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## COMMUNICATION

# Nanocrystalline cellulose grafted phthalocyanine: a heterogeneous catalyst for selective aerobic oxidation of alcohols and alkyl arenes at room temperature in green solvent†

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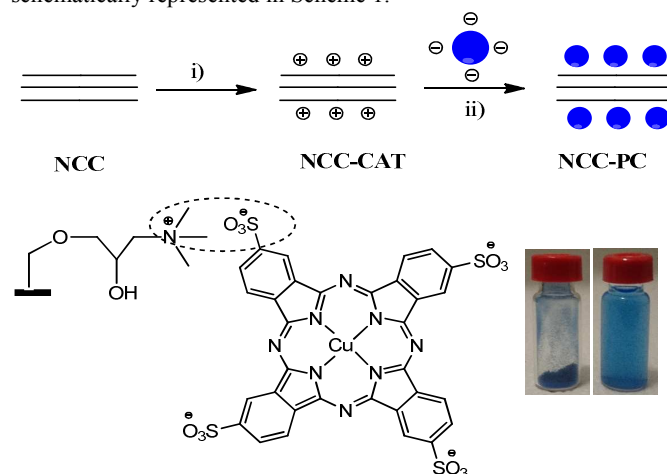
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**Copper-tetrasulfonate phthalocyanine was incorporated on cellulose nanocrystals to act as high yield, heterogeneous, and selective catalysts for aerobic oxidation of alcohols and alkyl arenes to the corresponding carbonyl groups in aqueous green solvent.**

Cellulose is one of the world's most abundant, inexpensive, biodegradable, and renewable biopolymers on earth. Nanocrystalline cellulose (NCC), a crystalline form of the cellulose, has recently drawn significant interests for different applications because of its outstanding physical and chemical properties. These properties originated from its molecular structure wherein microfibrils are held together by intra and intermolecular hydrogen bonding networks.<sup>1,2</sup> Cellulose contains a hierarchical architecture and is usually composed of both amorphous and crystalline regions. Applying mild hydrolysis with a mineral acid will selectively break amorphous regions in cellulose, but it will leave crystalline regions intact giving rise to individual nano-crystallites (NCC) with 'whisker' like morphologies.<sup>3</sup> Although, NCC contains many hydroxyl groups, only few of them are reactive limiting its applications. Meanwhile, surface functionalization technique is generally used to incorporate different functionalities onto the surface of the materials targeting specific applications, such as for an increased solubility in different solvents, without totally altering the intrinsic properties of the original materials. Recently, various reactive functional groups were introduced (like amino, carboxy, thio etc.) on the NCC surfaces that enabled NCC to be used in different forms for a wider range of products and applications.<sup>4</sup>

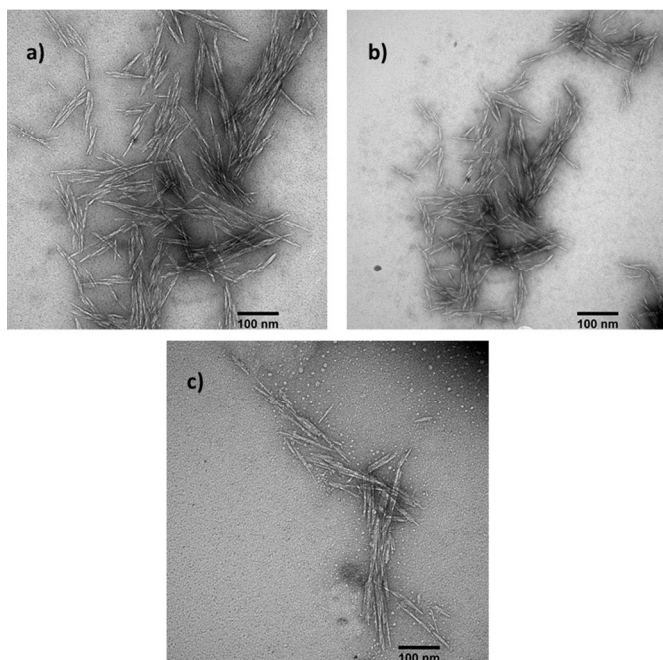
The selective aerobic oxidation reaction of alcohols and alkyl arenes are one of the most important reactions in organic synthesis for the transformation to corresponding carbonyl compounds.<sup>5</sup> Both for laboratory and industrial production: the oxidation of these organic compounds requires the usage of toxic-hazardous oxidants, expensive metals inorganic bases, and elevated temperature conditions.<sup>6</sup> These requirements are highly challenging and need to be specially addressed which will provide benefits to the industry specially agro-chemical, pharmaceutical, food and fragrances. Thus, there is an increasing demand for catalysts which are economic, efficient and greener in nature.<sup>7</sup>

Porphyrins and phthalocyanine based macro-cycles have been attached on the nano-particles to impart photo-physical, photo-electronic and catalytic properties to the nanoparticles.<sup>8</sup> In a recent study, a water soluble aminotrisulfonate tetraphenylporphyrin was covalently linked to cellulose nanocrystals which produced singlet oxygen under UV irradiation.<sup>9</sup> The modified macromolecules were used as efficient catalysts for carrying out different organic transformation reactions.<sup>10</sup> Despite many reported studies on porphyrin and phthalocyanine based catalysts, there are only limited examples in producing cellulose based catalysts for different applications.<sup>11</sup> Nevertheless, these reported cellulose supported catalysts still exhibited some disadvantages including: use of expensive metals (Pd), use of non-aqueous solvents, tedious workup conditions and difficulty in recovering the catalyst. To overcome some of these challenges, herein we report successful grafting of water soluble, anionic copper tetrasulfonate phthalocyanine (PC) onto NCC as an environmentally friendly solid support catalyst for aerobic oxidation of alcohols and alkyl arenes with high yields. The grafting of phthalocyanine on the crystalline nanocellulose is schematically represented in Scheme 1.



**Scheme 1:** Grafting of phthalocyanine on crystalline nanocellulose: i) EPTMAC, NaOH; ii) Cu-tetrasulfonate phthalocyanine. *Inset:* Digital photos of NCC-PC (solid) and NCC-PC (aqueous suspension).

Microcrystalline cellulose (from cotton linters) was used as the commercial sourced starting material for the production of **NCC** in this study. The preferential hydrolysis of amorphous cellulose was carried out with sulphuric acid (63%) at 45 °C for 2 hours, leaving the crystalline cellulose intact.<sup>12</sup> Later, the surface of **NCC** was made cationic by treatment with (2,3-Epoxypropyl)trimethylammonium chloride (EPTMAC) in aqueous environment of NaOH, wherein some hydroxyl (primary) groups were selectively converted to cationic groups (**NCC-CAT**).<sup>13</sup> The degree of functionalization of trimethylammonium chloride was determined by conductometric titration of each chloride with AgNO<sub>3</sub> solution, which was found to be  $0.1 \pm 0.52$  mmol per g of **NCC** (assuming existence of one chloride ion per trimethylammonium chloride). Furthermore, grafting of **NCC** with **PC** was accomplished by strong electrostatic interaction and hydrogen bonding between cationic **NCC** and anionic sulfonate Cu-**PC** by stirring the suspension overnight and later recovered by centrifugation process.

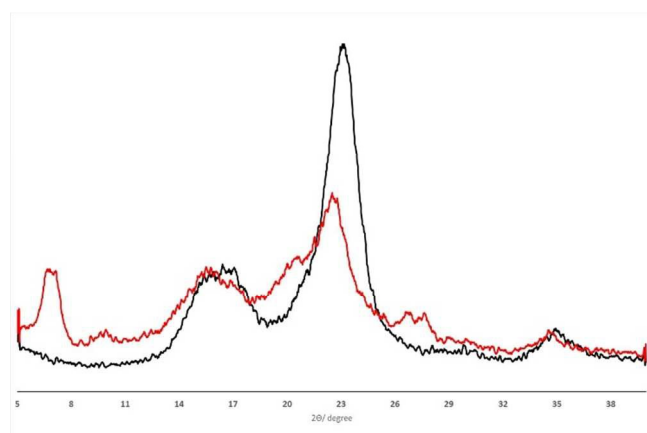


**Fig 1:** TEM images of cellulose derivatives: (a) **NCC**, (b) **NCC-CAT**, (c) **NCC-PC**.

Transmission Electron Microscopy (TEM) was used to substantiate the nano-crystalline structure of **NCC** (Fig. 1a) having the usual whisker like morphology. The measurement of these nano-whiskers gave an average length of  $165 \pm 33$  nm, while the Z-potential value was  $-26 \pm 5$  mV, due to the residual sulfonate groups on the surface of **NCC** from the sulphuric acid hydrolysis process. **NCC-CAT** obtained from the cationic functionalization showed a similar whisker like morphology (Fig. 1b), having an average length of  $152 \pm 45$  nm and a positive Z-potential value of  $16 \pm 5$  mV, due to the presence of cationic groups on the surface. TEM analysis of **NCC-PC** (Fig. 1c) showed the similar morphology with an average length of  $170 \pm 25$  nm and a polarity switch in Z-potential value to  $-33 \pm 8$  mV, due to anionic sulfonate groups from phthalocyanine macrocycles. In comparison to both **NCC** and **NCC-CAT**, **NCC-PC** showed an increased tendency for aggregation, which

could be due to the presence of phthalocyanine-phthalocyanine interactions.

The grafting of phthalocyanine was characterized by various spectroscopic techniques. Fig 2 represents the powder X-Ray Diffraction (XRD) pattern of **NCC** (black line) showing strong and sharp peaks at  $2\theta = 15.9^\circ$ ,  $23.0^\circ$  that are in accordance with the literature values for crystalline cellulose.<sup>14</sup> On the other hand, XRD pattern of **NCC-PC** (red line) shows the characteristics peaks of **NCC** and **PC** which are in consistent with ICDD Card no. 11-0893 of Cu-**PC**.<sup>15</sup> The success of grafting was also confirmed by FT-IR spectra (KBr) (see ESI†).



**Fig 2:** XRD patterns cellulose derivatives: (a) **NCC** (black line), (b) **NCC-PC** (red line)

In order to further confirm the grafting process, X-Ray Photoelectron Spectroscopy (XPS) was employed for the surface characterization of **NCC-PC** (see ESI†). The elemental measurement scan showed a prominent absorption band at 936 eV which can be easily assigned to Cu (II) 2p<sub>3/2</sub> in accordance with the literature recorded values for Cu (II) oxidation state.<sup>16</sup> Also, the band at 169.9 eV is associated with S 2p<sub>3/2</sub> from SO<sub>3</sub><sup>-</sup> groups from Cu-**PC**.<sup>17</sup> The Thermo Gravimetric Analysis (TGA), indicated that Cu-**PC** immobilization onto **NCC** did not change thermal behaviour of **NCCs** (see ESI†). It was found that both the **NCC** and **NCC-PC** started to decompose above 275 °C under nitrogen atmosphere and evenly stable under the oxygen atmosphere, which demonstrated good promises as solid supports for various catalytic reactions. The Cu loading in **NCC-PC** was determined by using Inductive Coupled Plasma Atomic Emission Spectroscopy (ICP-AES). For this purpose, the **NCC-PC** was dissolved in aqua regia (3:1 HCl:HNO<sub>3</sub>) solution, filtered and analysed. Based on ICP-AES, Cu loading in **NCC-PC** was found to be 0.91wt%.

The versatility of the newly constructed **NCC-PC** was illustrated as heterogeneous solid support catalysts for aerobic oxidation of alcohols and alkyl arenes to corresponding carbonyl groups. The optimum reaction conditions for oxidation of benzyl alcohol or tetralin, wherein **NCC-PC** acted as catalyst is included in Table 1. The optimum reaction condition involved very mild experimental conditions with 0.004 mole% Cu content, room temperature and water as the solvent. The ease of using **NCC-PC** as solid support catalyst is also in the recovery method *i.e.* by a simple centrifugation process. In order to establish the recyclability of this catalyst, aerobic oxidation of benzyl alcohol and tetralin were studied. As the oxidation process was finished, the blue coloured

catalyst was recovered by centrifugation. After 7 repetitive cycles, a very minor decrease in the product yield was observed (see ESI†), indicating a high productivity of the catalyst.

**Table 1:** Effect of the amount of catalyst on oxidation reactions<sup>a</sup>

Amount of NCC-PC catalyst (Cu content /mmole %)	Entry	Yield <sup>b</sup> (%)	Selectivity <sup>b</sup> (%)
None	benzyl alcohol	3	>99
	tetralin	1	>99
0.001	benzyl alcohol	20	>99
	tetralin	17	>99
0.002	benzyl alcohol	48	>99
	tetralin	32	>99
0.003	benzyl alcohol	85	>99
	tetralin	76	>99
0.004	benzyl alcohol	99	>99
	tetralin	92	>99

<sup>a</sup> Reaction conditions: benzyl alcohol or tetralin (1 mmol), NCC-PC, water (3 mL), air (1 atm), 5 hours, room temperature. <sup>b</sup> Yield and selectivity was determined by GC analysis.

A series of different alcohols and alkyl arenes for aerobic oxidation reactions was conducted to prove the catalytic application in high yields (see ESI†). In order to confirm the true heterogeneity of the catalyst especially when dealing with a nano-based system, scrutiny for leaching is a necessity.<sup>18</sup> For this purpose during the catalysis process, the reaction mixture was centrifuged and its supernatant was examined using ICP-AES where Cu content was found to be less than the detection limit. This was also confirmed by FTIR and XRD analysis wherein no changes were observed.

**Table 2:** Comparison of the results for oxidation of benzyl alcohol using NCC-PC and some other Cu-phthalocyanine catalysts

Entry	Catalyst	Oxidant	Temp (°C)	Time (h)	Yield (%)	Ref.
1	CuPC	n-Bu <sub>4</sub> NHSO <sub>5</sub>	70	0.5	25	19
2	CuPC@MCM-41	TBHP	100	4	36	20
3	NCC-PC	Air	Room temp	5	99	This work

As shown in Table 2, the NCC-PC has some advantages in comparison to some other copper-phthalocyanine based catalyst. In comparison to CuPC<sup>19</sup> and CuPC@MCM-41<sup>20</sup> catalysts, they both requires oxidants such tetra-n-butylammonium peroxomonosulfate (n-Bu<sub>4</sub>NHSO<sub>5</sub>) and tert-butyl hydroperoxide (TBHP), high temperature conditions and product thus formed are low yielding, whereas our NCC-PC based catalyst doesn't require any toxic, hazardous oxidant and product of oxidation reaction are high yielding which can be performed at room temperature using water as green solvent. Further, the versatility of newly constructed NCC-PC catalyst is that it doesn't require tedious workup conditions and catalyst can be recovered by simple centrifugation process. Unlike the other Copper based catalyst such as (Cu/SiO<sub>2</sub>)<sup>21</sup>, the NCC-PC doesn't suffer any deactivation, during its catalytic process. Also, no oxidation was observed on the nanocellulose backbone which was

also confirmed by FTIR and XRD spectroscopic analysis. Thus, all these observation led to the conclusion that NCC-PC catalyst displayed no leaching and maintained its heterogeneity.

In conclusion, we presented a novel nanocellulose grafted phthalocyanine for selective catalysis of alcohols and aryl arenes. The major advantages of this bio-nano-catalyst are as follows: inexpensive nanocellulose as the solid support, ease in synthetic process of catalyst, heterogeneous nature of the catalyst, in water as green solvent reaction condition, single step workup process, high catalytic activity at room temperature, and no need for any base requirement. The catalyst also displayed ease in recovery and reusability features with no significant loss in activity. Future research activities will be focused on application of this novel catalyst for other organic transformation reactions.

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† Electronic Supplementary Information (ESI) available: experimental details for the synthesis of cellulose nanocrystals and phthalocyanine grafting. See <http://www.rsc.org/suppdata/xx/b0/b000000x/>

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