Decoration of cellulose nanocrystals with iron oxide nanoparticles

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Abstract
Cellulose nanocrystals (CNCs) are excellent candidates for the design and development of multi-functional biomaterials systems to be used in a variety of technologically relevant applications. They may be used as the structural reinforcement phase of polymer matrices, act as catalyst support constituents, as well as drug delivery vectors. Modifying and functionalizing CNCs by introducing specific functional components can impart electronic, magnetic, catalytic, fluorescence and optical properties to the system. In this work we report the successful in situ tethering of iron oxide nanoparticles (IONPs) onto CNCs by the thermal decomposition of Fe(CO)5 in a H2O/DMF suspension. Following this procedure, IONPs consisting of mixtures of Fe3O4 and Fe2O3 with an average diameter of 20 nm were attached to the CNCs. The type of iron oxide species that was generated was determined by selected area electron diffraction (SAED) and energy dispersive spectroscopy (EDS), and the particle size was evaluated by transmission electron microscopy (TEM). Raman spectroscopy was used to characterize the presence and the nature of the molecular interaction between the IONPs and the CNCs.

1. Introduction
The development of novel, advanced biocompatible materials is consistent with the current drive for the creation of sustainable materials platforms for higher-value products, and reduction of the dependence on non-renewable raw materials, particularly those derived from petrochemicals [1–4]. Biocompatible materials based on cellulose nanocrystals (CNCs) derived from the acid hydrolysis of cellulosic materials [3, 5–9], constitute excellent candidates for the design and development of multi-functional systems to be used in a variety of technologically relevant applications, as shown schematically in figure 1 [10–14]. CNCs exhibit several attractive features, such as high surface area, a multitude of hydroxyl groups that can undergo further functionalization, colloidal stability, low toxicity, chirality and mechanical strength. These features make them suitable for a broad range of applications such as structural reinforcement, enzyme immobilization, antimicrobial shielding, green catalysis, biosensing, and drug delivery [15–22].

The utilization of CNCs for these various applications very often requires either their coupling with other components, such as polymer matrices to form nanocomposites [1, 23–25], or their surface chemical modification for targeted functionalization, again as shown schematically in figure 1 [5, 14, 26–28]. In recent years, the utilization of CNCs as components in functional material systems has become an active field of research. The abundance of hydroxyl groups on CNCs allows for extensive and diverse chemical modification options. The modification of the surface chemistry by introducing different functional groups translates into variations in the type of interactions of these materials with their environment. Some common surface functionalization reactions of CNCs include esterification, carboxylation, sulfonation, amination, nucleophilic substitution, surfactant attachment, polymer grafting, among others [5, 14, 26–28]. The main advantages of the chemical modification of CNCs are two-fold: They can introduce negative or positive electrostatic charges on the surface, and they can impart novel properties that are not intrinsic to the material and cannot be accessed otherwise. Because of their high surface reactivity due to the abundance of surface functional groups, CNCs tend to aggregate and thus, the impact of the properties of the individual nanocrystals is diminished. Therefore, the
surface modification of the CNCs may also provide a better dispersion in any solvent and polymer mixture. It also helps to tune the surface energy characteristics to improve compatibility, especially when used along with nonpolar or hydrophobic polymer matrices [29, 30].

The prospect of modifying and functionalizing CNCs is attractive as it enables the creation of advanced materials with new or improved properties [16]. By introducing the functional components (materials or chemical groups) to the system, synergistic effects can be achieved, which can impart electronic, magnetic, catalytic, fluorescence and optical properties. Thus, their functionalities will be improved and potential applications in specific fields can be expanded [2, 4, 18, 19, 31–34].

In the current work, we will present our recent developments in the functionalization of cellulose nanocrystals with magnetic nanoparticles. As previously stated, CNCs possess a large surface area and high surface energy, and hence, a high reactivity due to an abundance of surface functional groups. In order to expand the properties of CNCs and impart to them novel characteristic features, specifically, magnetic properties [35], we aimed to magnetize them through their decoration with maghemite/magnetite nanoparticles via an in situ reaction of iron precursors [20, 36, 37]. Kaushik et al thoroughly investigated the immobilizations of noble metal nanoparticles, such as Au, Ag or Pd, on CNCs using different methods [21]. The abundance of hydroxyl functional groups on the surface of the CNCs provides for convenient and accessible nucleation sites for the tethering of the metallic nanoparticles. Despite the relative ease of such tethering processes, there are very few reports on the growth of iron oxide nanoparticles (IONPs) onto CNCs. Hence, in this work we present the in situ formation of IONPs on CNCs by adopting a novel and facile thermal decomposition process of iron carbonyl precursors on the surface of CNCs. The tethering of IONPs onto CNCs was indeed confirmed and evaluated by various characterization techniques including TEM, EDS, SAED and Raman spectroscopy.

2. Experimental section

2.1. Materials
Microcrystalline cellulose (MCC), iron pentacarbonyl (>99.99%), N, N-dimethylformamide (DMF, 99%), and sulfuric acid (95%–98%) for hydrolysis were purchased from Sigma Aldrich and used without further treatment. All water used was deionized and purified using Millipore-Q purification system with a resistivity of 19.9 MΩ.cm at 24.9 °C.

2.2. Synthesis of CNCs
CNC suspensions were prepared from microcrystalline cellulose. A classic sulfuric acid hydrolysis method was carried out [7]. In particular, 2 g of MCC was hydrolysed with 20 ml 62% sulfuric acid at 45 °C for 1 h under...
continuous stirring. The hydrolysis step was stopped by adding 200 ml of cold deionized water. The suspension then was centrifuged at 7000 rpm for 20 min for three cycles to refine the solid residues. To remove excess acid, the solid residues in suspension were dialyzed using cellulose dialysis membranes with 12–14 kDa molecular weight cut off against deionized water for several days till constant pH was reached. Samples were then sonicated for 20 min in an ice bath. The concentration of obtained CNCs was around 0.2% w/w.

2.3. Synthesis of CNCs decorated with IONPs
CNCs were decorated with IONPs by the in situ thermal decomposition of iron pentacarbonyl, Fe(CO)$_5$ [38–41]. As a first step, 10 ml of a freshly-prepared CNC suspension was mixed with 10 ml DMF and sonicated (Qsonica, Q125) for 10 min (2 min for 5 cycles) to obtain a uniform dispersion. Then, the mixture was transferred to a three-neck round bottom flask equipped with a condenser, thermometer, and a rubber stopper, that was placed in an oil bath at 100 °C. A 200 μl aliquot of iron pentacarbonyl (1.52 mmol) was injected into the flask through the rubber stopper. The system was sealed under a nitrogen atmosphere and was then gradually heated to generate reflux for 1 h under continuous stirring. The yellowish solution gradually turned to reddish and then dark red. Then the suspension was exposed to air with continuous stirring for an additional 1 h at 80 °C and then cooled to room temperature, at which time a black precipitate formed. The precipitate was centrifuged (7000 rpm, 20 min) and washed repeatedly with water. Finally, the residue obtained at the end of this process was re-suspended in water and sonicated for 10 min. The final suspension had a concentration of ~0.04 wt%.

2.4. Characterization
Characterization of the morphology of decorated CNCs were performed on JEOL-1400, 120 kV transmission electron microscopy (TEM). TEM samples were prepared by drop casting freshly-synthesized suspensions on a 400 × 400 mesh copper grid coated with formamide-carbon (Ted Pella). The same TEM instrument was used for both selected area diffraction (SAED) and energy dispersive spectroscopy (EDS) analyses. Raman samples were prepared by drying a droplet on a polished stainless steel substrate. Raman spectra of CNCs and decorated CNCs were recorded in the range of 200–3500 cm$^{-1}$ using a HORIBA XploRA PLUS Raman spectrometer with an incident 638 nm laser.

3. Results and discussion
3.1. Mechanism of formation of IONPs on the surface of CNCs
In the presence of DMF, Fe(CO)$_5$ undergoes a disproportionation reaction resulting in the formation of Fe(II) moieties having six coordinated DMF molecules [40–42], as shown in figure 2. Variable amounts of CO gas are eliminated during the reaction, depending on the molar ratios of the Fe(CO)$_5$ and DMF compounds. There may be several mechanisms that account for the initial nucleation stage of the decomposition reaction. One possible mechanism may involve some of the residual sulfonic groups on the surface of the CNCs that have been retained following the sequential acid hydrolysis steps of hemicellulose using sulfuric acid. These negatively-charged surface groups could potentially attract the positively charged Fe(II) fragments and act as nucleating centers and anchoring points for the formation of IONPs. Alternatively, nucleophilic nucleation sites may result from –OH groups on the glucose molecules of CNCs, particularly the terminal groups on the C(6) carbons that have
enhanced polar character as a result of the acid hydrolysis and the aqueous environment, as later shown through Raman spectroscopy.

The subsequent thermal decomposition of the iron carbonyl/DMF complexes on the surface of the CNCs results in the in situ generation of iron nanoparticles on the surface of CNCs through the removal of the CO groups, followed by the oxidation of the iron moieties to Fe$_3$O$_4$ or γ-Fe$_2$O$_3$. The process may be catalyzed by the presence of the nucleophilic groups on the surface of the CNCs, which may also be involved in the decomposition of the iron carbonyl complexes during the process [39].

3.2. The morphological and structural characterization of CNCs decorated with IONPs

The morphology of the CNCs decorated with IONPs has been characterized by TEM and is shown in figure 3. CNCs can be easily distinguished as needle-like shapes with an average diameter of 20–70 nm and an average length of several microns. These rod/fiber nanoparticles tend to entangle with each other while drying due to the hydrogen bonding of their surface –OH groups (Habibi 2010), as shown in figure 3(a). The highlighted region in figure 3(a) is expanded in figure 3(b) to show in more detail the IONPs (black dots) present on the surface of the CNCs. As may be noted in figure 3(b), the concentration of the IONPs on the surface of the CNCs greatly exceeds their concentration in areas in which CNCs are not present. This suggests that while IONPs were formed throughout the CNC suspension, they preferentially nucleated and grew on the surfaces of the CNCs.

A section of one of the CNC fibers is shown at a higher magnification in figure 4(a). The IONPs on the surface of the CNC fiber have a relatively narrow size distribution of (19.78 ± 5.59 nm in diameter), as shown in figure 4(b), and exhibit a non-spherical morphology. This morphology is most likely due to the mechanism of nucleation and growth of the IONPs. The hydroxyl groups of CNCs, which have enhanced polarity in water, O^2− – H^+ ×, or alternatively, the residual sulfonic groups on the CNCs (remnants of the hydrolysis process), provided the nucleation sites and anchors for the Fe(II) fragments, thus restricting particle growth only in preferred directions [5, 26, 27]. This mechanism has been further verified by Raman spectroscopy and is described in a subsequent section.

One of the key issues associated with the characterization of the tethering process of the IONPs is the determination of their local distribution and the exclusivity of their presence on the CNC surfaces. Since the assumption is that the CNC surface groups provide the necessary nucleation sites for the generation of the IONPs, it is imperative to show that their location is primarily on the surface of the CNCs and that they are not randomly distributed in the suspension. Energy dispersive spectroscopic (EDS) analysis allows the determination of the elemental composition of a given site in the TEM sample and thus, this was used to perform two-point and line scans in selected regions of the sample. A two spot scan as well as a line scan were performed across an individual CNC fiber and its immediate environment as shown in figure 5. There were four elements of interest displayed in the results: C, O, Fe and Cu. The source of carbon is the underlying substrate carbon film of the TEM grid and the CNC under observation. Oxygen originates from the underlying copper oxide surface of the TEM grid and the CNC under observation, while Cu originates from the TEM grid itself. The only variable that was significant in this analysis was the presence (or absence) of a peak corresponding to Fe.

Figure 3. The morphology of the CNCs decorated with IONPs. (a) TEM of CNCs decorated with IONPs. (b) An expanded view of the highlighted region of (a) showing in greater detail the iron oxide nanoparticles (black dots) present on the surface of the CNCs.
Figure 5(a) shows the two spots that are compared: spot 1 that sits exactly on top of the black dot, which corresponds to a particle present on the surface of a CNC and is presumed to be iron oxide, and spot 2, which is a random site away from the CNC. The differences in the EDS profiles of the two spots are shown in figures 5(b) and (c). As expected, the spectrum obtained from the black dot (spot 1) exhibited the presence of the Fe moiety and an increased amount of O, in accordance with the characteristics of an iron oxide nanoparticle. Figure 5(d) shows the line EDS profile obtained along the trajectory between two arbitrary spots on both sides of a decorated CNC and through at least one black dot present on its surface. The intensity of the EDS peaks corresponding to the three elements of interest, C, O and Fe, was scanned across the line. The spectra show a sharp increase in the intensity of the Fe peak and a moderate increase in the intensity of the O peak precisely at the location of the black dot. A correlation of the spectra to the distance between the two spots shown in figure 5(e) indicate that the trajectory of the beam through an Fe-rich dot is about 20 nm, which is the average size of the IONPs as measured by TEM.

Selected area electron diffraction (SAED) was used to characterize the identity and structure of the nanoparticles present on the surface of the CNCs. The area selected for analysis is shown in figure 6(a) and the diffraction pattern with the assigned Miller indices is shown in figure 6(b). Spacing analysis, shown in table 1, closely matched the values of maghemite/magnetite, as obtained by x-ray diffraction.

The chemical composition of magnetite is Fe$^{2+}$Fe$^{3+}$O$_4$$^{2-}$ and the structure is an inverse spinel, with O$^{2-}$ ions forming a face centered cubic lattice and iron cations occupying interstitial sites. Tetrahedral sites are occupied
by half of the Fe\(^{3+}\) cations and octahedral sites are occupied by the other half of the Fe\(^{3+}\) cations together with the Fe\(^{2+}\) cations. The unit cell contains 32 O\(^{-}\) ions and the cubic unit cell dimension is \(a = 0.839\) nm [43].

Magnetite and maghemite, Fe\(_2\)O\(_3\) have very similar spacing characteristics so it is very difficult to separate the presence of the two moieties [43].

Additional confirmation of the nature of the IONPs has been obtained by probing the response of a water suspension in the presence of an external magnet (Neodymium disc magnet, 1" diameter, 1/4" in thickness and 14 lbs maximum pull). Figure 7(a) shows the image of a stable suspension of the decorated CNCs sample in water, and figure 7(b) shows the image of the same sample suspension after several weeks of being exposed to the magnet. As may be noted, the nanoparticles were attracted to the site of the magnet without settling, and the solution remained clear, further indicating the attachment of IONPs to the CNCs.

In addition to the spot and line EDX analyses showing that the IONPs were largely concentrated on the surface of the CNCs, we also used Raman spectroscopy to ascertain whether there was a chemical interaction between the surface groups of the CNCs and the IONPs that was responsible for the anchoring effect, as suggested by the anisotropic morphology of the nanoparticles. The Raman spectra of the full range of frequencies (200–3500 cm\(^{-1}\)) for bare CNCs and CNCs decorated with IONPs are shown in figure 8(a).

There are several absorption bands that are common to both samples, most notably the 1093 cm\(^{-1}\) strong band, assigned to the C–O–C asymmetric stretching modes along the cellulose backbone, the 1119 and 1147 cm\(^{-1}\) medium bands, assigned to C–C–O asymmetric stretch modes of the sugar molecules, the 2897 cm\(^{-1}\) band, assigned to C–H stretching vibrations, and the spectral regions beyond 3000 cm\(^{-1}\), which are associated with O–H stretching vibrations [3, 8, 44, 45]. The very intense band at 667 cm\(^{-1}\) in the IONP-decorated CNCs is assigned to the A\(_{1g}\) vibration mode of magnetite [46], and hence is due to the presence of IONPs on the surfaces of the CNCs.

The fingerprint spectral region of 1000–1550 cm\(^{-1}\) shown in figure 8(b) is of particular interest, given some subtle, but highly informative differences between the two samples. The peak intensities were normalized with the 1093 cm\(^{-1}\) cellulose backbone band of each sample, and hence the ratios between various bands could be

| Interplanar distance (Å) | Spacing (XRD) | Miller indices |
|-------------------------|--------------|---------------|
| 1.4784                  | 1.4845       | 4 4 0         |
| 1.6124                  | 1.6158       | 5 1 1         |
| 2.1019                  | 2.0990       | 4 0 0         |
| 2.5217                  | 2.5432       | 3 1 1         |
| 2.9614                  | 2.9670       | 2 2 0         |

Figure 6. Structure determination of IONPs by electron diffraction. (a) The TEM image of CNCs decorated with IONPs used for the structure analysis. (b) Selected area electron diffraction (SAED) pattern of this area, indicating that the IONPs were maghemite/magnetite.

Table 1. Electron diffraction analysis of the IONPs present on the surface of the CNCs (shown in the TEM image in figure 3). Calculated interplanar spacing values were compared to known d-spacing values for maghemite/magnetite and were assigned the corresponding Miller indices.
assessed quantitatively, as shown in table 2. The relevant bands at 1272, 1290, 1336, 1375, and 1408 cm$^{-1}$ were assigned to C–C–H bending, CH$_2$ rocking and wagging, and C–O–H bending modes [47–49]. The ratio between the 1336 and 1375 cm$^{-1}$ bands, both corresponding to O–H in-plane bending modes of the C–O–H moieties on secondary and primary carbons of the glucose molecules, respectively, increases by more than 20%. This is indicative that the –OH group on the C(6) primary carbon may be the main site for the nucleation of the IONPs. Further support for this assessment may be inferred by examining the 1464 cm$^{-1}$ band, which was assigned to the scissoring mode of the CH$_2$ group on C(6) carbon of the glucose molecule of the bare CNC. This band underwent a split into two corresponding bands at 1452 and 1478 cm$^{-1}$ in CNCs decorated with IONPs, suggesting the interaction between the sugar substrate and the nanoparticles on the cellulose backbone C(6).

4. Conclusions

CNCs were magnetized by their decoration with IONPs. TEM results confirmed the presence of IONPs on the surface of CNCs, having an average size of ~20 nm and a homogeneous distribution along the CNC fibers. Electron diffraction together with Raman spectroscopy analyses identified the IONPs as consisting primarily of
Table 2. The relevant peaks of the fingerprint spectral region of 1000–1550 cm\(^{-1}\). The peak intensities were normalized with the 1093 cm\(^{-1}\) band of each sample, and hence the ratios between various bands could be assessed quantitatively.

| Frequency (cm\(^{-1}\)) | Band intensity | Normalized intensity | Frequency (cm\(^{-1}\)) | Band intensity | Normalized intensity |
|-------------------------|---------------|----------------------|-------------------------|---------------|----------------------|
| 1061                    | 73            | 0.46                 | 1059                    | 48            | 0.29                 |
| 1093                    | 160           | 1.00                 | 1093                    | 166           | 1.00                 |
| 1119                    | 90            | 0.56                 | 1119                    | 84            | 0.51                 |
| 1147                    | 43            | 0.27                 | 1148                    | 44            | 0.27                 |
| 1272                    | 17            | 0.11                 | 1278                    | 27            | 0.16                 |
| 1336                    | 51            | 0.32                 | 1336                    | 80            | 0.48                 |
| 1375                    | 51            | 0.32                 | 1377                    | 66            | 0.40                 |
| 1408                    | 36            | 0.23                 | 1412                    | 48            | 0.29                 |
| 1464                    | 32            | 0.20                 | 1452                    | 39            | 0.23                 |
| 1478                    | 21            | 0.13                 |                         |               |                      |

The peak intensities were normalized with the 1093 cm\(^{-1}\) band of each sample, and hence the ratios between various bands could be assessed quantitatively.

maghemite/magnetite. The enhanced magnetic properties of the IONP-decorated CNCs was highlighted by the migration and aggregation of the particles in the direction of an external magnet without precipitation. Detailed Raman analysis provided evidence of the presence of molecular-level interactions between CNCs and IONPs in decorated CNC samples, and it suggested that IONP binding sites on the cellulose backbone, resulting from the thermal decomposition reaction, was at the C(6) carbon of the glucose moiety. The magnetization of CNCs could open up new avenues for the utilization of these nanoparticles in applications that would not have been accessible given their intrinsic non-magnetic properties. For example, this could potentially allow their alignment in various matrices by externally-applied magnetic fields, thus selectively enhancing their mechanical properties in a preferred direction. Such options could potentially contribute to the utilization of such CNC-based composites as relevant functional materials. Moreover, the method developed in this work for the functionalization of nanostructures by their decoration with magnetic nanoparticles could be extended to a wide range of materials, thus expanding and tailoring their surface properties.

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