

A facile one-pot route to cationic cellulose nanocrystals

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1. Experimental

Materials Cotton wool (BP grade, 100%), sulfuric acid (> 95%), ethanol (95%), dichloromethane (99%), potassium bromide for IR spectroscopy (> 99%), and orange II sodium salt (Acros, pure, certified, 90%) were purchased from Fisher Scientific (UK). Pyridine (AnalaR NORMAPUR, 99.7%), Amberlite MB6113 mixed bed ion exchange resin, H+/OH- with indicator (Merck), Spectrum Laboratories Spectra/Por 4 regenerated cellulose dialysis tubing (MWCO, 12 - 14 kDa) and Whatman type 603 cellulose extraction thimbles were purchased from VWR international. p-Toluenesulfonyl chloride (98%), 4-(1-bromoethyl)benzoic acid (98%) and 4-(bromomethyl)benzoic acid (97%) were purchased from Alfa Aesar. Chloroform-d (99.8 atom % D) was purchased from Sigma-Aldrich.

Characterization Elemental analysis (C, H, N, Hal) was carried out by the University of Leeds Elemental Analysis Service. FTIR spectra were collected on a Thermo-Nicolet 380 FTIR spectrometer in transmission mode using KBr sample disks. Solution NMR spectra were acquired on Bruker DPX300, AV400 and AV(III) 400 spectrometers and shift referenced to either TMS or the residual solvent signal. High resolution mass spectra were recorded on a Bruker microTOF spectrometer with electrospray ionization using acetonitrile as a solvent. Zeta potential measurements were carried out on 0.1% suspensions of cellulose nanocrystals in deionized water, using a Malvern Zetasizer Nano. Recorded zeta potentials were averaged over a minimum of 10 measurements. UV-Vis spectra of Orange II dye solutions were recorded on a Perkin-Elmer Lambda 25 Spectrophotometer using quartz cells with a 1 cm path length between 190-600 nm with a resolution of 1 nm. X-ray diffractograms were recorded on a PANalytical X'Pert Pro multi-purpose diffractometer (MPD) in Bragg-Brentano parafocusing geometry, with monochromated Cu K α_1 ($\lambda = 1.5406\text{\AA}$, 40 kV, 40mA) radiation, automated divergence and receiving slits (10mm illuminated length), 10mm beam mask, 0.04 rad soller slits and a step size of 0.08°. Samples were analysed on a silicon "zero-background" sample holder as a loose powder with the packing density influencing the amount of sample in the beam (freeze dried samples are less aggregated). The sample stage was rotated during acquisition to reduce preferred orientation effects in the plane of the stage. X-ray photoelectron spectra were recorded on a Kratos Axis Ultra X-ray Photoelectron Spectrometer employing a monochromated Al K α ($h\nu = 1486.6\text{ eV}$, 120W) X-ray source, hybrid (magnetic/electrostatic) optics (300 x 700 μm

aperture), hemispherical analyser, multichannel plate and delay line detector (DLD) with a take-off angle of 90° and an acceptance angle of 30°. The analyser was operated in fixed analyser transmission (FAT) mode with survey scans taken with a pass energy of 80 eV and high resolution scans with a pass energy of 20 eV. All scans were acquired under charge neutralization conditions using a low energy electron gun within the field of the magnetic lens. The resulting spectra were processed using CasaXPS software. Binding energy was referenced to adventitious carbon at 285 eV. AFM images were obtained using an Asylum Research MFP-3D microscope in tapping mode. Samples were prepared from a 0.001% w/w suspension and dried on mica sheets. Micrographs of CNCs and pyridinium-g-CNCs suspension were taken using polarized light microscope (PriorLuxPol Polarizing Microscope). Pyridinium-g-CNCs suspensions at the desired concentrations were prepared and placed in a rectangular glass capillary tube (0.4 x 4.0 mm, VitroCom) where they were left to dry under ambient temperature. The capillary containing the modified film was then observed under microscope between crossed polarizing filters.

Synthesis of cellulose nanocrystals Cotton wool (80 g) was added to sulfuric acid (64% w/w, 700 ml) and heated at 45°C with mechanical stirring. The acid hydrolysis was left to occur for 40 minutes. Following hydrolysis, the suspension was diluted with an equal volume of cold deionized water and subjected to centrifugation. Three successive centrifugations were carried out at 10,000 rpm for 40, 60 and 20 mins, using a Sigma 6K15 Refrigerated Centrifuge. After centrifugation, the suspension was dialysed using cellulose membrane tubing (MWCO 12K-14K diameter 48mm) against running tap water. The suspension was then sonicated using a Branson Digital Sonifier to homogenize the suspension and separate aggregates prior to filtration through a fritted-glass filter (porosity 2). After sonication, the filtrate obtained was mixed with Amberlite MB6113 mixed bed ion exchange resin and filtered again before freeze-drying using Thermo Heto PowerDry PL6000 Freeze Drier. The resulting cellulose nanocrystals were Soxhlet extracted with ethanol for 72 hours before drying *in vacuo*. Found: C, 42.5; H, 6.3 %. Calc. for (C₆H₁₀O₅)_n: C, 44.3; H, 6.23 %. $\bar{\nu}_{\max}$ (KBr) /cm⁻¹ 3346 ν (O-H), 2900 ν (C-H), 1643 δ (H₂O), 1430 δ (C-O-H), 1337 δ (C-O-H), 1317 δ (C-O-H), 1206 ν (C-O-C, glycosidic), 1163 ν (C-O-C, glycosidic, asym.), 1113 ν (C₂-OH), 1059 ν (C₃-OH), 1034 ν (C₆-OH), 706 ω (C-OH), 666 ω (C-OH).

Synthesis of N-benzylpyridinium cellulose nanocrystals To a two-necked 100 ml round bottom flask equipped with magnetic stir bar was added CNCs (0.5 g), 4-(bromomethyl)benzoic acid (587 mg, 2.74 mmol) and *p*-toluenesulfonyl chloride (520 mg, 2.73 mmol). The flask was purged with argon before adding dry pyridine (50 ml) and subsequently attached to a condenser. The reaction was heated at 80°C for 16 hours under an atmosphere of argon. The resulting suspension was filtered through cellulose extraction thimble. The resulting modified CNCs were Soxhlet extracted with dichloromethane for 24 hours and subsequently with ethanol for 72 hours. Found: C, 45.4; H, 5.69; N, 0.71; Br, 4.80 %. Calc. for C_{7.25}H_{10.96}O_{5.10}N_{0.10}Br_{0.10} (DS (N) = 0.38): C, 46.1; H, 5.86; N, 0.71; Br, 4.05 %. $\bar{\nu}_{\max}$ (KBr) /cm⁻¹ 3344 ν (O-H), 2901 ν (C-H), 1720 ν (C=O), 1634 ν (C=C), 1580 ν (arom.), 1428 δ (C-O-H), 1337 δ (C-O-H), 1317 δ (C-O-H), 1206 ν (C-O-C, glycosidic), 1163 ν (C-O-C, glycosidic, asym.), 1113 ν (C₂-OH), 1059 ν (C₃-OH), 1034 ν (C₆-OH), 708 ω (C-OH), 668 ω (C-OH).

Synthesis of N-(α -methylbenzyl)pyridinium cellulose nanocrystals To a two-necked 100 ml round bottom flask equipped with a magnetic stir bar, was added CNCs (0.5 g), 4-(1-bromoethyl)benzoic acid (628 mg, 2.74 mmol) and *p*-toluenesulfonyl chloride (523 mg, 2.74 mmol). The flask was purged with argon before adding dry pyridine (50 ml) and subsequently attached to a condenser. The

reaction was heated at 80°C for 16 hours under an atmosphere of argon. The modified CNCs were filtered through a cellulose extraction thimble and Soxhlet extracted with dichloromethane for 24 hours and subsequently with ethanol for 72 hours. Found: C, 48.3; H, 5.46; N, 1.59; Br, 8.60 %. Calc. for $C_{9.84}H_{13.29}O_{5.27}N_{0.27}Br_{0.27}$ (DS (N) = 1.10): C, 48.9; H, 5.54; N, 1.59; Br, 9.07 %. $\bar{\nu}_{\max}$ (KBr) / cm^{-1} 3346 ν (O-H), 2901 ν (C-H), 1723 ν (C=O), 1632 ν (C=C), 1580 ν (arom.), 1424 δ (C-O-H), 1337 δ (C-O-H), 1317 δ (C-O-H), 1206 ν (C-O-C, glycosidic), 1162 ν (C-O-C, glycosidic, asym.), 1112 ν (C₂-OH), 1059 ν (C₃-OH), 1034 ν (C₆-OH), 708 ω (C-OH), 668 ω (C-OH).

Calculation of degree of substitution The degree of substitution was calculated based on elemental analysis using an iterative method in which the empirical formulae for anhydroglucose units was determined assuming a degree of substitution of 1, along with its respective expected atomic and weight percentage compositions. This bulk degree of substitution was then divided by the ratio of surface chains to total chains in the nanocrystals to obtain the degree of substitution at the surface.

Using the dimensions of the long ($L=14$ nm) and short ($l=7.3$ nm) sides of nanocrystal cross section,¹ and taking into account that the (1 $\bar{1}$ 0) planes ($d=0.594$ nm) are parallel to the long side and the (110) planes ($d=0.533$ nm) parallel to the short side, the chain ratio accessible on the surface can be calculated using method by Gousse *et al.* and Habibi *et al.*^{2,3}

$$\begin{aligned}\frac{\text{Surface chains}}{\text{Total chains}} &= \frac{\left(\frac{2L}{d_{(110)}}\right) + \left(\frac{2l}{d_{(1\bar{1}0)}}\right)}{\left(\frac{Ll}{d_{(1\bar{1}0)}d_{(110)}}\right)} \\ &= \frac{\left(\frac{2 \times 14}{0.533}\right) + \left(\frac{2 \times 7.3}{0.594}\right)}{\left(\frac{14 \times 7.3}{0.594 \times 0.533}\right)} \\ &= 0.24\end{aligned}$$

As can be seen, the ratio of surface chains to total chains is heavily dependent on the dimensions of the nanoparticles (e.g. using dimensions of 6 x 6.1 nm which are values obtained for the elementary crystals,⁴ this ratio increases to 0.37). We have used the widely reported values of 14 x 7.3 nm which allows direct comparison with existing literature modification results.

2. FTIR Spectra

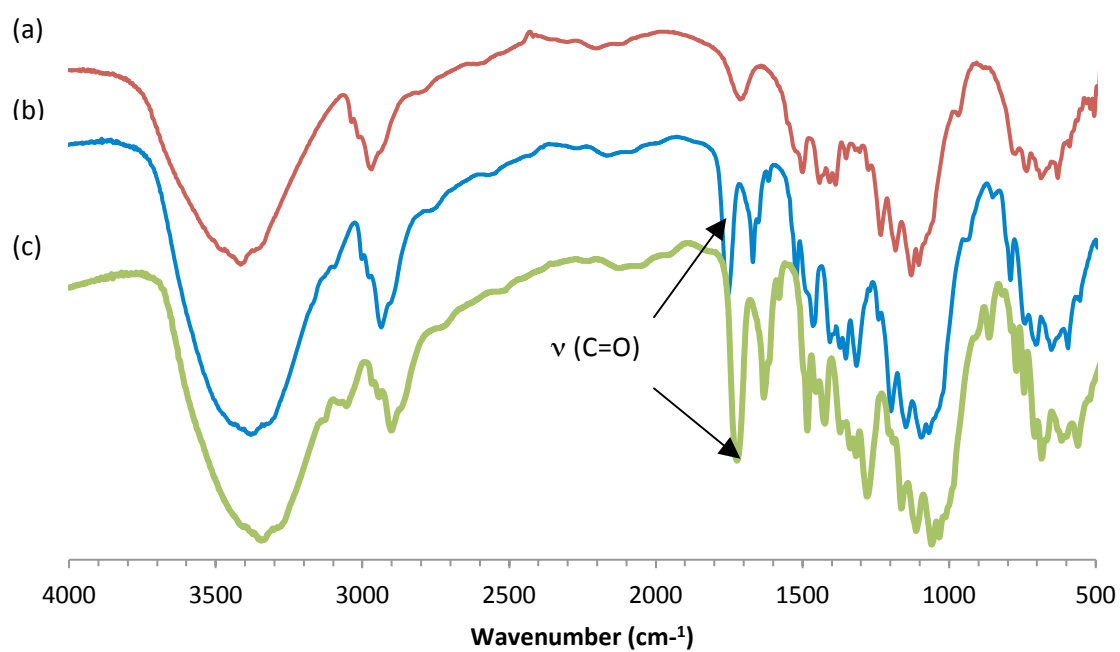


Figure 1 FTIR spectra of (a) CNCs and (b) [Br][BnPy]-g-CNCs (c) [Br][MeBnPy]-g-CNCs

3. X-ray Photoelectron Spectroscopy

Table 1 XPS data of CNCs

Element	Orbital	Binding energy (eV)	At %
Carbon	1s	286.1	54.4
Oxygen	1s	532.6	45.6

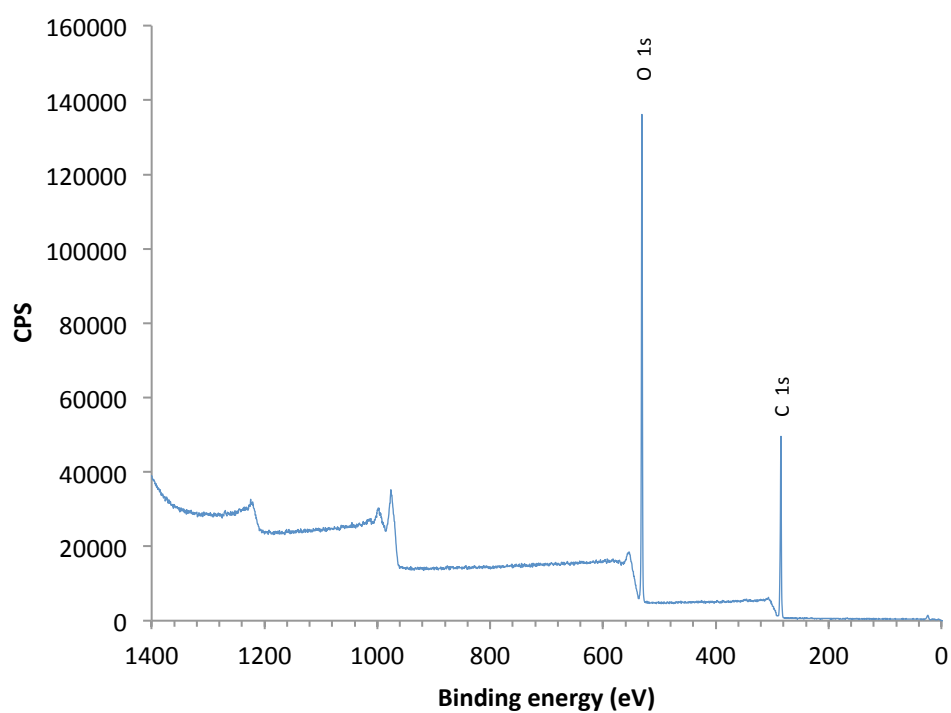


Figure 2 XPS wide scan of CNCs

Table 2 XPS data of [Br][BnPy]-g-CNCs

Element	Orbital	Binding energy (eV)	At %
Carbon	1s	286.1	64.6
Oxygen	1s	532.6	33.0
Nitrogen	1s	402.1	1.75
Bromine	3d	67.6	0.65

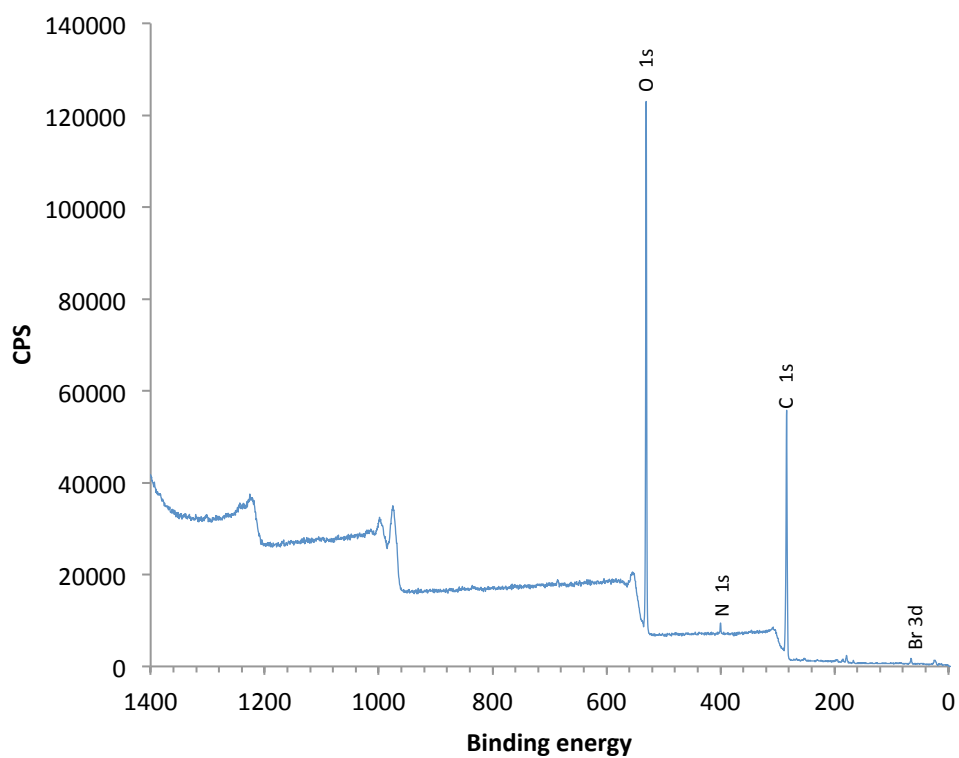


Figure 3 XPS wide scan of [Br][BnPy]-g-CNCs

Table 3 XPS data of [Br][MeBnPy]-g-CNCs

Element	Orbital	Binding energy (eV)	At %
Carbon	1s	286.1	69.8
Oxygen	1s	532.6	26.9
Nitrogen	1s	402.1	2.50
Bromine	3d	67.6	0.81

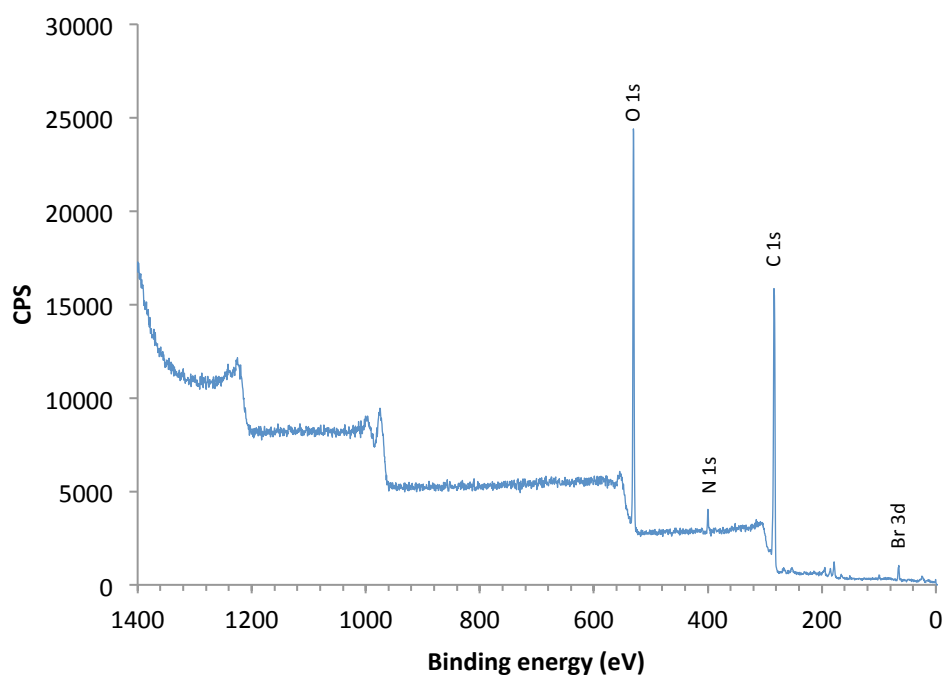


Figure 4 XPS wide scan for [Br][MeBnPy]-g-CNCs

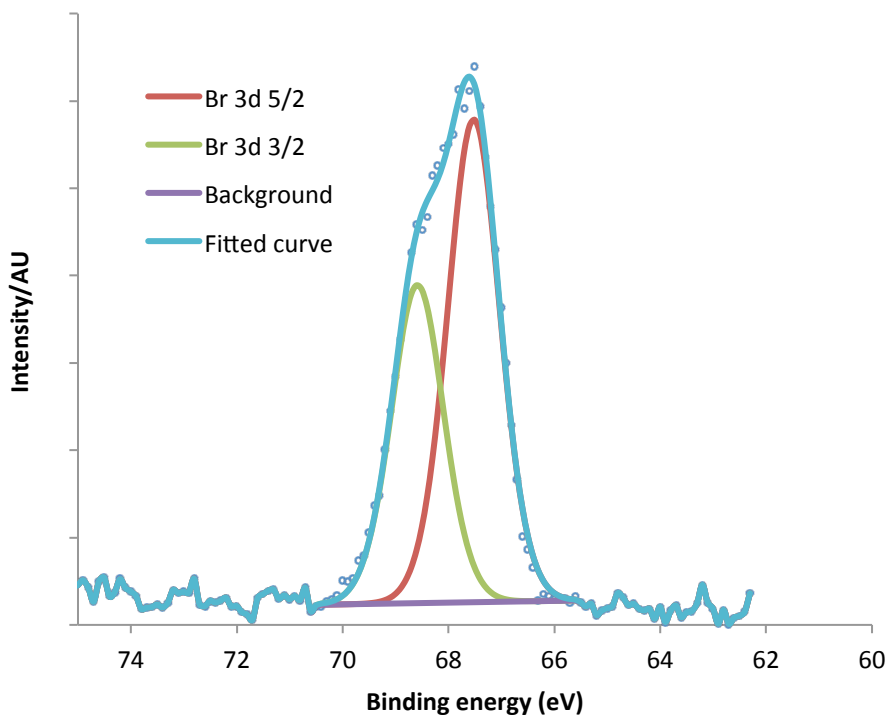


Figure 5 XPS high resolution scan of Bromine 3d for [Br][BnPy]-g-CNCs

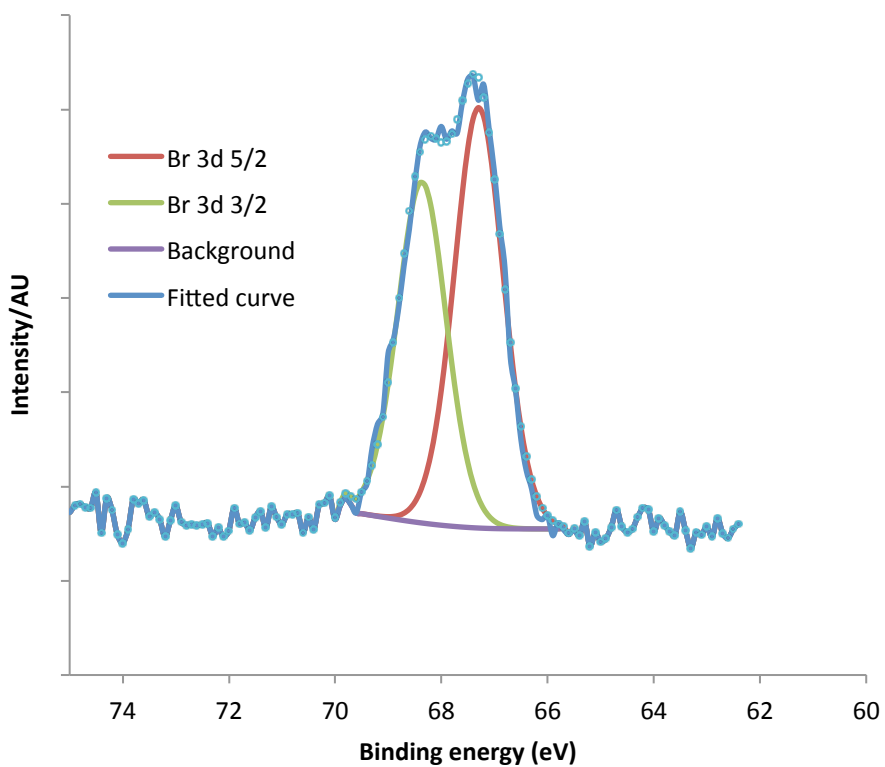


Figure 6 XPS high resolution scan of Bromine 3d for [Br][MeBnPy]-g-CNCs

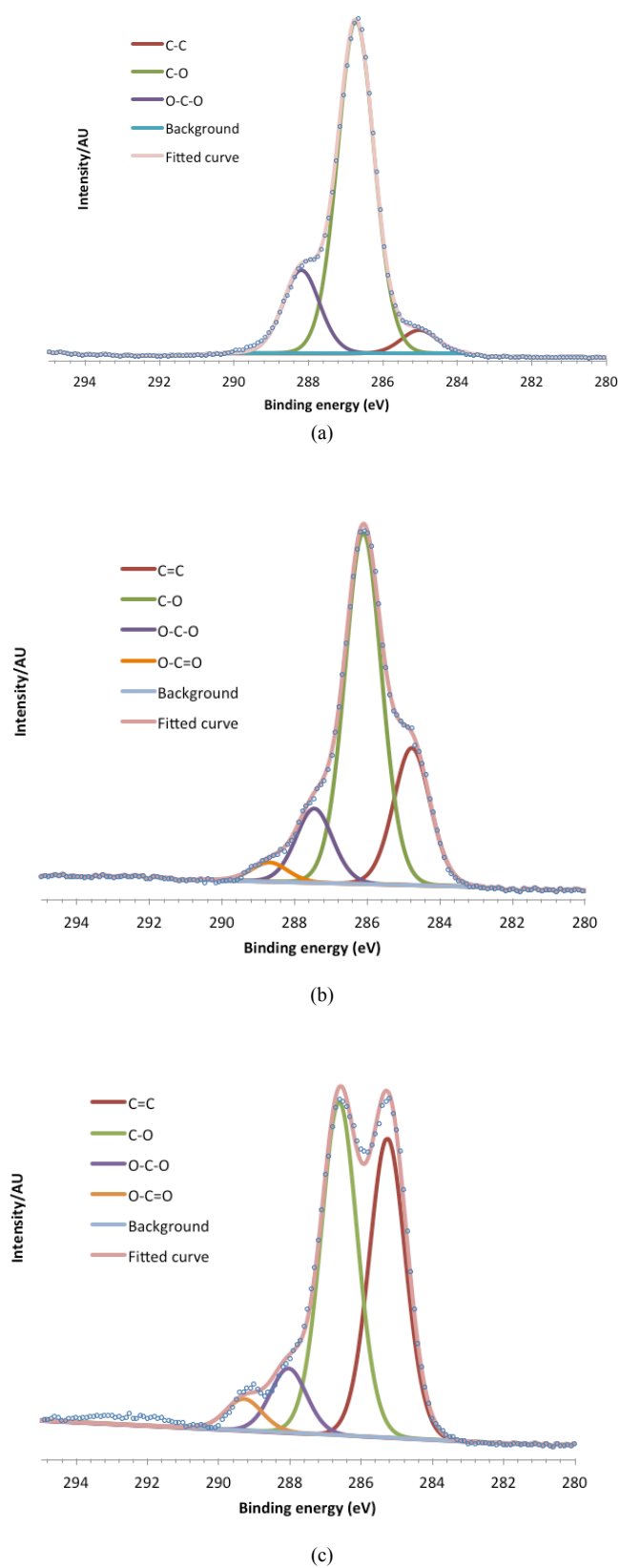
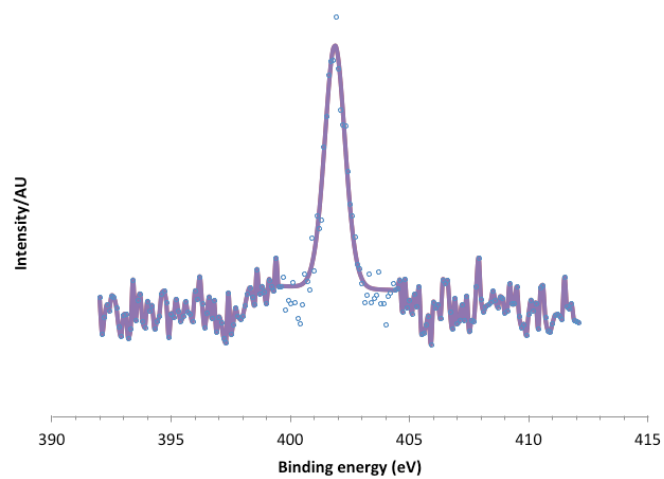
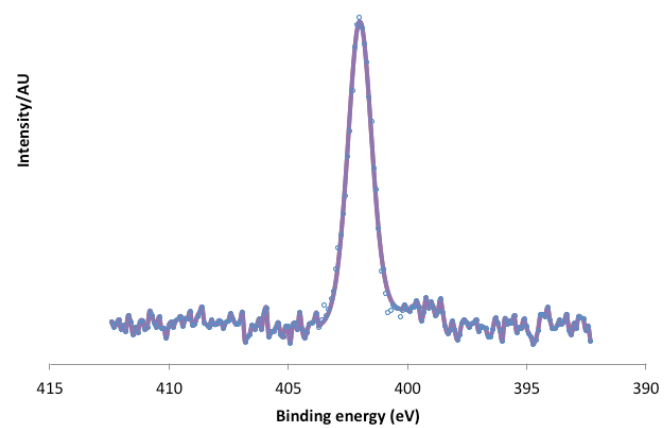


Figure 7 (a) XPS high resolution scan of C1s of unmodified CNCs (b) [Br][BnPy]-g-CNCs (c) [Br][MeBnPy]-g-CNCs



(a)



(b)

Figure 8 (a) XPS high resolution scan of the N1s signals of [Br][BnPy]-g-CNCs (b) [Br][MeBnPy]-g-CNCs.

5. Powder X-ray Diffraction

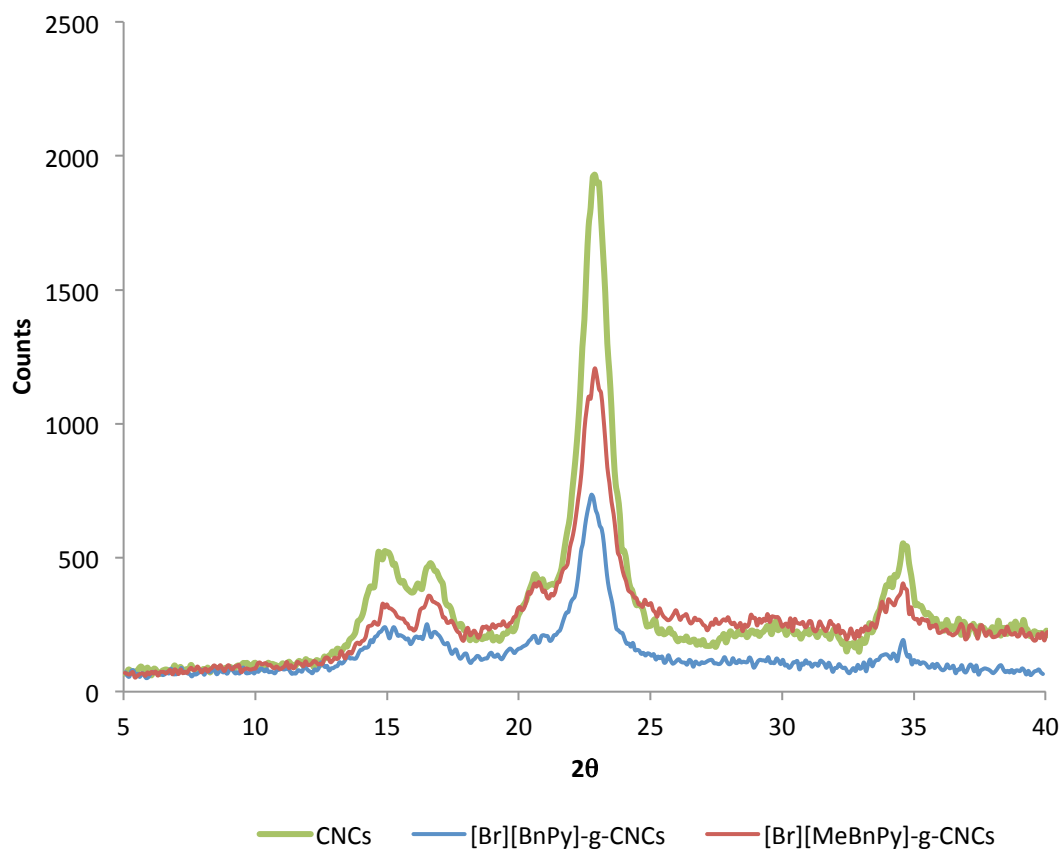


Figure 9 Diffractogram of CNCs and pyridinium-modified-CNCs

References

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