Correction to “Direct Visualization of Crystalline Domains in Carboxylated Nanocellulose Fibers”

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(1) We note that the TEM images for the carboxylated nanocellulose fiber (C-NCF) sample given in published article (Figure S1d and S1e, Supporting Information) are ambiguous due to its short length morphology resulted from an experimental error that occurred in the batchwise preparation. We regret for this error and we have provided the reimaged TEM data (Figure 1) for the C-NCF sample. Although the length is not on the micrometer scale, the calculation of percentage crystallinity from the XRD pattern in the published article (Figure S5, Supporting Information) supports the fibrous nature nanocellulose.

Figure 1. TEM image of C-NCF stained with 1% PTA.

(2) We understand that the sheet-like appearance that is observed in the low-magnification TEM analysis of the C-NCF/Ag⁺ system appeared to be unclear (Figure 4a in the original article). However, consistently similar observations were made each time for a different batch of samples. We presume that the sheet-like morphology is probably originated from the associated nature of the C-NCF when combined with Ag⁺ ions. The finer the fiber, the more flexible it is, and numerous C-NCFs not only easily entangle but also are capable of closer packing and internanofibril association. In addition, the negative surface charges of the C-NCF may get neutralized to some extent by the anchoring of Ag⁺ ions present in the medium, which lessens the Van der Waal’s repulsion between individual fibers and assembles them into sheet-like C-NCF/Ag⁺ bundled morphologies. This assumption is further supported by the HR-TEM images obtained from PTA-stained C-NCF/Ag⁺ samples, as shown in Figure 2. However, the particles that formed on cellulose fibers pose problems for further magnifying images under high-resolution TEM.

Figure 2. TEM images of aligned C-NCF fiber bundles in the C-NCF/Ag⁺ system imaged after staining with PTA.

(3) In a few cases, the TEM images presented in Figure 1a and Figure 5 of the original article showed coiled nanostructures at the periphery of the C-NCF samples. A recent report by Toth et al.¹ has demonstrated the possibility that the electron-beam-induced damage and the subsequent carbonization resulted in the formation of coiled nanostructures under high vacuum conditions.¹ With TEMPO-oxidized C-NCFs being a carbonaceous fragile material, the coiled structural features could therefore possibly originate under high electron beam irradiation.

To check whether there is any possibility of the presence of carbon fiber or graphene in our original samples (that were used for TEM analysis), we performed a Raman spectroscopy analysis of C-NCF/Ag⁺ and C-NCF/Ag⁺/TiO₂ samples and...
compared that with the C-NCF/rGO sample under similar probing conditions. The results are presented in Figure 3a. Black, red, and blue spectra were obtained for C-NCF/rGO, C-NCF/Ag+, and C-NCF/Ag+/TiO2, respectively. The Raman spectrum of the C-NCF/rGO sample features D and G Raman bands positioned at 1335 and 1593 cm\(^{-1}\), respectively, characteristics of graphene-related structures, whereas, the absence of band peaks in the other two systems indicates that graphitic carbon nanostructures were initially absent in the C-NCF/Ag+ and C-NCF/Ag+/TiO2 samples that were used for the TEM analysis.

As a result, the high energy of the electron beam is more likely to break the intermolecular hydrogen bonds that hold \( \beta \) (1 \( \rightarrow \) 4) glucan chains together. Furthermore, the C-NCF possesses several hydroxyl and carboxyl groups that evaporate to keep the temperature from rising during heating. This assumption is further supported by Raman studies (Figure 3b) and TGA results (Figure 4). The results indicate that a higher laser power could induce the emergence of D and G bands, suggesting the transformation of the C-NCF to graphitic carbon-like nanostructures. Our observation on the C-NCF/Ag+/TiO2 sample is in agreement with the previous reports, suggesting that the as-prepared C-NCF is composed of randomly curved graphene layers. Thus the HR-TEM imaging performed under a high-intensity electron beam would probably result in coiled structures due to thermal heating at the edges of the C-NCF bundles, as observed in our report.

Figure 3. (a) Raman spectra of: (1) C-NCF/rGO, (2) C-NCF/Ag+, and (3) C-NCF/TiO2/Ag+ systems under laser power of 1 mW. (b) Raman patterns for C-NCF/Ag+ acquired with increasing order of laser power: (1) 1 mW, (2, 3, 4) >4 mW. (c) Raman spectrum of C-NCF/rGO acquired under laser power of 1 mW (given for comparison). Laser wavelength, 633 nm.

Nevertheless, considering the report by Lee et al.\(^3\) who highlighted the possibility of graphitization under laser beam irradiation, we studied the effects of different lasering conditions of Raman analysis and present them in Figure 3b. Here we have noticed a gradual emergence of D and D** bands upon high power laser irradiation (>4 mW), indicating the transformation of C-NCF/Ag+ to graphitic structures (Figure 3b, spectra 2, 3, and 4). The increased intensity of the D and D** bands at higher laser power (Figure 3b, spectrum 4) suggests the emergence of graphitic structures but with highly disordered features. The appearance of peaks at 1505 cm\(^{-1}\) corresponds to D** being attributed to the formation of more defective graphitic nanostructures or amorphous carbon.\(^1\) The Raman spectrum of C-NCF/rGO acquired under laser power of 1 mW is also shown for the purpose of comparison. These results suggest that the C-NCFs used in our study are vulnerable to electron beam damage, and hence one cannot rule out the possibility of graphitization during HR-TEM imaging.

Interestingly, similar observations were reported for the possible graphitization phenomenon that happened during the HR-TEM imaging of cellulose under a high energy electron beam.\(^2,5\) It is reported that high energy beams could introduce an upsurge in the local surface temperature in the range of 1000–2000 K that may cause local damage to samples.\(^6\) Considering these possibilities, electron beam damage would occur to form graphite nanostructures during HR-TEM imaging of the cellulose samples (having a low thermal decomposition temperature), resulting in the formation of coiled nanostructures. This is not surprising because the maximum energy transfer to a carbon atom even under 60 keV electron beam irradiation is \( \sim 10.8 \) eV, which is higher than the bonding energy of hydrogen bonds (0.5 eV) and the activation energy for cellulose depolymerization (2.68 eV).\(^4,5\)
conductive graphitic carbon and could find potential applications like flexible electronic devices and sensors.

Figure 5. TEM images of three systems stained using 1% PTA taken under TEM: (a) C-NCF/rGO, (b,c) C-NCF/Ag+, and (d and e) C-NCF/Ag+/TiO2.

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