Supporting Information for "Preparation of Aldehyde-functionalized cellulose nanocrystals via aerobic oxidation of cellulose in a recyclable triisopropoxy vanadium oxidation system"

Xianqing Lv, Chengke Zhao, Xiwei Zhang, Zhuotong Wu *, Li Shuai *

[†] College of Materials Engineering, Fujian Agriculture and Forestry University, Fuzhou 350002, PR China

Corresponding Author

*E-mail: wuzt@fafu.edu.cn; lishuai@fafu.edu.cn

Method and calculation

Aldehyde content determination: Hydroxylamine hydrochloride reacts with the aldehyde group of cellulose to form hydrochloric acid, and sodium hydroxide titration is used to determine the content of aldehyde groups in cellulose. The calculation was as follows:

$$H = \frac{0.03X}{W}$$

In the equations,

H: is the mass molar concentration of aldehyde groups in cellulose, mmol/g;

W: is the mass of the cellulose sample, g;

X: Volume of sodium hydroxide/methanol solution consumed in titration, mL.

XRD: The surface chemical composition and structure were analyzed by X-ray photoelectron spectrometer (ESCALAB250, Thermo-Fisher Scientific), and the analysis conditions were: anode aluminum target (1486.8 eV), X-ray source was standard X - ray, current 10 mA, accelerating voltage was 15 kV, and the full spectrum scanning range was 0-1100 eV. The scanning speed is 4 °/min, and the scanning range is $2\theta = 10° - 60°$

The CrI of cellulose was calculated using the following equation

$$CrI\ (\%) = \frac{I_{002} - I_{am}}{I_{002}} \times 100\%$$

where I_{002} is XRD peak at $2\theta = 22.6°$ and I_{am} is diffraction pattern of amorphous area at $2\theta = 18.0°$.

PD: The polymerization degree of cellulose was determined by copper ethylenediamine method. Weigh an appropriate amount of cellulose into a 60 mL dissolveable bottle, add glass beads to cover the bottom of the bottle, add 25 mL of deionized water and 2-3 pieces of copper, and shake vigorously until the cellulose is fully dispersed. Then add 25 mL of copper ethylenediamine solution, fill the bottle with glass beads to about 1 cm, and continue to vigorously shake to completely

dissolve the cellulose. Finally, the polymerization degree of cellulose was measured by the cellulose viscosity tester.

(1) Relative viscosity (η_γ)

$$\eta_\gamma = h_n \times t_n$$

In the formula, hn is the viscometer constant (0.08561 s^{-1}) measured during calibration, s-1; t_n represents the outflow time of the sample solution, s.

(2) Intrinsic viscosity (η)

$$\eta = \frac{C}{\rho}$$

Where, C represents the constant C corresponding to the relative viscosity in Martin's equation; ρ represents the slurry concentration calculated from the sample mass and solution volume (50.0 mL), mL/g.

(3) Polymerization degree DP

$$DP^{0.905} = 0.75[\eta]$$

By substituting the intrinsic viscosity η, the average polymerization degree of cellulose can be calculated by equation (3).

Inductively Coupled Plasma-Mass Spectrometry (ICP-MS): Weigh 40 mg of the sample into the microwave digestion tube, add 7 mL of aqua regia and 1 mL of hydrogen peroxide. Place the digestion tank and the lining cup of the support into the microwave digestion instrument and digest at temperatures ranging from 150°C to 220°C for 150 minutes. Post-digestion, transfer the solution to a beaker, rinse it with ultra-pure water into a 10 mL volumetric flask, and then proceed with the analysis.

Hydrolysis of reaction solution: The oxidized reaction solution is first filtered and cleaned with acetone. The acetone is subsequently removed through spin evaporation. The solution is then transferred to a 10 mL volumetric flask. From this, draw 1 mL into a 15-mL vial and add 3 mL of 4% H_2SO_4 aqueous solution. Finally, place the vial at 120°C for a 1 h reaction. Then 10 μL of the reaction solution was silanized and determined by GC.

The following temprature program was used for Gas chromatogram (GC) analysis: the column temperature was initially set at 50°C and held at 50°C for 5 min, then heated at a rate of 10°C/min to 300°C and held at 300°C for 5 min.
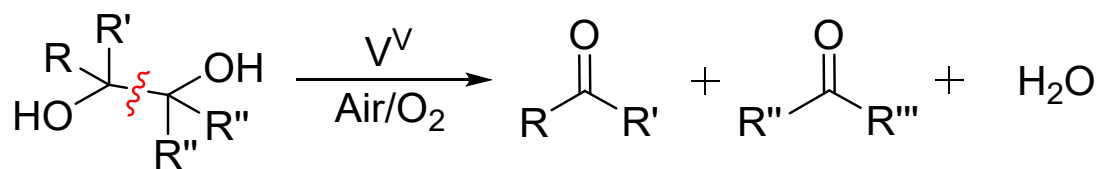

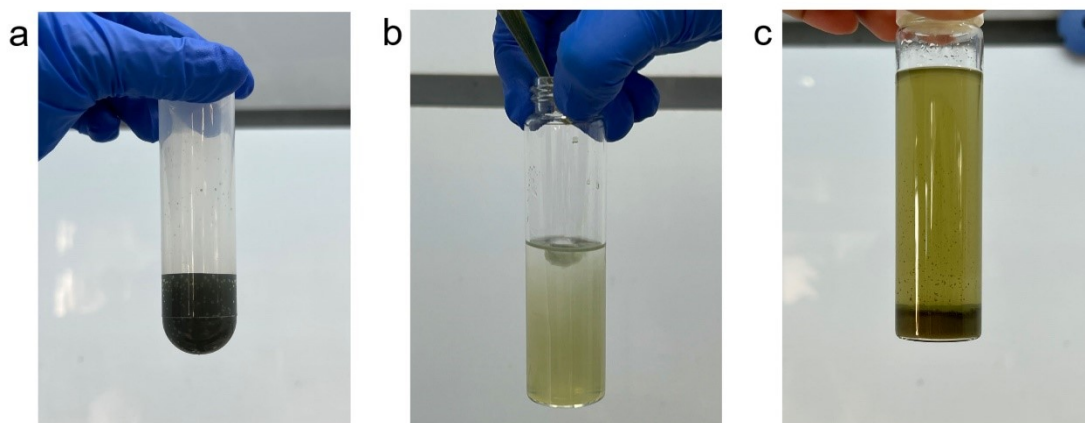Fig. S1 Aerobic C-C oxidative cleavage of diols to the corresponding carbonyl derivatives.

Fig. S2 (a) The solution becomes dark green after the oxidation reaction; (b) The reaction solution was dropwise added to acetone, and O-NC was observed to precipitate in acetone; (c) Deposition of O-NC in acetone solution after a short period of standing.
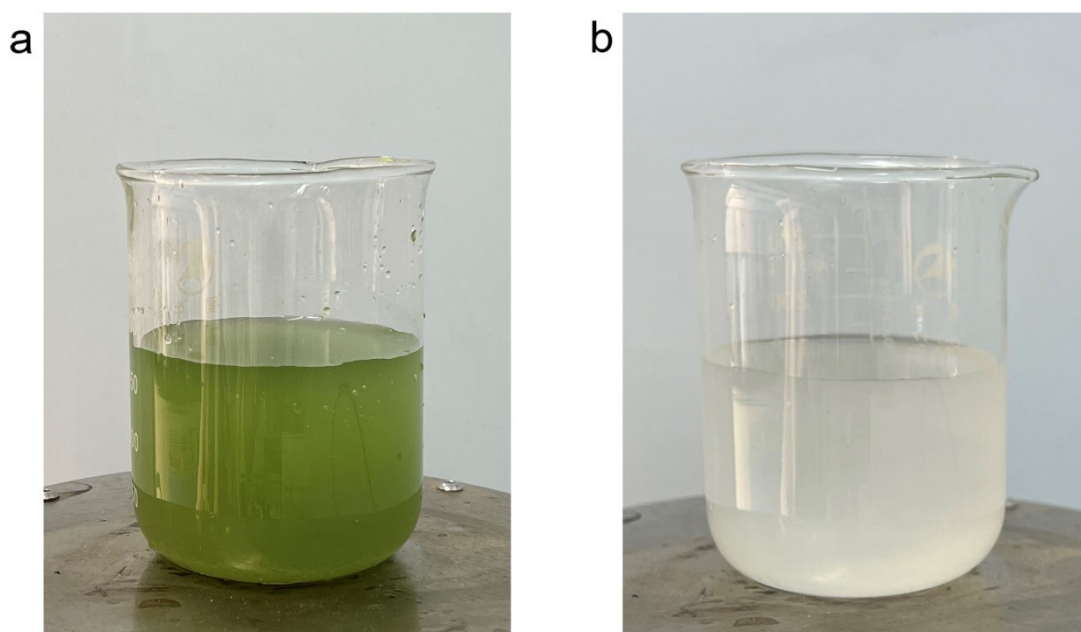
Fig. S3 (a) The O-NC washed three times by acetone is dispersed in deionized water to form a green suspension containing oxidizing agent VO(OiPr)$_3$, DMSO and a small amount of acetone, which can be removed by deionized water washing; (b) After full washing in deionized water, the white O-NC is evenly dispersed in the deionized water.
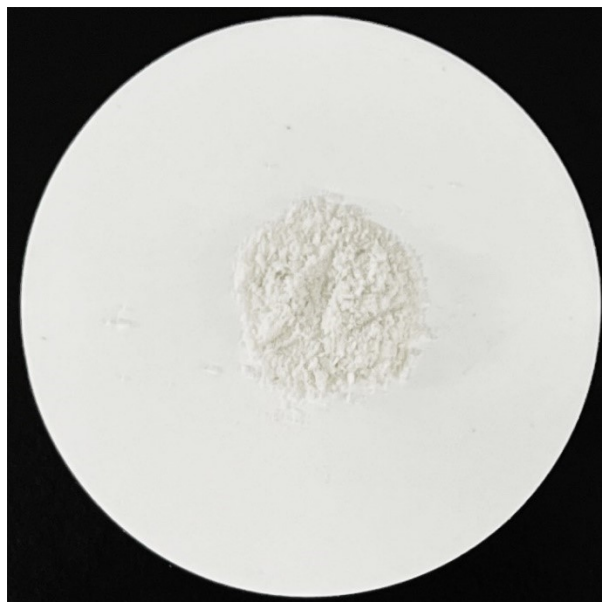

Fig.S4 Vacuum freeze-dried O-NC sample.

Table S1 The yield of O-NC prepared by oxidation of MCC in VO(OiPr)$_3$ system.

MCC (g)	O-NC (g)	Yield (%)
0.5002	0.2616	52.30

Table S2 The crystallinity of O-NC prepared by different oxidation time and different cycles of catalyst.

Item	CrI (%)
MCC	81.58
MCC-3 h	74.37
MCC-6 h	71.75
MCC-9 h	71.39
MCC-12 h	70.81
Cycle 1	70.69
Cycle 2	74.05
Cycle 3	76.40

Cycle 4	78.39

Table S3 T_{D1} of MCC and MCC oxidized at different reaction in VO(OiPr)$_3$ system.

Item	T_{D1} (°C)
MCC	336.33
MCC-3 h	314.33
MCC-6 h	314.5
MCC-9 h	305.67
MCC-12 h	288.5

Table S4 ICP-MS test results for O-NC.

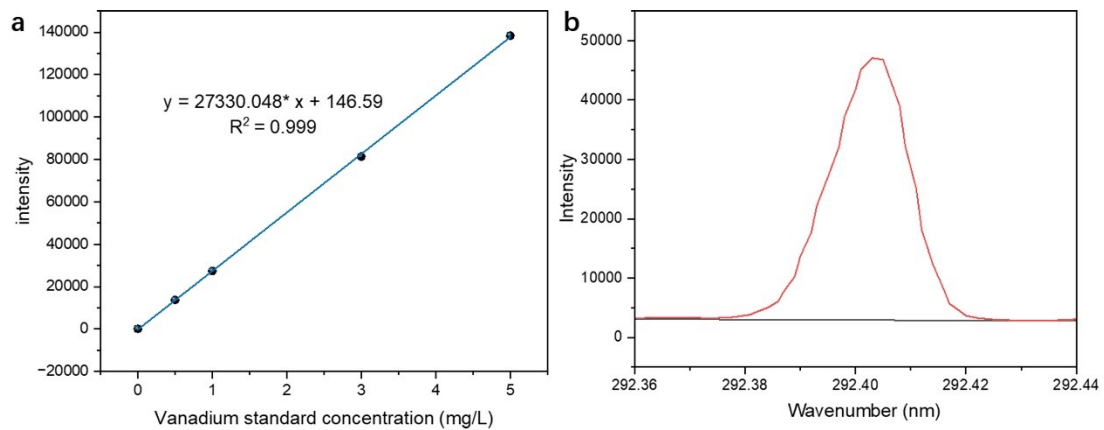| Element	weight (g)	Volume (mL)	Dilution coefficient	concentration (mg/L)	Vanadium content (mg/kg)
V	0.0419	10	1	1.4234	339.7131

Fig.S5 (a) Vanadium marking curve; (b) ICP-MS spectra of O-NC.

According to the test results of Inductively Coupled Plasma-Mass Spectrometry (ICP-MS), the residual content of vanadium metal in the aldehyde functional group nanocellulose prepared is 0.03%, which is very low and does not affect its different applications, and even a small amount of metal ions in some hydrogels can improve
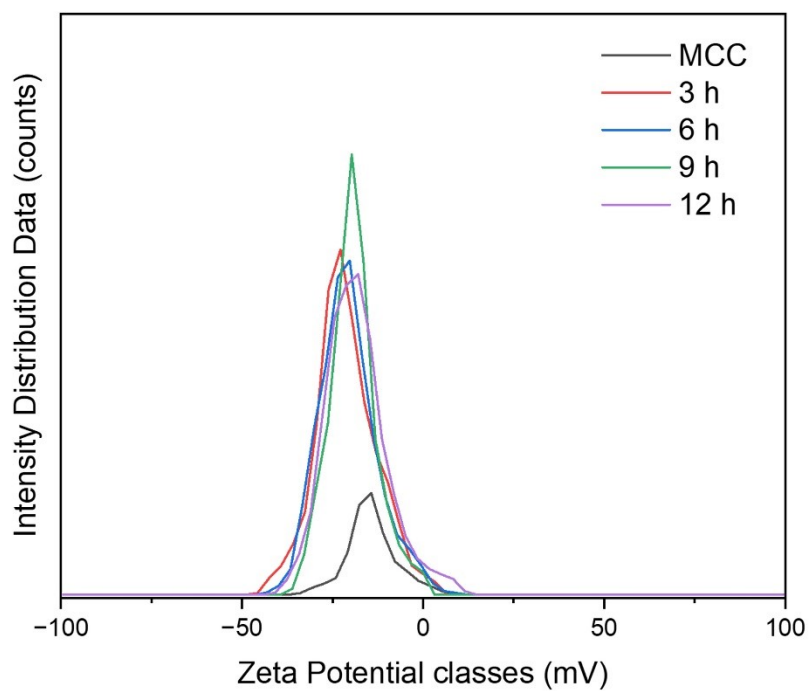
its mechanical properties.[1, 2]

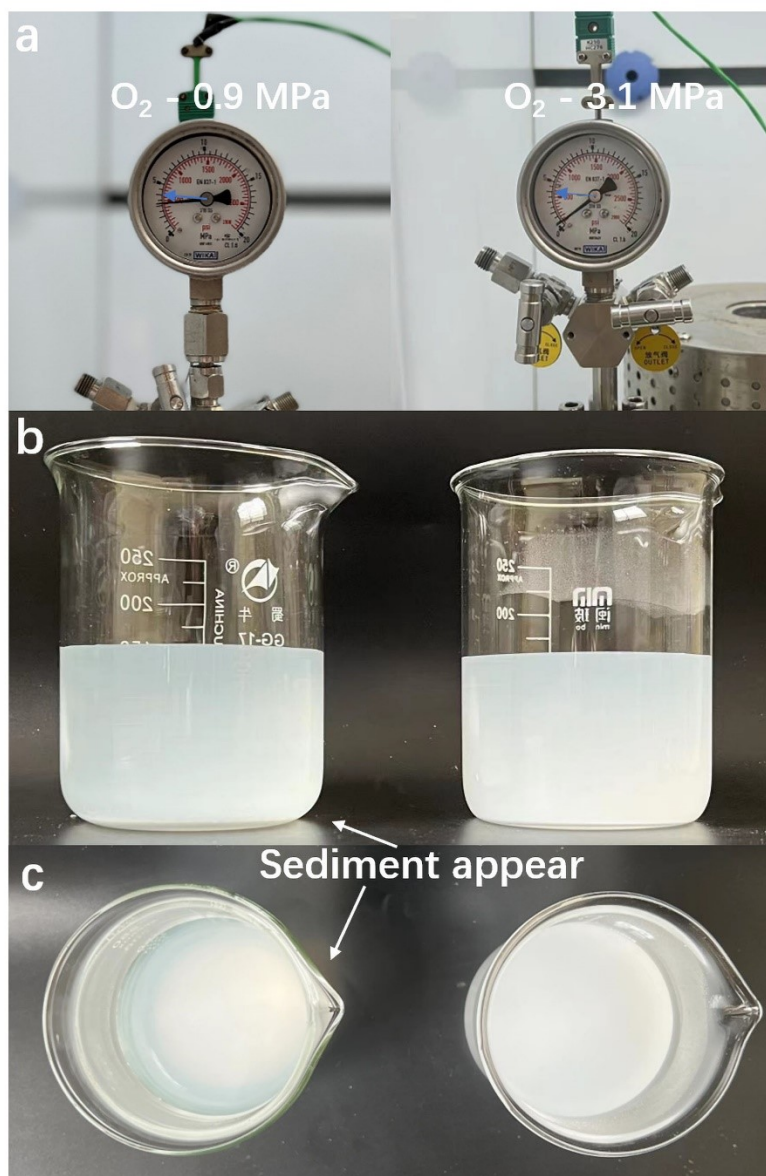Fig.S6 Zeta point curve of MCC and MCC oxidized at different reaction in VO(OiPr)$_3$ system.

Fig.S7 A comparison of oxidizing MCC products in the persence and/or absence of VO(OiPr)$_3$ as a catalyst. (a) The remaining oxygen in the reactor at the end of the oxidation reaction without (left) and with (right) the VO(OiPr)$_3$; (b) and (c) show the front view and top view of the cellulose samples prepared by MCC reaction with and without catalyst VO(OiPr)$_3$ dispersed in deionized water after standing for 72 h, respectively.（Left :0.5 g MCC, 10 mL DMSO, 4 MPa O$_2$, 120°C, 12 h；Right: 0.5 g MCC, 10 mL DMSO, 136 μL VO(OiPr)$_3$, 4 MPa O$_2$, 120°C, 12 h.）

Fig.S8 A comparison of oxidizing MCC products in the persence and/or absence of O_2 as an oxidant. The figures show the front view and top view of the cellulose samples dispersed in deionized water after standing for 1 h, respectively.（Left :0.5 g MCC, 10 mL DMSO, 4 MPa O_2, VO(OiPr), 120°C, 12 h；middle: 0.5 g MCC, 10 mL DMSO, 4 MPa N_2, VO(OiPr), 120°C, 12 h; right: 0.5 g MCC, 10 mL DMSO, 4 MPa N_2, 120°C, 12 h.）
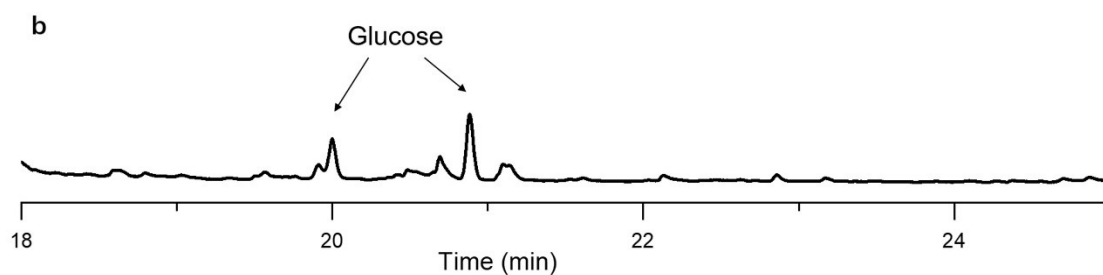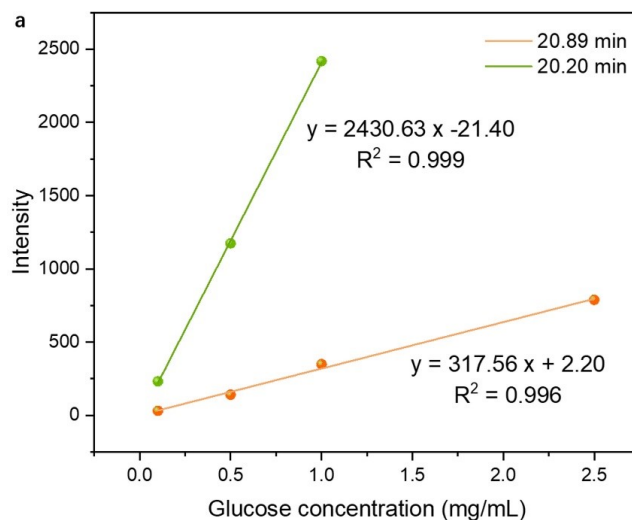
Fig. S9 (a) Glucose standard curve; (b) Gas chromatogram of DMSO reaction solution hydrolyzed by H_2SO_4. Acid hydrolysis of the waste liquid after oxidation was conducted to hydrolyze oligosaccharides in the liquid into glucose. The reaction solution was diluted into a 3% sulfuric acid aqueous solution and reacted at 120°C for 1 h. We detected 105 mg glucose per 500 mg MCC, which is around a glucose yield of 20% (original data is shown below). Surely, these oligosaccharides will accumulate in the reused solvent, which will affect the reuse of the liquid after a few recycles. To solve the issue, the residues mainly including oligosaccharides can be separated from DMSO for glucose production after evaporating DMSO while DMSO can be recovered as a fresh solvent for the oxidation.
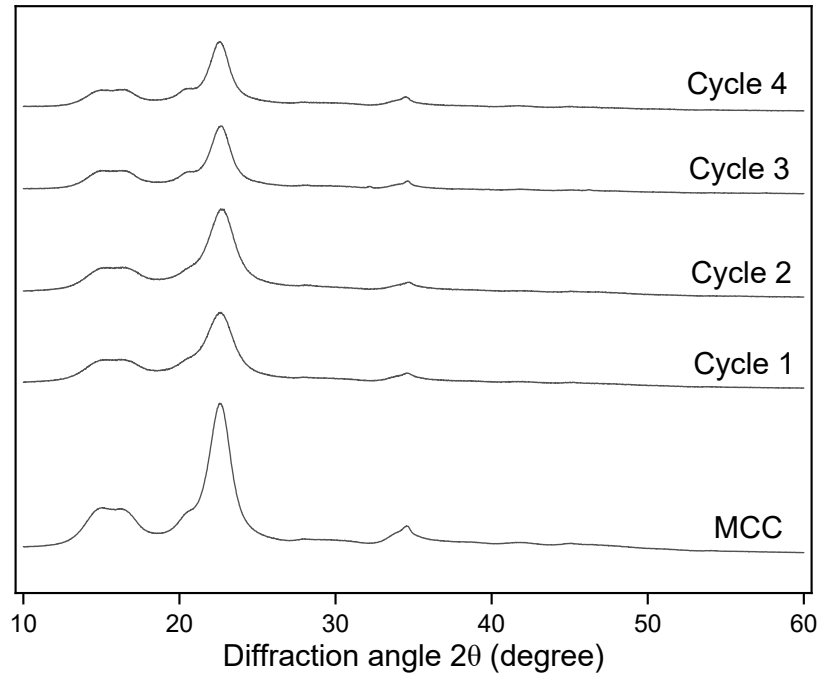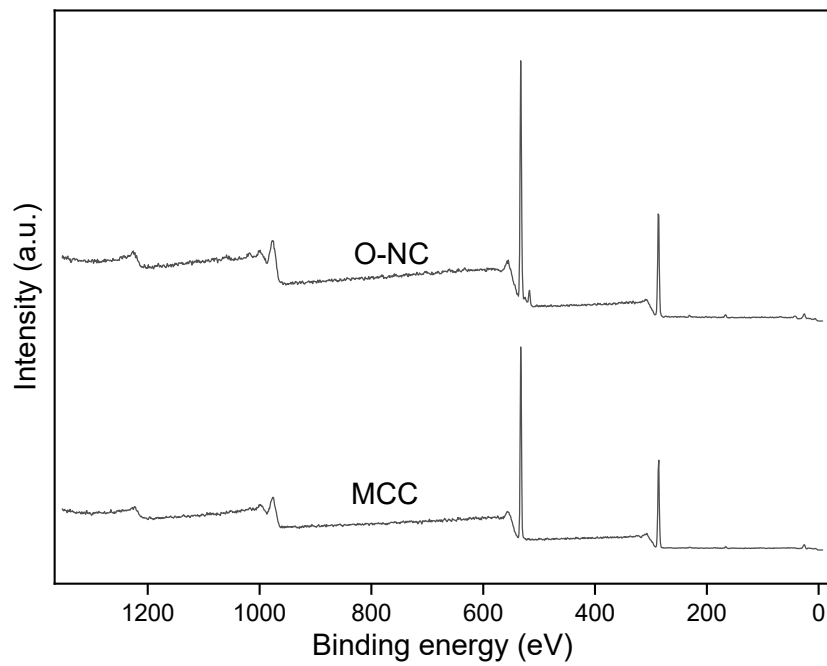
Raw spectral data:
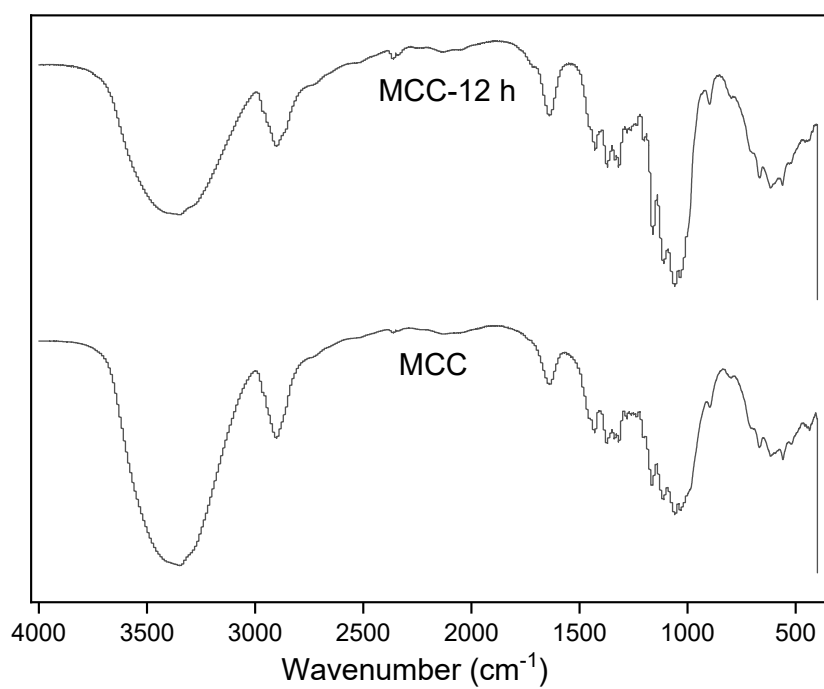
FT-IR spectra of MCC before and after oxidation.
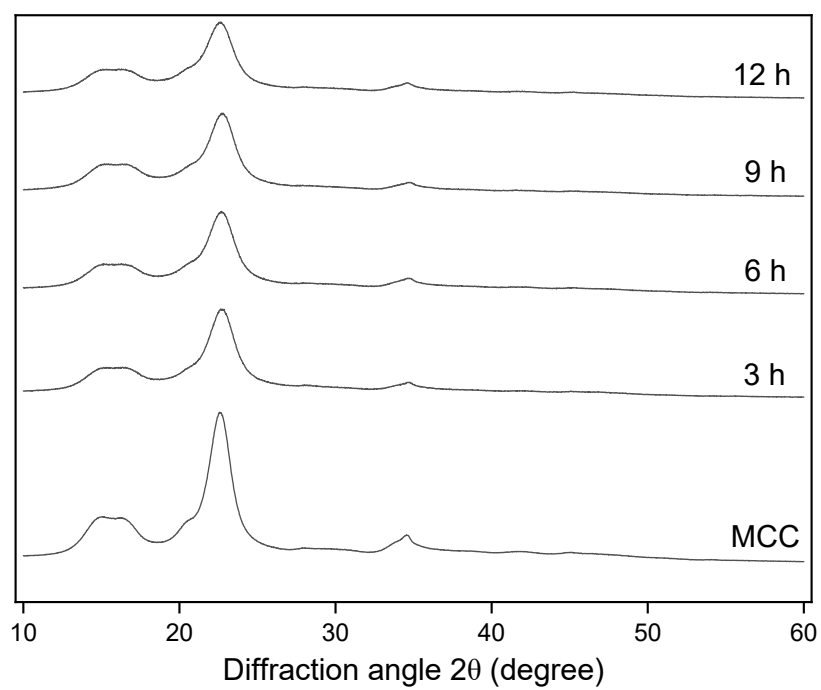
XRD of MCC at different oxidation times.

XRD of MCC at different oxidation times.

XPS spectra of MCC and O-NC.

Referenc

1.   F. Wahid, Y. N. Zhou, H. S. Wang, T. Wan, C. Zhong and L. Q. Chu, *Int. J. Biol. Macromol.*, 2018, **114**, 1233-1239.

2.   I. Hussain, S. M. Sayed, S. Liu, F. Yao, O. Oderinde and G. Fu, *Eur. Polym. J.*, 2018, **100**,

219-227.