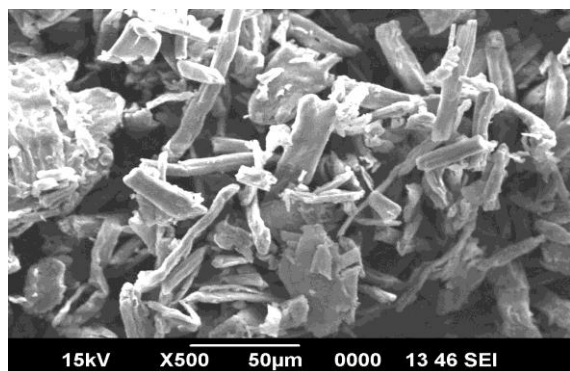
a   b
Figure 2 SEM micrographs of CuO nps@ modified AC

TEM Analysis

TEM analysis was performed on Jeol/JEM 2100. The information inferred from transmission electron micrographs **(Fig. 3a, 3b)** involves the black observable particles can be attributed to CuO nanoparticles adhered to modified activated charcoal which appears as a mesh.
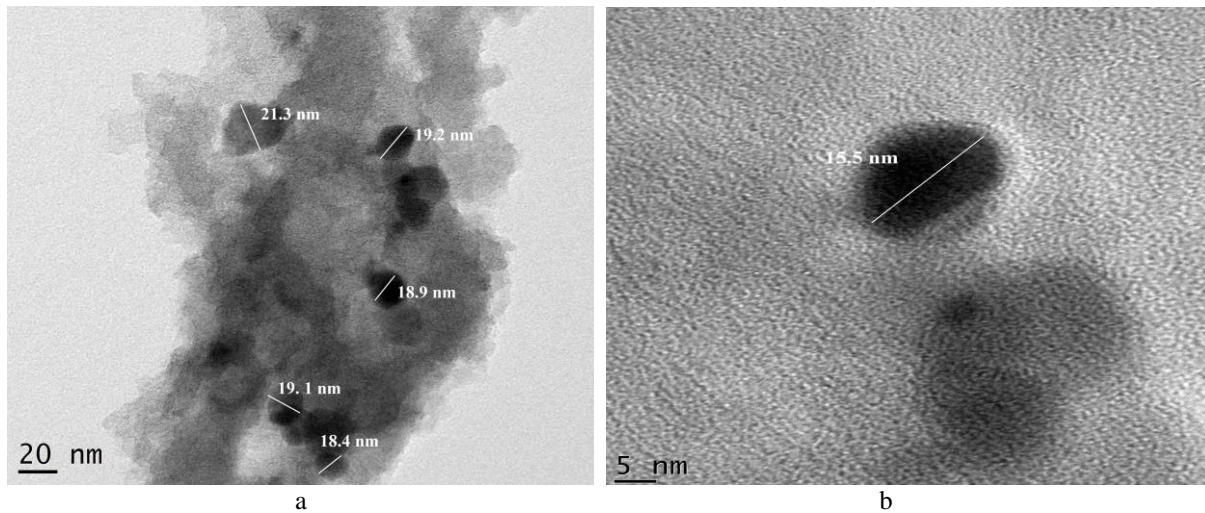

a   b

Figure 3. TEM micrographs of CuO nps@ modified AC

UV-Vis Analysis

The UV spectrum was recorded on Varian, Cary 5000 and it showed two peaks, one at 203 nm and the other at 283 nm (low absorbance) **(Fig. 4)**. Both the peaks correspond to CuO nanoparticles as also observed by.[12,13]
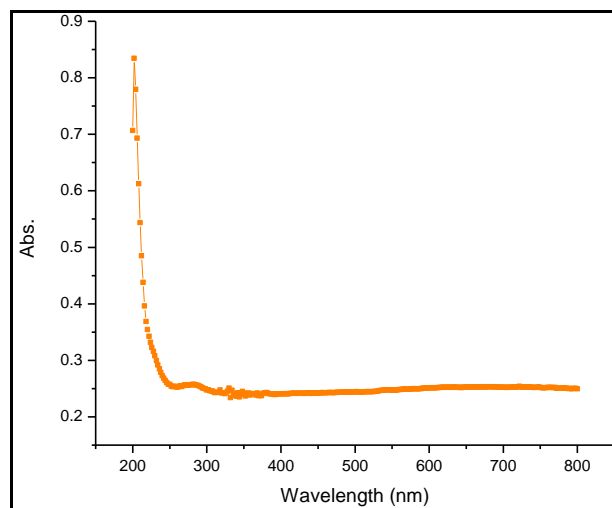

Figure 4. UV-Vis analysis of CuO nps@ modified AC

XRD Analysis

XRD analysis was studied on Bruker AXS D8 Advance. The results obtained shows a peak at 22 dgree corresponding to 002 plane of graphitic carbon. Also peaks at 35 degree corresponding to 110, 002 planes of CuO nanoparticles and at 38 degree corresponding to 111 plane of CuO nanoparticles were observed **(Fig. 5)**.[14]
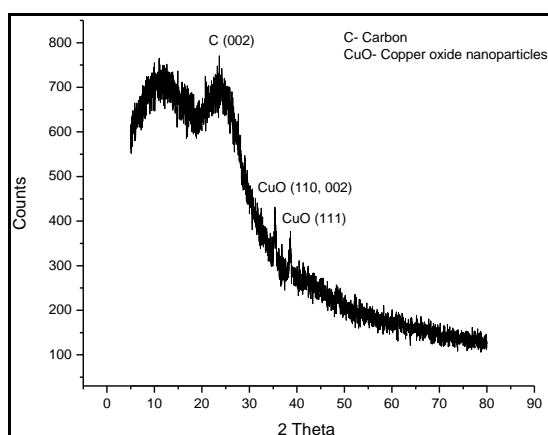
Figure 5. XRD Analysis of CuO nps@ modified AC

FTIR Analysis

FTIR analysis of CuO nps@ modified AC was taken up on Thermo Nicolet, Avatar 370. It showed peaks at 1711 cm^{-1} corresponding to C=O stretching vibration of carboxyl group, 3489 cm^{-1} corresponding to O-H stretching vibration of carboxyl group and a broad peak at 1113 cm^{-1} due to C-O stretching vibration along with shoulder band at 1085 cm^{-1} corresponding to carboxylic O-H vibration. The peaks at 2920 cm^{-1} and 2842 cm^{-1} are atrributed to C-H asymmetric and symmetric stretching vibrations of CH, CH$_2$ and CH$_3$ groups. Also a peak observed at 2320 cm^{-1} corresponds to C-O bond of ketene moiety present.[15] In addition, a weak strength peak at 562 cm^{-1} is attributed Cu-O bond vibration **(Fig. 6)**.[16]
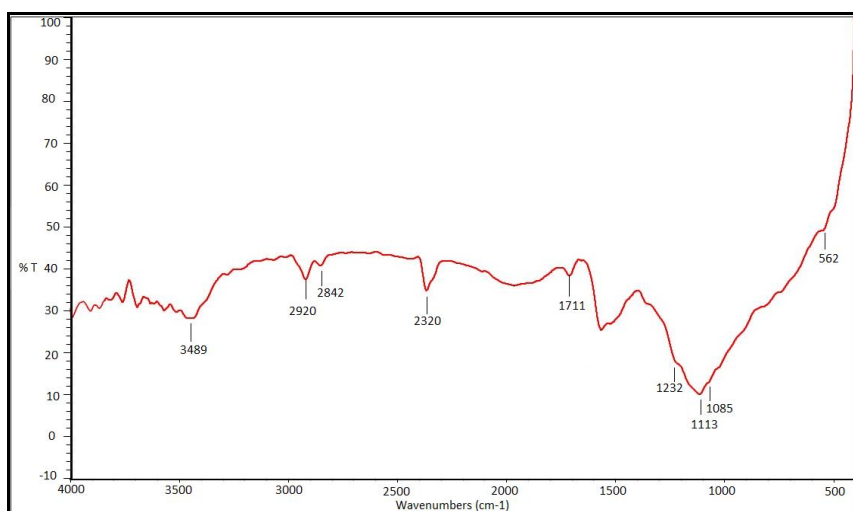

Figure 6. FTIR Analysis of CuO nps@ midified AC

TGA

Thermogravimetric analysis was recorded on Linesis Thermal Analyser and the results show an initial weight loss of upto 7.8% at 152 ºC and continues upto 20.4% at 507 ºC which further continues upto 36% at 842 ºC. The initial loss can be attributed to physically adsorbed water. The loss of upto 20.4% and 36% corresponds to the loss of surface oxygen modified functionalties as carbon dioxide from loss of carboxyl groups **(Fig. 7)**.
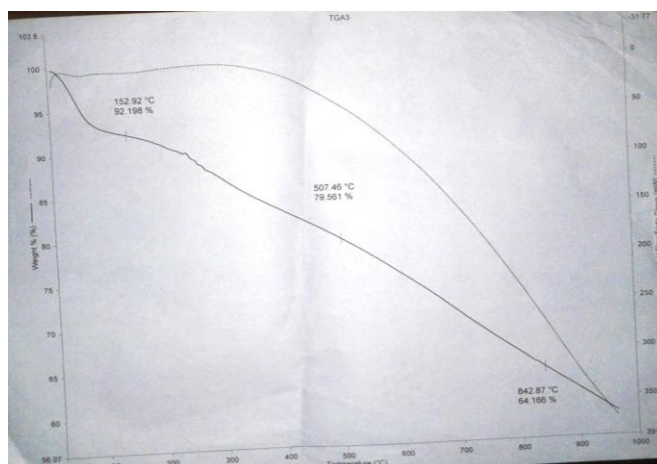
Figure 7. TGA of CuO nps@ modified AC

VSM Ananlysis

VSM analysis was done on model: 7410 series made by Lakeshore. The magnetization curves for CuO nps@ modified shows the material to be ferromagnetic in nature having a magnetization of 0.0082 emu/ g **(Fig. 8)**.
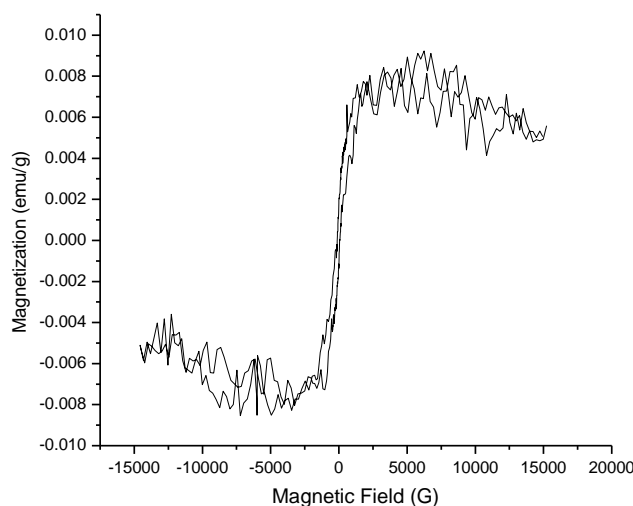

Figure 8. VSM plot of CuO nps@ modified AC

ICP Analysis

ICP analysis was studied on ARCOS, Simultaneous ICP Spectrometer made by SPECTRO Analytical Instruments GmbH, Germany. The given sample was digested in 5ml HNO_3 and 10ml H_2O_2 and made up to 50ml. The filtered solution was analyzed with ICP-AES system. The amount of copper metal present in CuO nps@ modified AC was found to be 6.68 wt%.

Optimization of reaction conditions for the oxidation of benzyl alcohols

To optimize the reaction conditions, *p*-nitrobenzyl alcohol (1 mmol) was randomly chosen as test substrate and catalyst (0.1 g), oxygen (balloon) as oxidant, base (1 mmol) and tested solvents (2 mL). Firstly, caesium carbonate was the base chosen and reactions in water for 6 h were observed at r.t., no reaction was observed (entry 1, Table 1) but at 80 °C and 100 °C (entry 2 and 3, Table 1) and no product was observed along with consumption of reactants. The same base was tried in toluene as solvent at r.t. and again no reaction took place for 6 h run but at 80 °C and 110 °C conditions again no product along with reactant consumption was found (entry 4-6, Table 1). The

reaction with caesium carbonate at lesser reaction time was also observed and the data has been added to Table 1 which indicates decomposition of aldehyde formed to gaseous substrates like CO_2 along with other substrates the presenceof which has not been studied in the present work. Next potassium carbonate was tried as a base and it was seen that at room temperature, there was no reaction observed (entry 7, Table 1). Further the temperature was increased to 80 ^oC and 95 % yield was obtained (entry 8, Table 1). So here, temperature is playing an important role for the conversion and for the catalyst to substitute that energy gap. The temperature was further increased to see if there is an increase in yields but the results were still the same (entry 9, Table 1). The reaction was also carried out in toluene if the yields can be increased at 110 ^oC the yields were almost same (entry 10, Table 1). As water is a green solvent so the optimized condition was confirmed with water as solvent.

To reach some mechanistic insights and know the vitality of CuO nps@ modified AC in selective oxidation of benzyl alcohols, experiments with parallel analogues were also conducted under optimized set of conditions. Again p-nitobenzyl alcohol was takenas the test substrate and a reaction was carried out with bare CuO nanoparticles and only 30% yields were observed (entry 1, Table 3). Agglomeration of particles was also an addition issue with bare nanoparticles. The lower yields can be attributed to low reduction potential of Cu^{2+}/Cu^+ (0.153) which initiated the reaction but unable to complete. Also, a reaction was tried with modified AC only as catalyst and no reaction was observed (entry 2, Table 3). So the modified AC is playing a role in enhancing the activity of CuO and not itself involved in the mechanism.

Further, a set of oxidation reactions with different substituted benzyl alcohols were taken up under the optimized set of conditions. It was observed that the electron withdrawing groups substituted alcohols gave best results in lesser time (p-nitrobenzyl alcohol, 45 min) while the benzyl alcohols substituted with electron releasing groups gave a comparatively lower yield in longer time (p-methylbenzaldehyde, 87%, 1.30 h). Among halogen substituted, p-chlorobenzyl alcohol (90%) gave the better yield than other halogen substituted benzyl alcohols. Reactions with lower aliphatic alcohols, ethanol and propanol was also tried and the corresponding aldehyde conversion was observed in traces while the reactant consumption was observed signifying presence of other products such as carbon dioxide and water along with the presence of acetaldehyde and propanal in traces.

Table 1 Optimization of reaction conditions for oxidation of benzyl alcohols using p-nitrobenzyl alcohol as test substrate

S.No.	Solvent	Base	Time	Temperature (^oC)	Yield%[b]
1	water	Cs_2CO_3	6 h	r.t.	NR
2	water	Cs_2CO_3	6 h	80	-
3	water	Cs_2CO_3	45 min.	80	-
4	water	Cs_2CO_3	6 h	100	-
5	water	Cs_2CO_3	45 min.	100	-
6	Toluene	Cs_2CO_3	6 h	r.t.	-
4	Toluene	Cs_2CO_3	45 min.	r.t.	NR
5	Toluene	Cs_2CO_3	45 min.	80	-
6	Toluene	Cs_2CO_3	45 min.	110	-
7	water	K_2CO_3	6 h	r.t.	NR

8	water	K_2CO_3	45 min.	80	95
8	**water**	**K_2CO_3**	**45 min.**	**100**	**95**
9	Toluene	K_2CO_3	1.5 h	110	94

[a]Catalyst (0.1 g), Base (0.5 mmol), *p*-nitrobenzylalcohol (1mmol),
O₂ (balloon), solvent (2 mL)
[b]Isolated yields

Table 2 Comaparison of CuOnps@ modified AC with parallel
analogues using *p*-nitrobenzylalcohol as test substrate

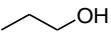| S.No.	Catalyst	Time	Yield%[b]
1	CuO nps	5 h	30
2	Modified AC	6 h	NR
3	**CuO nps@ modified AC**	**45 min.**	**95**

[a]Catalyst (0.1 g), Base (0.5 mmol), *p*-nitrobenzylalcohol (1mmol),
O₂ (balloon), solvent (water, 2 mL) at 80 ℃
[b]Isolated yields

Table 3 Selective oxidation of benzyl alcohols to corresponding
aldehydes using CuO nps@ modified AC as catalyst

S.No.	R	Product	Time	Yield%	M.Pt./ Lit. M.Pt.(℃)
1	H	2a	1 h	92	Liq.
2	4-CH₃	2b	1.30 h	87	Liq.
3	4-OCH₃	2c	2 h	85	Liq.
4	4-Cl	2d	1.30 h	90	48-50/ 47-49[17]
5	2-Cl	2e	2 h	86	Liq.
6	4-Br	2f	1 h	89	56-58/ 55-58[18]
7	3-Br	2g	1.30 h	87	Liq.

8	2-NO$_2$	2h	1.30 h	85	42-44/ 42-44[18]
9	3-NO$_2$	2i	1 h	95	54-56/ 55-58[18]
10	4-NO$_2$	2j	45 min	95	102-104/ 103-105[18]
11	⌒OH	-	30 min.	trace	-
12	⌒⌒OH	2k	50 min.	trace	-

[a]Catalyst (0.1 g), Base (0.5 mmol), benzylalcohols (1mmol),
O$_2$ (balloon), solvent (water, 2 mL) at 80 °C
[b]Isolated yields

Recyclability of CuO nps@ modified AC

To test the recyclability of CuO nps@ modified AC in the oxidation of benzyl alcohols, *p*-nitrobenzyl alcohol **(entry 10, Table 3)** (2 mmol) was taken as the test substrate under the optimized set of conditions (also made doubled for doubled amount of reactant) for consecutively five runs and it was found that there is little drop in activity by fifth run as indicated by a drop in yield%. After every run, the catalyst was thoroughly washed with warm water (10 mL) and ethanol (10 mL) and dried in oven at 50 °C for 5 h. As after every run, the catalyst needs to be conditioned to be used for the next run, there was some manual loss of catalyst amount and so each time the reactant and other conditions were adjusted respectively **(Fig. 9)**.
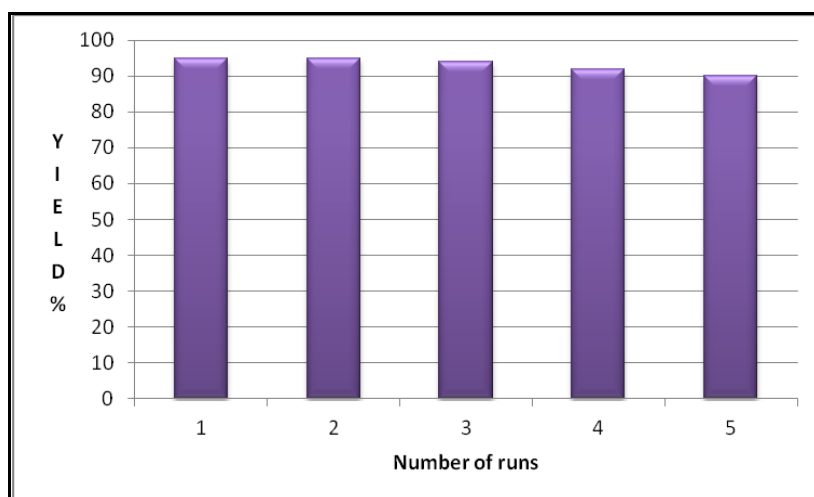

Figure 9. Recyclability of CuO nps@ modified AC in case of *p*-nitrobenzyl alcohol as test substrate **(entry 10, Table 3)**

Proposed mechanism for oxidation of benzyl alcohols using CuO nps@ modified AC as nanocatalyst

The mechanism involves first alcohol addition to CuO nps @ modified AC to form a complex (A). In the presence of base (potassium

carbonate) there occurs deprotonation of benzyl alcohol by the catalyst to form an alkoxide type transition phase (B) and buffering action of base is involved balance the pH by involving a transitory phase in equilibrium with alkoxide transitory phase (B). The next step in the cycle involves a β-hydride elimination giving away the product formation. Finally the hydrogen peroxide is removed from the catalyst by the addition of oxygen to regenerate the catalyst in its previous condition (**Scheme 1**).

Further, there is an indirect role of modified active carbon in catalyzing the oxidation process. Modified active carbon itself and also increases the catalytic activity of CuO nps in decomposition of hydrogen peroxide to release oxygen thus creating a consistent O_2 environment inside the vessel. Also, modified active carbon surface provides a suitable negatively charged surface to enhance the activity of CuO nps for the requisite catalytic performance in the oxidation reaction.
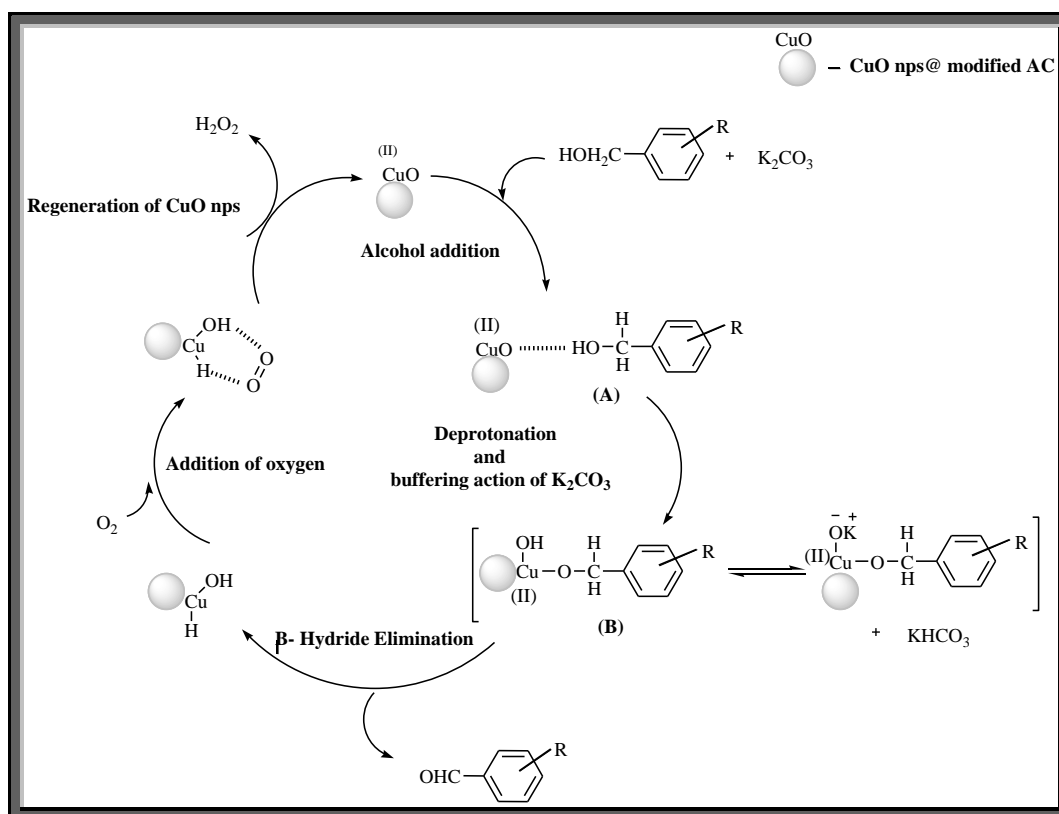
Scheme 1

Experimental
Synthesis of CuO nps@ modified activated carbon
Synthesis of modified activated carbon
Commercially available activated charcoal (5 g) was taken in a round bottomed flask (250 mL) and to it was added conc. HNO_3 (25 mL) and the flask was equipped with magnetic stirrer and a reflux condenser. The contents of the flask were heated at 120 °C for 4 h. After that the contents of the flask were cooled and filtered. The filtered solid was thoroughly washed with distilled water until the filterate was neutral. The neutralized solid was then given washings with ethanol (20 mL) and the filterate was colourless. The solid thus obtained

was dried in oven at 100 °C for 4 h. Thus carboxyl group modified activated charcoal was prepared.
*Synthesis of CuO nanoparticles using sol-gel method*
A $CuCl_2$. 2 H_2O (0.3 M) solution was prepared by dissolving $CuCl_2$. 2 H_2O in distilled water (25 mL) in a beaker. To this was added acetic acid (1 mL) and heated to 110 °C in an oil bath on a magnetic stirrer. After 20 min. stirring aq. NaOH solution was added till the pH reaches 7. When the pH became neutral, the colour of the sol. thus prepared changed from green to black and lead to formation of CuO nanoparticles (CuO nps).
Synthesis of CuO nps@ modified activated carbon

The modified activated charcoal (4.8 g) prepared before was taken in a round bottomed flask (250 mL) and the freshly prepared CuO nps sol. was poured to it. The mixture was stirred at room temperature for 5 h. After stirring for 5 h, the CuO nps@modified AC thus obtained was filtered, washed with distilled water (15 mL), ethanol (15 mL) and acetone (15 mL). This material was then dried in oven at 60 $^{\circ}$C for 5 h (**Scheme 1**).
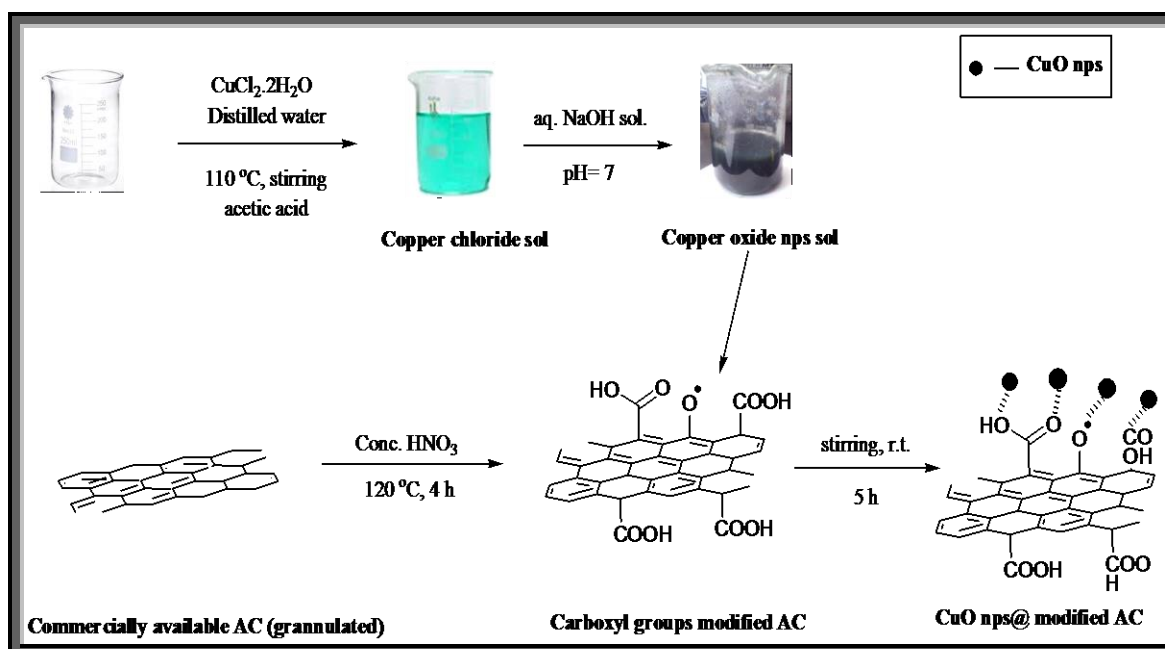
Scheme 1. Synthesis of CuO nps@ modified AC

Genereal procedure for the oxidation of benzyl alcohols

In a round bottomed flask (100 mL) was taken benzyl alcohol (1 mmol). To it was added CuO Nps@ modified AC (0.1 g), potassium carbonate (0.5 mmol), distilled water (2 mL) and stirred at 80 $^{\circ}$C under oxygen atmosphere for reasonable time. When the reaction was complete, the products were extracted with ethyl acetate (15 mL) and the catalyst was filtered off. The extract was then given water washings (three times) to remove any impurities and dried overnight on sodium sulphate. Finally the sodium sulphate was filtered off and the crude products were recrystallized using ethyl acetate or pure compounds were obtained using column chromatography. The reactions were monitored through thin layer chromatography in petroleum ether : ethyl acetate as elutents. All the products were confirmed with ^{1}H NMR and ^{13}C NMR spectroscopy techniques.

III.   Conclusion

We have prepared CuO nps@ modified AC and its activity was observed in the selective oxidation of variable benzyl alcohols to corresponding aldehydes in good to excellent yields. The protocol involves usage of water as solvent system and oxygen as oxidant which is a Green parameter and recyclability of catalyst also makes the reaction green. As lesser reaction times are involved the protocol is quite suitable for industrial application too. The synthesized catalyst has shown good tolerance of functional groups and temperature conditions along with the mild basic conditions.

Spectral Data
Benzaldehyde (2a)
^{1}H NMR (CDCl$_3$, 400 MHz): δ 10.04 (s, 1H, CHO), 7.77 (d, 2H, ArH), 7.52 (m, 3H, Ar-H).
^{13}C NMR (CDCl$_3$, 400 MHz): δ 190.5, 136.2, 133.5, 128.9, 128.7.

4-methylbenzaldehyde (2b)
^{1}H NMR (CDCl$_3$, 400 MHz): δ 9.72 (s, 1H, CHO), 7.52 (d, 2H, ArH) 7.05 (d, 2H, Ar-H), 2.16 (s, 3H, CH$_3$).
^{13}C NMR (CDCl$_3$, 400 MHz): δ 191.6, 145.2, 134.1, 129.5, 129.5, 21.4.

4-methoxybenzaldehyde (2c)
^{1}H NMR (CDCl$_3$, 400 MHz): δ 9.96 (s, 1H, CHO), 7.76 (d, 2H, ArH), 7.04 (d, 2H, Ar-H), 3.42 (s, 3H, CH$_3$).
^{13}C NMR (CDCl$_3$, 400 MHz): δ 191.4, 165.4, 134.0, 130.6, 114.1, 57.0.

4-chlorobenzaldehyde (2d)
^{1}H NMR (CDCl$_3$, 400 MHz): δ 9.92 (s, 1H, CHO), 7.64 (d, 2H, ArH), 7.44 (d, 2H, Ar-H), 3.42.
^{13}C NMR (CDCl$_3$, 400 MHz): δ 191.6, 142.1, 135.7, 131.8, 130.0.

2-chlorobenzaldehyde (2e)
^{1}H NMR (CDCl$_3$, 400 MHz): δ 9.98 (s, 1H, CHO), 7.32-7.56 (m, 4H, ArH).
^{13}C NMR (CDCl$_3$, 400 MHz): δ 188.2.6, 136.8, 134.7, 133.9, 131.6, 129.4, 119.2.

4-bromobenzaldehyde (2f)
^{1}H NMR (CDCl$_3$, 400 MHz): δ 9.93 (s, 1H, CHO), 7.69 (d, 2H, ArH), 7.38 (d, 2H, ArH).
^{13}C NMR (CDCl$_3$, 400 MHz): δ 191.2, 143.9, 135.0, 132.4, 129.1.

3-bromobenzaldehyde (2g)
^{1}H NMR (CDCl$_3$, 400 MHz): δ 10.02 (s, 1H, CHO), 8.02 (s, 1H, ArH), 7.72 (d, 2H, ArH).
^{13}C NMR (CDCl$_3$, 400 MHz): δ 191.6, 134.2, 133.2, 131.6, 130.5, 129.7.

2-nitrobenzaldehyde (2h)
^{1}H NMR (CDCl$_3$, 400 MHz): δ 9.91 (s, 1H, CHO), 7.38-7.86 (m, 4H, ArH).
^{13}C NMR (CDCl$_3$, 400 MHz): δ 185.6, 163.1, 135.4, 133.6, 131.8, 128.6, 117.0.

3-nitrobenzaldehyde (2i)
^{1}H NMR (CDCl$_3$, 400 MHz): δ 9.94 (s, 1H, CHO), 8.49 (s, 1H, Ar-H), 8.23 (d, 1H, ArH), 8.10 (d, 1H, ArH), 7.64 (t, 1H, ArH).
^{13}C NMR (CDCl$_3$, 400 MHz): δ 190.4, 135.2, 133.5, 132.0, 129.4, 128.6.

4-nitrobenzaldehyde (2i)
^{1}H NMR (CDCl$_3$, 400 MHz): δ 10.18 (s, 1H, CHO), 8.41 (d, 2H, Ar-H), 8.09 (d, 2H, ArH).
^{13}C NMR (CDCl$_3$, 400 MHz): δ 190.2, 152.2, 151.4, 140.6, 130.4, 124.3.

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