

SURFACE MODIFICATION ON CELLULOSE NANOCRYSTALS (CNC) TOWARDS ORGANIC REDOX - BATTERIES

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Classification: New materials and processes in nanotechnology and its applications in agribusiness

Abstract

The global mission is achieving sustainable growth for humankind within this century has demanded the development of novel materials that meet our needs and at the same time “eco-friendly” from the renewable resources. In this context, we report, here in, the surface modification of cellulose nanocrystals (CNC) with 4-hydroxy-2,2,6,6-Tetramethylpiperidin-1-oxyl (4-hydroxy TEMPO) *via mitsunobu* reaction. The modified CNC were characterized from Fourier-transform infrared (FT-IR), Electron paramagnetic resonance (EPR) and elemental analysis. Further the electrochemical measurements and battery properties are under progress.

Keywords: Cellulose nanocrystals (CNC); TEMPO; Mitsunobu and organic redox-batteries

1 INTRODUCTION

The global mission is achieving sustainable growth for humankind within this century has demanded the development of novel materials that meet our needs and at the same time “eco-friendly” from the renewable resources. Furthermore, the ability to take a cheap and abundant material and generate products with value-added properties is desirable. Polymers derived from plants, especially those from non-food resources, are gaining more attention of governments, industries and institutes, mainly due to their environmental compatibility, superior physical properties and low stable market prices which are becoming competitive with petroleum-derived polymers.

Cellulose constitutes the most abundant renewable polymer resource available today, with an annual production estimated to be over 7.5×10^{10} tons. This fascinating and almost inexhaustible sustainable polymer possesses remarkable chemical and physical attributes allowing its use in different forms for a wide range of materials and products. Acid hydrolysis of cellulose fibers yield defect-free, rod-like crystalline residues, the “so called” cellulose nanocrystals (CNC). CNC have gained a tremendous level of attention because of their unsurpassed quintessential physical and chemical properties along with their inherent renewability and sustainability in addition to their abundance. They have been the subject of a wide array of research efforts as reinforcing agents in nanocomposites due to their low cost, availability, renewability, light weight, nanoscale dimension, and unique morphology (HABIBI, 2010; TONOLI, 2012). Besides, they play a pivotal role in energy applications such as fuel cell, solar cell and Li-ion batteries (LIBs) (WEI et al., 2014).

Organic radical compounds have extensively been explored as the electrode materials in energy storage applications because of their fast transport kinetics of ions and electrons, cost effective and environmentally friendly (ZHANG et al., 2016). The 4-hydroxy-2,2,6,6-tetramethylpiperidin-1-oxyl (4-hydroxy TEMPO), a representative example of most used organic radical, is a promising electrode material owing to their two redox couple process of the nitroxide radicals (DU et al., 2014). Thus for most of the studies have been carried out with synthetic polymers. However there is growing interest in natural polymers and their derivatives for practical applications from the viewpoint of biotechnology, environmental protection and so forth (QU et al., 2008).

In the present investigation, we report the surface modification of cellulose nanocrystals (CNC) by a simple etherification reaction with organic radicals (4-hydroxy TEMPO). Generally etherification of cellulose materials has been reported in harsh condition like high basic condition and elevated temperature, but, for the first time, we report the etherification of cellulose nanocrystals

(CNC) under an ambient condition using the Mitsunobu reaction. The TEMPO modified CNC characterized by Fourier transform infrared (FTIR), electron paramagnetic resonance (EPR) and elemental analysis (CHN).

2 MATERIALS AND METHODS

White (commercial type) (CW) cotton linter were supplied from Cremer. S. A; Indústria Brasileira. Cellulose was hydrolyzed with 6.5 M sulfuric acid (Synth) and cellulose membrane (Sigma–Aldrich: D9402) was used to dialyze the products. 4-hydroxy-TEMPO, diisopropyl azodicarboxylate (DIAD), triphenyl phosphine (TPP) and DMF were purchased from Sigma-Aldrich and used without further purification.

2.1 Preparation of cellulose nanocrystals (CNC):

Cellulose nanocrystals were prepared according to the literature reported from our research group earlier (TEIXEIRA et al., 2010). Briefly, about 5.0 g of fibers were dispersed in 100 mL of 6.5 M sulfuric acid at 45 °C and stirred vigorously for 75 min. After that, 500 mL of cold distilled water was added to stop the reaction. The sulfuric acid was partially removed from the resulting suspension by centrifugation at 10,000 rpm for 10 min. The non reactive sulfate groups are removed by centrifugation following by dialysis. Then the fibers were resuspended and dialyzed against tap water with a cellulose membrane, until the pH reached 6-7. The resulting suspension was ultrasonicated for 5 min and stored in a refrigerator after the addition of drops of chloroform. The yield of cellulose nanocrystals was determined by weighing a 10 mL aliquot of the suspension after standing overnight to dry. Yield (%) and concentration (g mL⁻¹) were calculated from the difference between initial and final weight.

2.2 Synthesis of CNC - TEMPO:

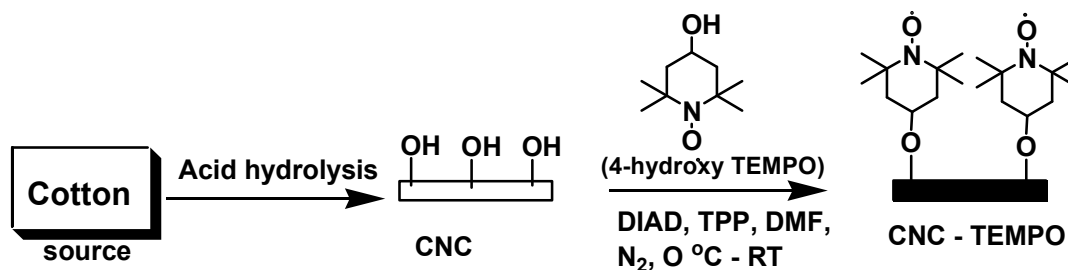
This surface modification was carried out based on the literature reported earlier (YANG et al., 2001). Briefly, DIAD (1.31 mL, 13.4 mmol) was added to the mixture of CNC (0.25 g, 3.1 mmol glucopyranose units), 4-hydroxy TEMPO (0.97 g, 11.4 mmol), TPP (1.30 g), and 30 mL of anhydrous DMF in a 250 mL flask cooled in ice bath. The mixture was stirred for one week at room temperature under nitrogen atmosphere and then added into 150 mL of methanol. The precipitate was isolated by centrifuge. Any unreacted 4-hydroxy TEMPO was removed by repeated dissolutions and precipitations with DMF and methanol. The precipitate was then washed with distilled water and freeze-dried to give surface modified CNC. The degree of substitution (DS) of polymer was determined on the basis of the %N determined by elemental analysis. The DS for the surface modified CNC is 0.47. Theoretically, the maximum DS would be 3 if all the hydroxyl groups were substituted by 4-hydroxy TEMPO chromophores on each glucose ring. yield 85%. FT-IR: 2977, 2931, 2850, 1643, 1566, 1457 (N-O), 1376, 1311, 1241, 1107, 918, 879, 555, 505. Anal. Calcd for C₃₂H₅₆O₁₂N (Scheme 1): C, 41.33; H, 5.87; N, 1.16. Found: C, 41.60; H, 5.81; N, 1.01.

2.3. Characterization:

Infrared spectra were recorded on a BRUKER VERTEX 70 FT-IR spectrometer with ATR diamond crystal technique. Elemental analysis was performed with Perkin Elmer EA2400 CHN elemental analyzer. EPR spectra were measured on a BRUKER EMX X-band 9.6 GHz spectrometer.

3 RESULTS AND DISCUSSION

Nanocellulose carrying TEMPO radicals were synthesized by the reaction of 4-hydroxy-TEMPO with cellulose nanocrystals (CNC) *via* a Mitsunobu reaction. In this reaction, CNC treated with TEMPO in the presence of diisopropyl azodicarboxylate (DIAD) and triphenyl phosphine (TPP) in DMF under N₂ at room temperature for one week afforded the radical functionalized CNC in 85 % of yield. The schematic representation is depicted in Scheme 1.



Schem1. Synthesis of CNC-TEMPO by the Mitsunobu reaction.

The IR spectrum of CNC displays a broad peak characteristic of the residual hydroxyl groups (3550 cm^{-1}), while CNC-TEMPO newly showed an absorption at 1457 cm^{-1} , which is attributable to the N-O stretching of the TEMPO radical (Qu J et al).

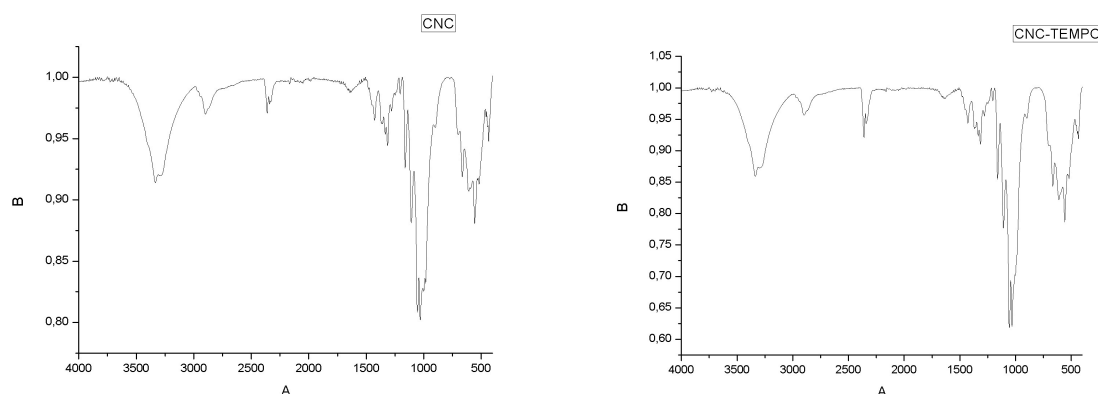


Figure 1. FT-IR spectrum of CNC (left) and CNC-TEMPO (right)

Fig. 2 shows the derivative spectra of the electron spin resonance (EPR) of CNC-TEMPO. EPR spectra is further revealed that the presence of TEMPO radicals on CNC after surface modification. The shape which is similar to that of the TEMPOL (4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl) radical crystals.

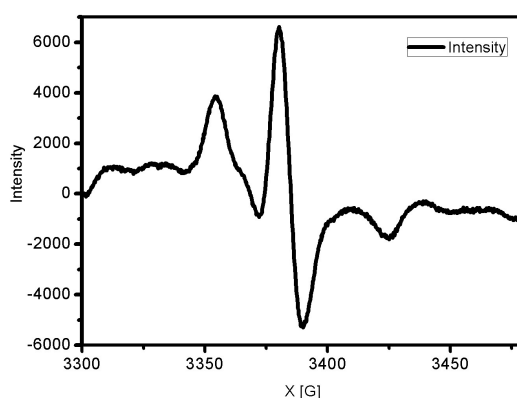


Figure 2. EPR spectrum of CNC-TEMPO

4 CONCLUSION

We have successfully synthesized a new category of cellulose nanocrystal (CNC) carrying TEMPO radicals by Mitsunobu reaction for the first time. The nitroso radical on the surface of CNC were confirmed from FT-IR, EPR and elemental analysis. Further, the electrochemical and battery properties are under progress.

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