Electronic Supplementary Material (ESI) for RSC Advances.

Supplementary information for

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

by

Prashant Chauhan[a] and Ning Yan[a,b*]

[a] *Faculty of Forestry, University of Toronto, 33 Willcock Street, Toronto, ON, Canada, M5S3B3. Email: ning.yan@utoronto.ca ; Phone: +1 (416) 946-8070.*

[b] *Department of Chemical Engineering and Applied Chemistry, University of Toronto, 200 College Street, Toronto, ON, Canada, M5S 3E5.*

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1. General Information

All the reagents were purchased from Sigma Aldrich® and used without further purification. The cellulose starting material having crystallinity index of 66% was purchased from Sigma. Copper tetrasulfonated phthalocyanine having ~50% dye content was purched from Sigma. FTIR was carried out in KBr on a Bruker Tensor 27 Fourier Transfer Infrared Microscope instrument. Z-potential experiments were conducted on a Brookhaven Instruments Corporation instrument (Zeta Plus). Thermal analysis were performed on a TGA Q5000 TA instrument. Centrifugations were carried out with a Beckman Coulter centrifuge. TEM analysis was performed on a Hitachi H7000 transmission electron microscope and the images where analysed with the ImageJ software for crystal size measurements and the data were evaluated with Origin 7.0 software. XRD analysis were performed on a Philips PW 3710 X-Ray Diffractometer. GC experiments were performed on a Perkin Elmer Gas Chromatography Mass Spectrometer. ICP-AES analysis for Cu detection was performed on Perkin Elmer Optima 7300 DV instrument. XPS analysis were performed on a Thermo Scientific K-Alpha X-ray Photoelectron Spectrometer (XPS) having a monochromated Al Kα X-ray source.

2. Synthesis of NCC

5 gr of microcrystalline cellulose was added to a sulfuric acid (63% w/w, 21.5 mL of 95-98% H_2SO_4 with 22.5 mL of water) solution. The suspension was stirred at 45° C temperature. After 2 hours, the hydrolysis was stopped by adding 10 folds of water. The suspension was transferred to the centrifuge tubes and centrifuged at 5000 rpm for 5 minutes to remove the acidic supernatant. The solid cellulose so obtained was again washed with water and recovered by centrifugation at 10,000 rpm for 5 minutes. The suspension thus obtained was transferred in dialysis tubes having 12 kD cut off and dialyzed against milliQ water for 3 days. The nanocrystalline cellulose was recovered in ~ 60% yield by lyophilization.

NCC (1mg/mL aqueous suspension)	Zeta Potential (mV)
1st measurement	-26.4
2nd measurement	-24.5
3rd measurement	-26.5
4th measurement	-28.8
arithmetic average	**-26.5**

Table S1: Measured Zeta potential values for NCC

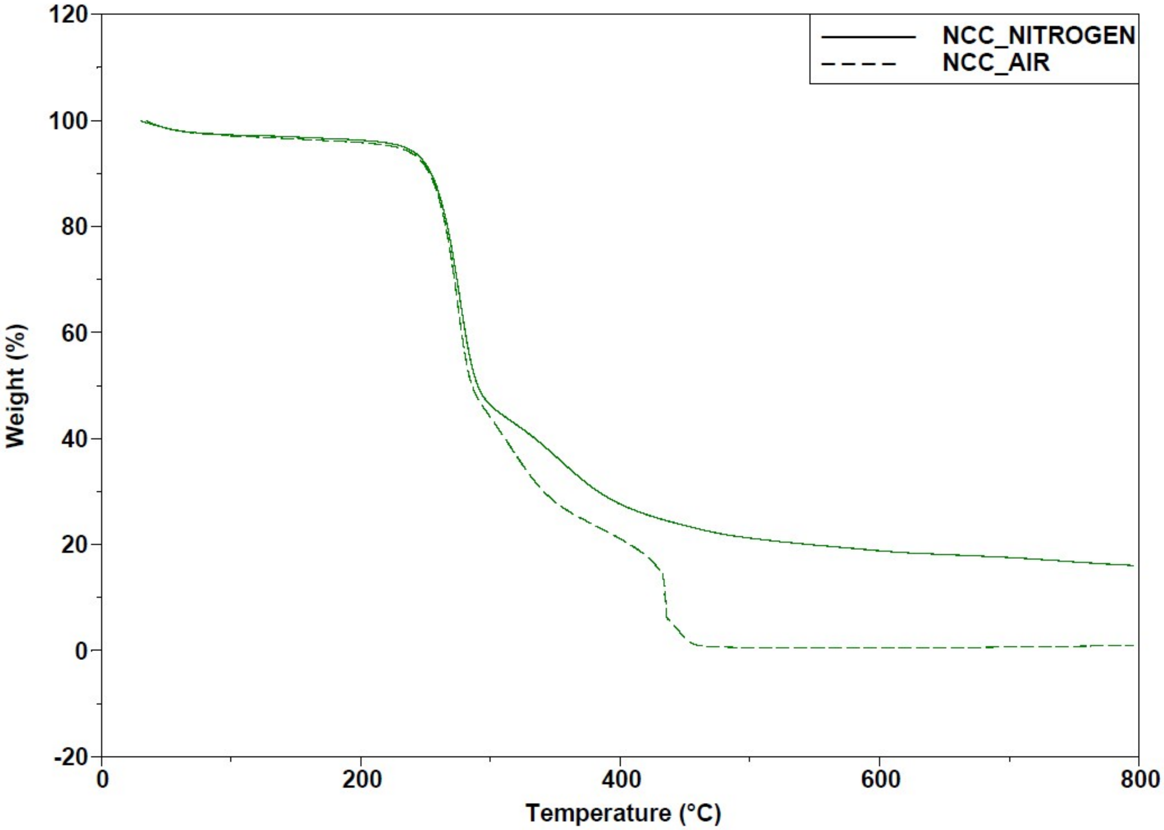


Figure S2: Weight loss vs. temperature plots for NCC obtained by TGA measurements (in air and nitrogen)

3. Synthesis of NCC-CAT

Firstly 7% w/v NaOH solution was prepared dissolving (2.34 g, 0.57 mol in 33mL water). To this, NCC (300 mg) was added and stirred for 30 minutes at room temperature in order to achieve a stable homogenous suspension. Afterwards, 2,3-epoxypropyltrimethylammonium chloride (8.1 g, 0.054 mol) was added and stirred at 65° C temperature. After stirring for 5 hours, the suspension was diluted with 10 folds of water. The product was washed extensively with water and recovered by centrifugation process (7500 rpm for 5 min). Later, it was dialyzed against distilled water for 3 days. The cationic cellulose was recovered by lyophilization in 50% yield. The degree of cationization was determined by conductometric titration with a silver nitrate solution. The degree of functionalization was found to be 0.1±25 mmol per g of NCC.

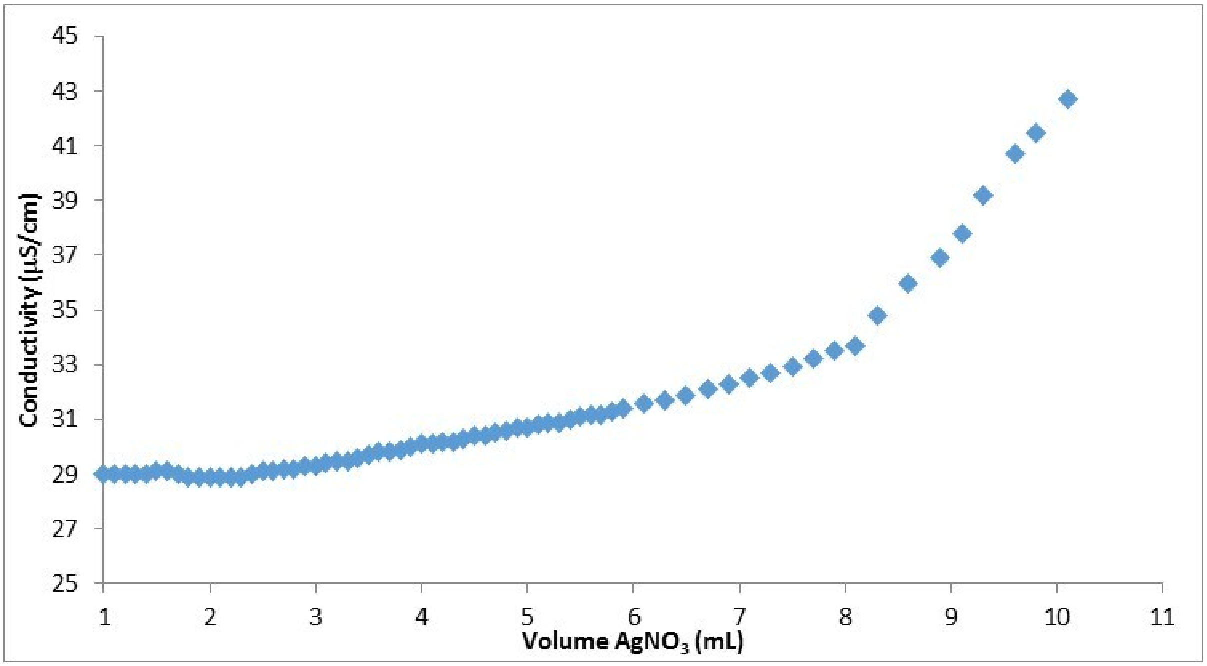


Figure S3: Conductometric titration for the degree of cationization of NCC-CAT

NCC-CAT (1mg/mL aqueous suspension)	Zeta Potential (mV)
1st measurement	15.5
2nd measurement	17.0
3rd measurement	17.0
4th measurement	16.5
arithmetic average	**16.5**

Table S2: Measured Zeta potential values for NCC-CAT

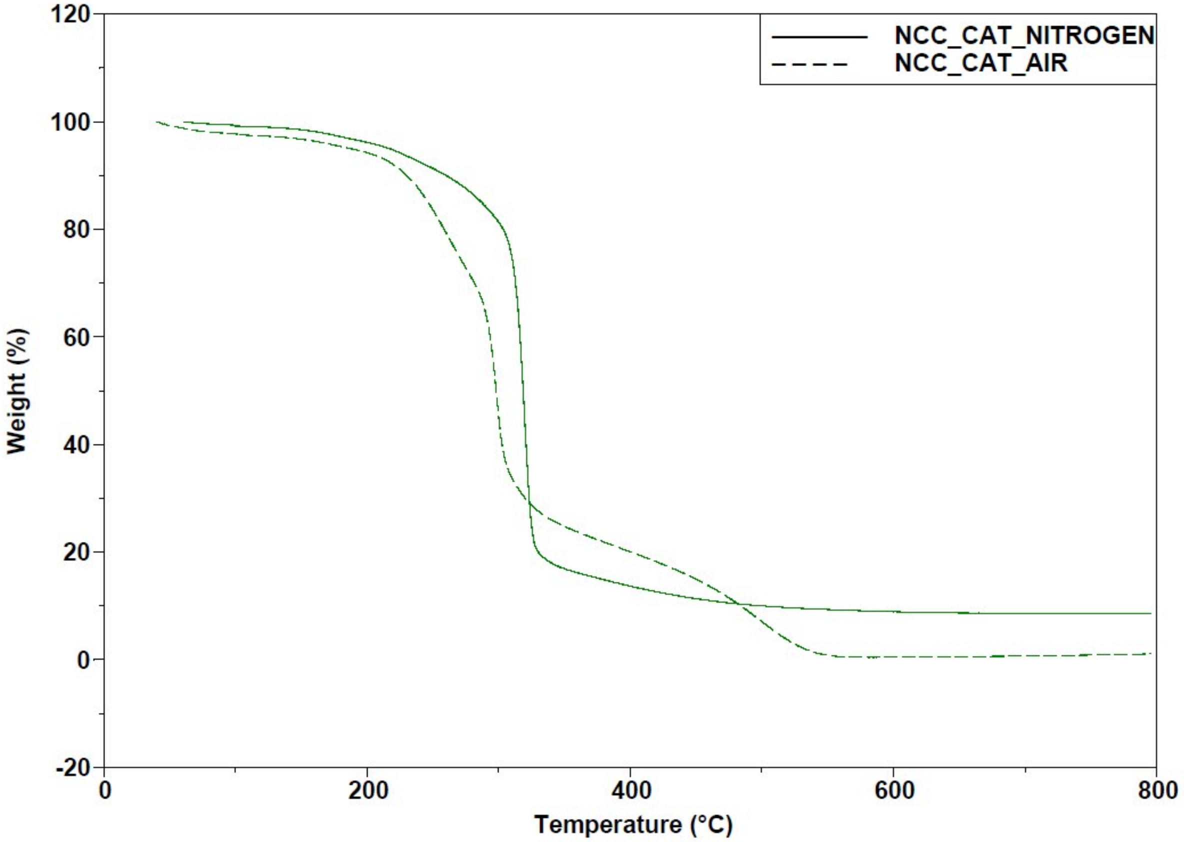


Figure S4: Weight vs. temperature plots for NCC-CAT obtained by TGA (in air and nitrogen)

4. Synthesis of NCC-PC

Firstly, 300 mg of cationic cellulose was dissolved in 30mL distilled water. It was sonicated for 15 minutes to obtain a stable homogenous suspension. To this suspension, Copper tetrasulfonated phthaolcyanine (0.5 g, 5 mol) was added. The resultant blue colored suspension was stirred at room temperature for 12 hours. The blue suspension was transferred in the centrifuged tube and washed extensively first with methanol, then with water, to remove excess of phthalocyanine until clear supernatant was observed. The suspension was centrifugated at 10,000 rpm for 5 min. The solid product was obtained by lyophilization in 80% yield.

5. Characterization of NCC-PC

Determination of Cu(II) content by ICP-AES analysis

An accurate amount of NCC-PC sample (29.7 mg) was weighed and placed into a small beaker and 8 ml of aqua regia (3:1 HCl:HNO_3) was added. The mixture was covered by a watch glass, followed by mild heating for 2 hours. The resultant solution was cooled, filtered (to remove particulates) and diluted to 50 mL with 18.2 MOhm water (deionized water). The resultant solution was then analyzed by ICP-AES directly and Cu content was found to be 0.91wt%.

FT-IR spectrum analysis

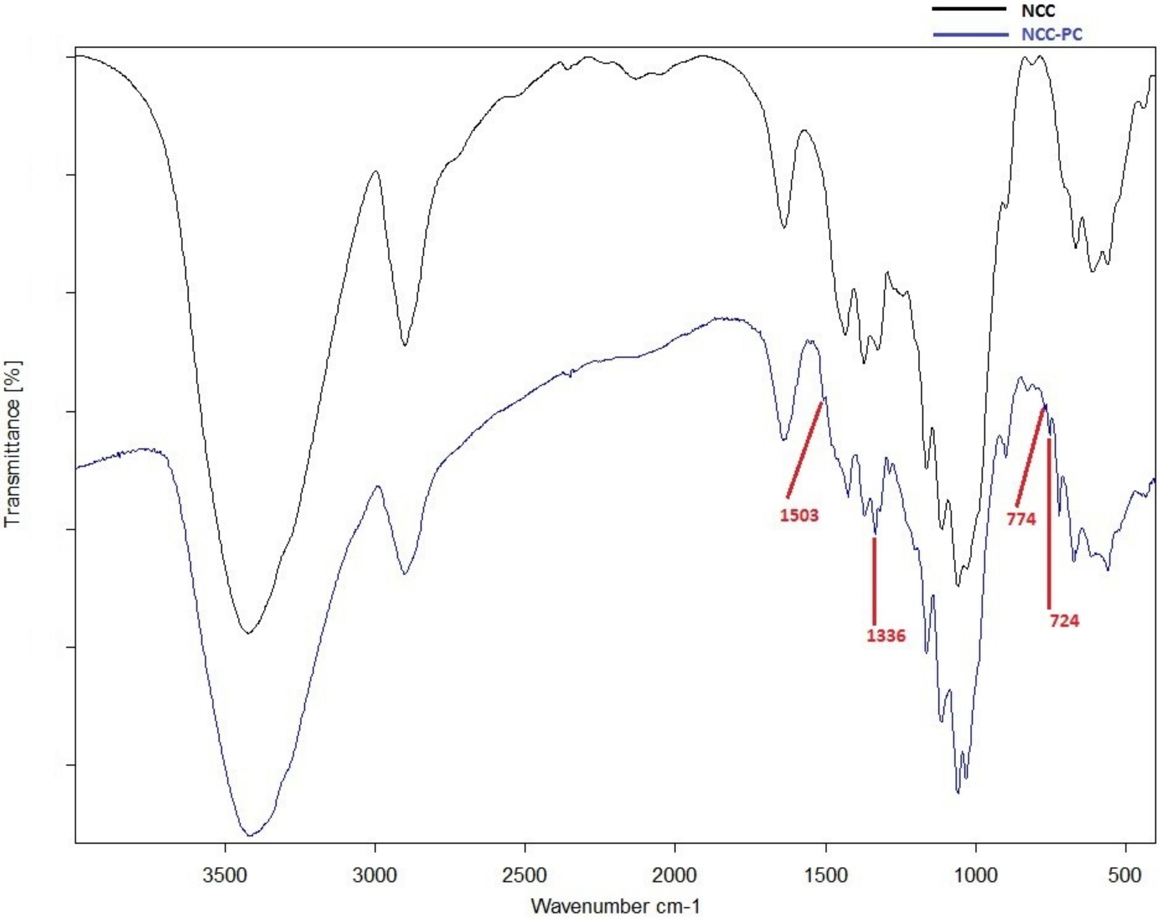


Figure S5: FTIR spectra for NCC and NCC-PC in KBr

The comparison of FTIR spectrum of NCC and NCC-PC clearly showed appearance of new absorption peaks in case of NCC-PC at 1503 cm^{-1}, 1336 cm^{-1}, 774 cm^{-1}, 724 cm^{-1} originated from copper phthalocyanine.

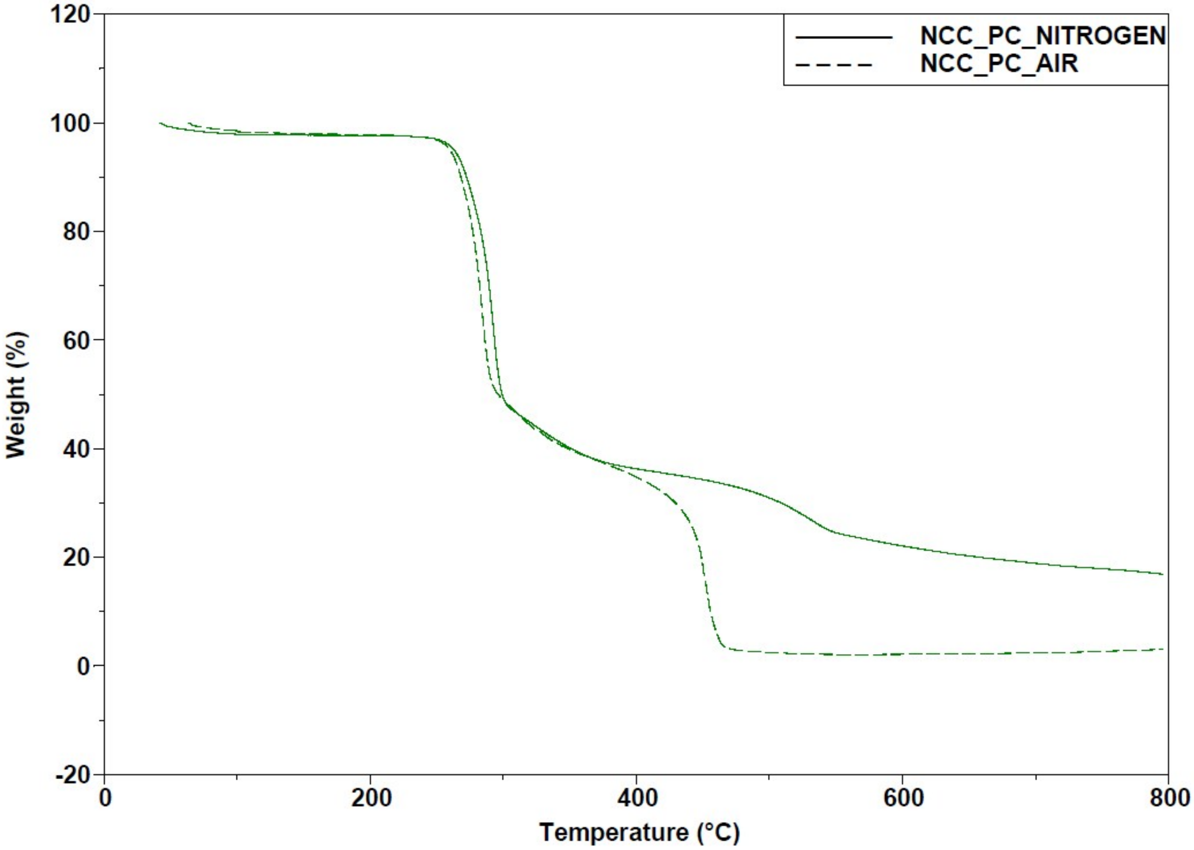


Figure S6: Weight vs. temperature plots for NCC-PC obtained by TGA (in air and nitrogen)

NCC-PC (1mg/mL aqueous suspension)	**Zeta Potential (mV)**
1st measurement	-34.0
2nd measurement	-33.8
3rd measurement	-33.8
4th measurement	-33.6
arithmetic average	**-33.8**

Table S3: Measured Zeta potential values for NCC-PC

XPS analysis

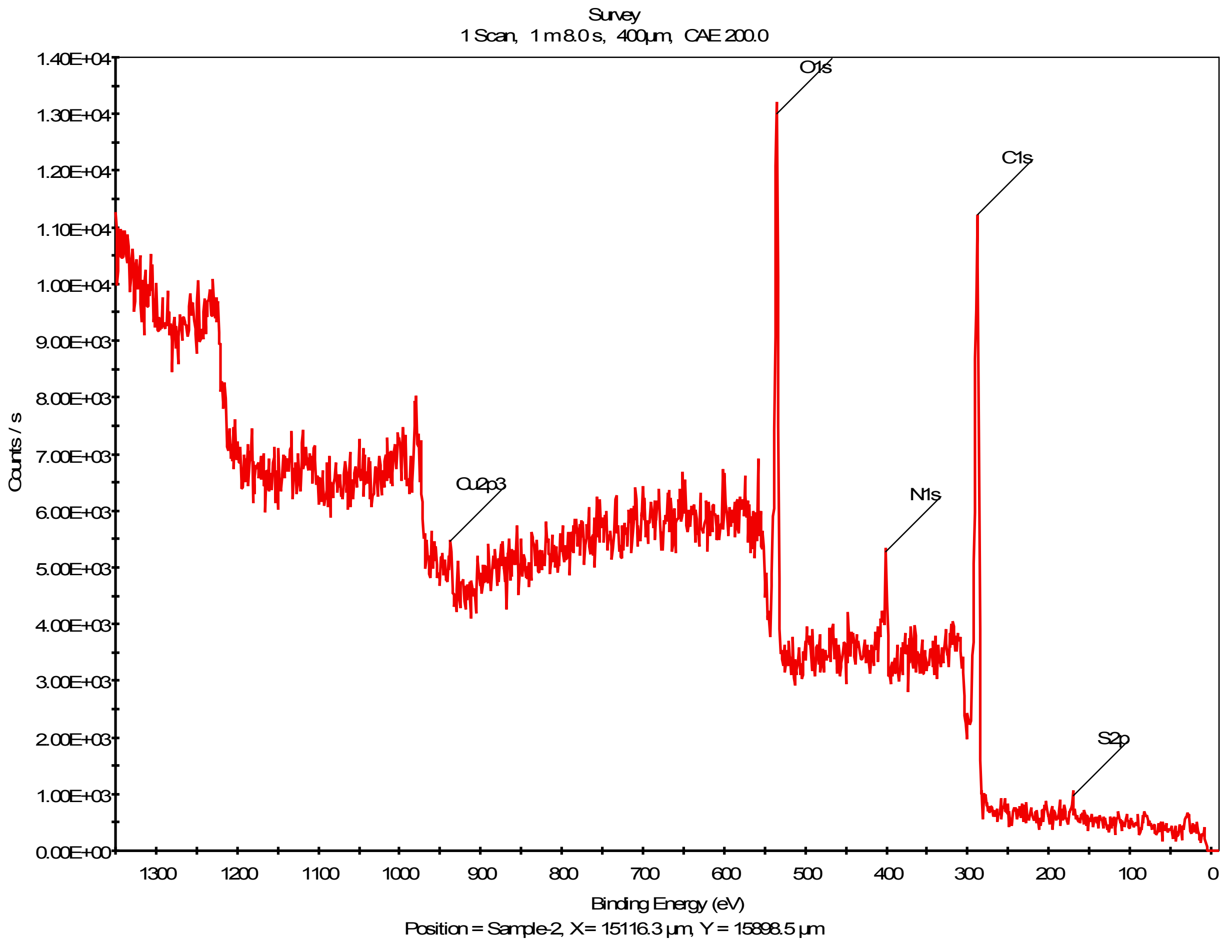


Figure S6: XPS absorption spectrum for NCC-PC

Elemental ID and Quantification

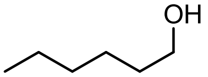
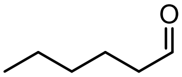
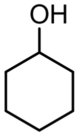
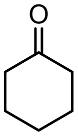
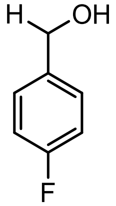
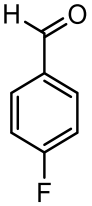
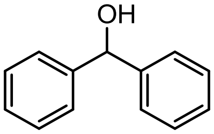
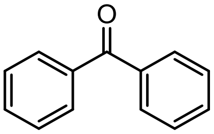
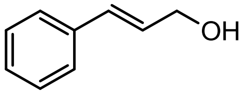
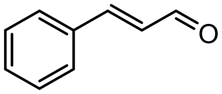
Name	*Peak BE*	*FWHM eV*	*Area (P) CPS.eV*	*Atomic %*	*Q*	*SF*
C1s	287.46	4.79	59201.83	69.54	1	1.000
Cu2p3	936.37	3.26	6709.88	0.75	1	16.730
N1s	399.84	2.84	8571.18	5.93	1	1.800
O1s	534.52	3.25	49509.02	22.79	1	2.930
S2p	169.98	3.67	1474.49	0.98	1	1.670

Table S3: XPS analysis for NCC-PC

6. General procedure for oxidation of alcohols and aryl arenes

Firstly, the NCC-PC catalyst (0.004 mol% Cu, 0.276 g) was added to a vial containing 5 mL water and was stirred well to obtain a homogenous suspension. To this suspension, an organic compound (1 mmol) was added with constant bubbling of air at room temperature. The progress of the reaction was followed by gas chromatography (GC). The GC yield and selectivity were obtained by using n-decane as the internal standard. When the reaction was completed, the NCC-PC catalyst was removed by centrifugation at 10,000 rpm for 5 minutes. The aqueous suspension was extracted thrice with DCM. The combined organic layers were passed to magnesium sulfate to remove any trace of water. Finally, the solvent was evaporated over a rotavapour to give the product.

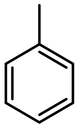
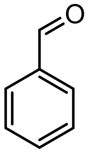
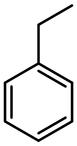
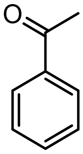
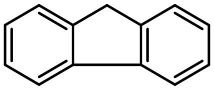
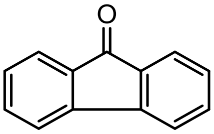
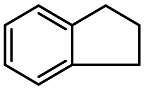
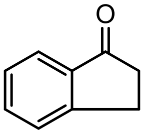
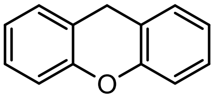
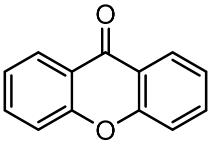
Table S4: Oxidation of alcohols using NCC-PC based catalyst[a]

Reactant	Product	Time (hours)	Yield[b] (%)	Selectivity[b] (%)
		10	93	>99
		10	92	>99
		10	93	>99
		10	92	>99
		10	90	>99

[a] Reaction condition: NCC-PC catalyst (0.004 mol% Cu, 0.276 g), 5 mL water, 1 atm air, 1 mmol organic compound

[b] Conversion and selectivity determined by GC analysis

Table S5: Oxidation of aryl arenes using NCC-PC based catalyst[a]

Reactant	Product	Time (hours)	Yield[b] (%)	Selectivity[b] (%)
		10	89	>99
		10	90	>99
		10	88	>99
		10	90	>99
		10	89	>99

[a] Reaction condition: NCC-PC catalyst (0.004 mol% Cu, 0.276 g), 5 mL water, 1 atm air, 1 mmol organic compound

[b] Conversion and selectivity determined by GC analysis

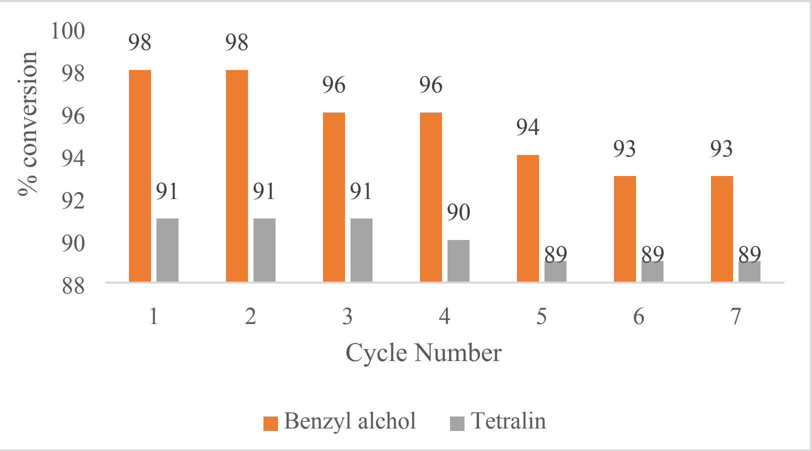


Figure S6: Recyclability of NCC-PC based catalysts