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Imidazolium Grafted Cellulose Nanocrystals for Ion Exchange Applications†

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An imidazolium salt was grafted to cellulose nanocrystals (also called nanowhiskers) using copper(I) catalysed azide-alkyne cycloaddition and the bromide anion was successfully exchanged for bistriflimide and an anionic dye, providing the opportunity to synthesize a wide variety of ion exchange systems or catalysts using cellulose nanocrystals as a support medium.

Cellulose nanocrystals are long rigid ribbons produced by acid hydrolysis of native cellulose which have a surface area in excess of $300\,m^2\,g^{-1}$. Their ample surface hydroxyl groups ($2-3$ mmol/g) enable targeted surface modification to introduce virtually any desired surface functionality. Reported surface modifications include surface initiated polymerization, esterification, etherification controlled oxidation, fluorescently dyed (thiol-ene click reaction), and cationization of the surface, to name but a few.[1]

Recently, cationized nanocrystals have been prepared by the introduction of quaternary amine groups,[2] and azide groups were introduced away from the surface using an aliphatic linker molecule. Use of the linker molecule led to only a limited extent of modification, however, the azide groups were successfully used to perform the well known azide-alkyne cycloaddition "click" reaction.[3] Direct introduction of the azide group onto the surface of the cellulose nanowhiskers should result in a significantly higher extent of modification, enabling potentially a near complete modification of the nanocrystal surface using "click" chemistry.

The renewable nature of cellulose combined with the ability to functionalize the surface easily means that charged cellulose nanocrystals may form an attractive alternative to traditional cross-linked polystyrene divinylbenzene co-polymer ion exchange resins. Cellulose nanocrystals can also be transformed into aerogel porous structures with surface areas of up to $605\,m^2\,g^{-1}$,[4] giving rise to the possibility of production of heterogeneous catalyst systems similar in nature to the supported aqueous phase system created by Quignard *et al.* using chitosan.[5] Described herein is the surface modification of cellulose nanocrystals to incorporate imidazolium cations by grafting of an imidazolium bromide salt using "click" chemistry onto an azidated cellulose nanocrystal surface to produce a heterogeneous system with facile anion exchange capability.

Cellulose nanocrystals were produced from bleached cotton by hydrolysis with 64 wt% sulfuric acid.[6] The resulting nanocrystals were soxhlet extracted for 48 hrs with ethanol to remove low molecular weight organic contaminants before surface modification.[7] Copper(I) mediated azide-alkyne cycloaddition was chosen as the preferred method for surface modification due to its tolerance to a wide variety of solvents and functional groups,[8] along with established methods for modification of cellulose using this reaction.[3;9]

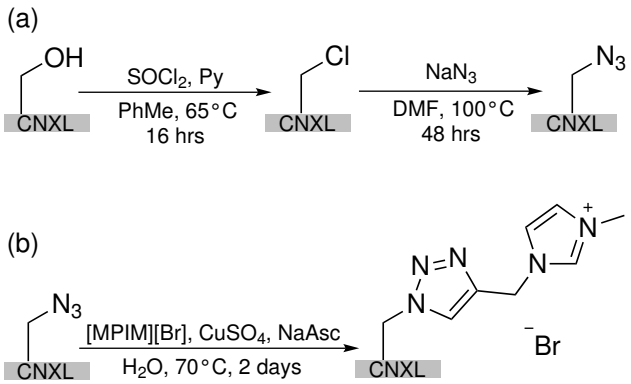
The cellulose nanocrystals were azidated to allow grafting of an alkyne terminated ionic liquid. The azidation conditions were adapted from those used by Liebert *et al.*[9] to use chlorination instead of tosylation to activate the nanocrystals, due to the inconsistent results of heterogeneous tosylation reactions on cotton.[10] The chlorination was performed following the previously described procedure by Carré *et al.*[11] and the product purified by soxhlet extraction with dichloromethane and ethanol. The chlorinated nanocrystals were subsequently azidated using sodium azide (39 mmol/g) in dimethylformamide and purified by dialysis against deionized water for five days before isolation by freeze drying the aqueous suspension (Scheme 1(a)).

The ionic liquid 1-methyl-3-propargylimidazolium bromide ([MPIM][Br]) was synthesized according to a literature procedure,[12] and grafted to the azidocellulose nanocrystals in an aqueous solution using copper(II) sulfate (5 mol%) as a pre-catalyst and sodium ascorbate (10 mol%) as the reductant (Scheme 1(b)). The product was purified by successive centrifugations with deionized water followed by dialysis against deionized water.

Infrared spectroscopy shows evidence of chlorination through formation of ν(C-Cl) $= 750\,cm^{-1}$. Reduction in ν(O-H) intensity is not visible however, due to the large number of

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Scheme 1 (a) Synthetic route for azidation of CNXLs. (b) Grafting of [MPIM][Br] using heterogeneous click chemistry.

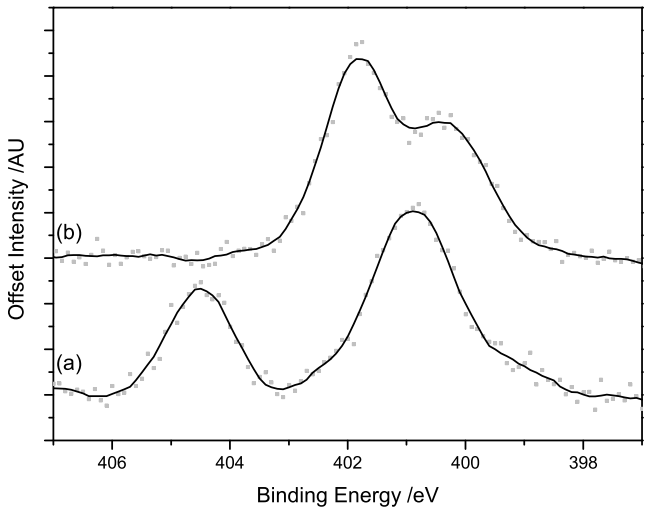


Fig. 1 XPS Nitrogen 1s high resolution spectra showing conversion of (a) azide to (b) 1,2,3-triazole during grafting.

hydroxyl groups within the nanocrystal structure unaffected by the chlorination. Subsequent azidation is also clearly visible in the infrared spectrum through appearance of the strongly absorbing $\nu(N_3) = 2114\ cm^{-1}$ band which subsequently disappears on formation of the 1,2,3-triazole linker during the imidazolium grafting reaction. The imidazolium graft is visible from appearance of a new band at $1566\ cm^{-1}$ which is present in the ionic liquid starting material.[†]

Following each stage of the modification of the cellulose nanocrystals, the crystallinity of the sample was monitored using powder x-ray diffraction, and the crystallinity indices of each product were calculated according to the literature method.[13] The crystallinity index for the product decreases slightly from 0.89 to 0.80 during the chlorination procedure, and remains constant through the other modification reactions showing high stability of the nanocrystal structure throughout the chemical modifications.

X-ray photoelectron spectroscopy (XPS) was used to further elucidate the structure of the IL grafted cellulose nanocrystals. The azidated nanocrystals show the characteristic nitrogen 1s peaks at 401 eV and 405 eV.[14] Following the grafting reaction, two overlapping nitrogen 1s peaks at 402 eV and 401 eV are present (Fig. 1). The peak at 402 eV is consistent with literature data for the nitrogen 1s binding energy of imidazolium cations,[15] while the broad peak at 401 eV provides good agreement with values for 1,2,3-triazoles obtained from heterogeneous click reactions.[14] XPS wide scans did not show bromide within the sample, however, degradation of samples containing bromine in XPS analysis is a known phenomenon,[16] and filtration of a suspension of the nanocrystals and subsequent ion chromatography revealed almost exclusive presence of bromide as the anion in the sample.

The degree of substitution (DS) for the imidazolium graft was calculated using nitrogen concentration by elemental analysis as 0.36; assuming that all azide moieties were converted to triazoles (consistent with the nitrogen 1s peaks in XPS). The maximum DS for this method of modification is 0.5, because the S_N2 mechanism dictates an inversion of configuration at the carbon centre which is severely hindered for the secondary hydroxyl groups, therefore only accessible primary hydroxyl groups can be modified.

The ion exchange capability of the modified nanocrystals was tested by suspending them in an aqueous solution of lithium bis(trifluoromethanesulfonyl)imide overnight. The ion exchanged nanocrystals were extracted by successive centrifugations with deionized water, and freeze dried before characterization. XPS shows that the ion exchange was successful with a significant fluorine 1s peak at 689 eV, and sulfur 2p peaks at 169 eV (Fig. 2: Left). Further evidence is provided by the high resolution carbon 1s scan showing CF_3 C-F character at 293 eV (Fig. 2: Right). We have therefore developed a method to immobilize imidazolium salts producing a heterogeneous system in which the anion can easily be exchanged

The ζ-potential of the imidazolium-grafted nanocrystals was determined to be +47 mV (cf. −9.49 mV for unmodified cellulose nanocrystals), from which a positive surface charge consistent with cationization of the surface can be inferred. Using the DS from elemental analysis, the concentration of imidazolium residues on the surface of the nanocrystals can be calculated as 0.53 mmol/g, giving a surface charge density of $1.17\ e\,nm^{-2}$. The ion exchange potential of the nanocrystals was quantified using Orange II (monoanionic dye) and UV/Vis spectroscopy (Fig. 3). The amount of dye adsorbed was 0.28 mmol/g, corresponding to a surface charge density of $0.73\ e\,nm^{-2}$. This value is lower than the value derived from the grafting, as can be expected from the steric bulk of the dye molecule and the possibility of blocking adjacent modified sites on the cellulose

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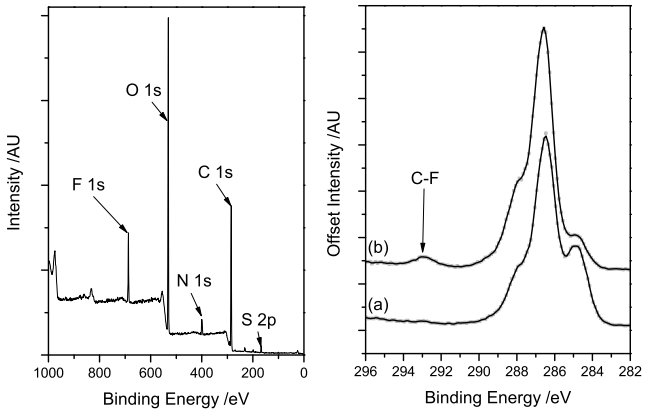


Fig. 2 Left: XPS wide scan of bistriflimide exchanged CNXLs. Right: XPS Carbon 1s (a) MPIM-g-CNXL (b) $[NTf_2][MPIM]$-g-CNXL.

surface favoured by $\pi - \pi$ stacking interactions between the aromatic rings of the dye and the imidazolium residues. Both values for the surface charge density are higher than previously reported by Hasani *et al*. for the cationisation of cellulose nanocrystals using quaternary ammonium substituents.[2]

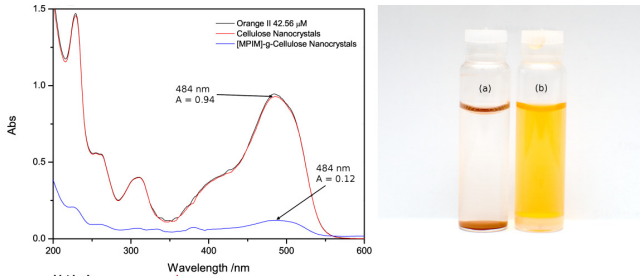


Fig. 3 UV/Vis spectrum showing adsorption of Orange II dye by (a) [MPIM]-g-cellulose nanocrystals and (b) cellulose nanocrystals

In summary, we have synthesized cellulose nanocrystals grafted with an imidazolium group (DS = 0.36) using heterogeneous copper(I) catalysed azide-alkyne cycloaddition giving a surface with a charge density of 1.17 $e\,\mathrm{nm}^{-2}$. We have demonstrated the ability to exchange the anion present at the surface of the nanocrystals, presenting the opportunity to exchange the anion for catalytically active species and produce a wide variety of, supported catalysts and ion exchange systems. These applications are currently under investigation.

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