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Cellulose nanocrystals: A versatile precursor for the preparation of different carbon structures and luminescent carbon dots

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ABSTRACT

The current study demonstrates that cellulose nanocrystals (CNCs) that are assembled in different arrangements can be thermally decomposed under controlled conditions to produce different carbon nanostructures. The results from FTIR, Raman, TGA, SEM, TEM and potentiometric titration indicated that thermal decomposition in the 300–1000 °C range produced carbons containing surface oxygen groups with different morphologies. The obtained results suggest that the obtained carbon structures are defined by the CNC precursor arrangement; i.e., CNCs organized as filaments produce carbon fibers, CNCs sheets result in carbon films and CNCs agglomerated as spheres will produce carbon spheres. Furthermore, the thermal decomposition of CNCs also produced water-soluble 4–8 nm carbon dots (CDs), exhibiting photoluminescence emission as a function of the excitation energy that covered the blue-to-green visible light region.

1. Introduction

The development of new substances, processes and materials from cellulose is currently of much interest both from an environmental perspective and from a socio-economic point of view due to its high availability and intrinsic renewable nature (Eyley and Thielemans, 2014; Habibi et al., 2010). In nature, cellulose chains are arranged into repeating crystalline structures to form microfibrils. These elementary microfibrils also aggregate to form larger fibers, which contain amorphous and crystalline regions (Klemm et al., 2011; Eichhorn et al., 2010; Zhang and Lynd, 2004).

Biomass, such as cellulose, which does not compete with the food supply, may be an excellent choice for the production of carbon materials. These carbon materials have wide potential application in different research and industrial areas due their unique properties, such as a high surface area, conductivity, porous structure and surface functional groups that allow various chemical modifications (Titirici et al., 2015; Baker and Baker, 2010).

Among these carbons materials, carbon dots (CDs) represent a new family of nanocarbons with a spherical shape and size less than 10 nm (Baker and Baker, 2010; Sahu et al., 2012). These nanocarbons were accidentally discovered during the electrophoretic purification of single-walled carbon nanotubes (SWCNTs) when researchers looked beyond the SWCNTs and discovered a mixture of nanoparticles that exhibited photoluminescence behavior (Xu et al., 2004). Since their discovery, these very small particles have attracted much interest due to their high photoluminescence and good biocompatibility for biomedical applications compared to that of nanoparticles prepared with heavy metals (Puvvada et al., 2012; Du et al., 2014). Moreover, CDs are also considered emerging materials for energy-related and photocatalytic applications (Zhang et al., 2012; Wang et al., 2014) due to the possibility of tuning their emissions from the near-infrared region to the ultraviolet region.

Cellulose and lignocellulose-based biomass have been converted using pyrolysis and hydrothermal carbonization to produce carbon materials from renewable precursors with distinct properties (Wan et al., 2015; Guiotoku et al., 2009; Falco et al., 2011).

In general, the cellulose-derived carbon structures that have been described in the literature are composed of microspheres in the 2–5 μm size range and have been obtained using different methods, such as chemical vapour deposition, pyrolysis and hydrothermal treatments (Zhao et al., 2013b; Sevilla and Fuertes, 2009). These cellulose-derived carbon spheres, which can be pre-

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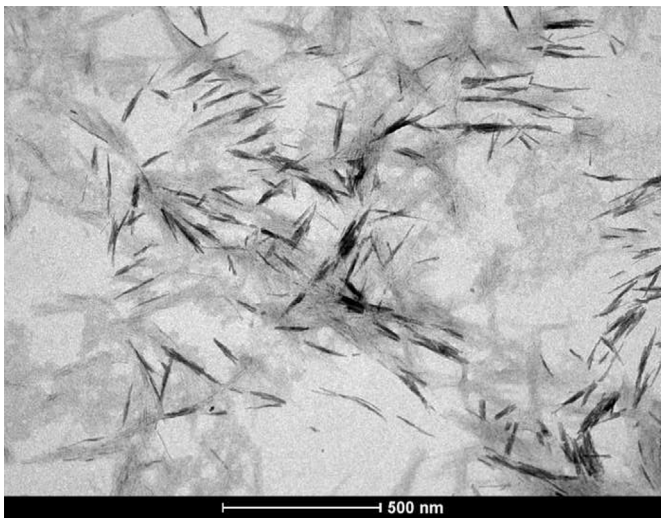

Fig. 1. TEM image of the eucalyptus CNC precursor used in this study.

pared in different sizes and with oxygenated functional groups on their surface, have attracted much attention due to their different applications, such as super capacitors, catalyst supports, and adsorbents (Titirici et al., 2015).

Cellulose nanocrystals (CNCs), which are also known as cellulose nanowhiskers (CNWs) or nanocellulose, consist of highly crystalline nanosize segments obtained from cellulose fibers when the amorphous regions are eliminated by acid hydrolysis (Eichhorn, 2011). These promising and advanced nanomaterials that are 100–250 nm long and 4–10 nm wide, have received considerable attention in recent years due to their remarkable features, such as excellent mechanical properties, low density and inherent renewable character, making them interesting candidates as reinforcing nanofillers for different polymers (Samir et al., 2005). Additionally, the CNCs can be easily prepared, present nanoscale sizes, differentiated morphology (high aspect ratio) and high surface areas.

In this study, CNCs have been investigated as precursors for the production of different carbon nanostructures using conventional pyrolysis. CNCs exhibit several advantages as precursors for the production of carbon structures including a relatively high fixed carbon yield and relatively low cost as well as the unique possibility for assembly into different morphologies (e.g., single nanoparticles, films, filaments or aggregates). Then, these different CNC assemblies can be thermally decomposed to produce specific carbon structures. Herein, for the first time, we report the use of CNCs as precursors for the production of very interesting nanostructured carbon dots (CDs).

2. Materials and methods

2.1. Preparation of cellulose nanocrystals

Sulfuric acid hydrolysis of eucalyptus kraft wood pulp was performed according to a previously reported procedure with some modifications (de Rodriguez et al., 2006; Brito et al., 2012). First, 20 g of bleached cellulose pulp was added to 160 mL of 64 wt% sulfuric acid under strong mechanical stirring at 55 °C for approximately 30 min. After hydrolysis, the dispersion was diluted in water and washed three times with deionized water using centrifugation. Dialysis against deionized water (until the dispersion reached a pH of ~7) was used as the final purification step. The dispersions were ultrasonicated with an Ultrasonic Processor Cole Parmer CPX750 equipped with a microtip, and a stable suspension of CNCs was obtained after sonication for approximately 1 min. The obtained

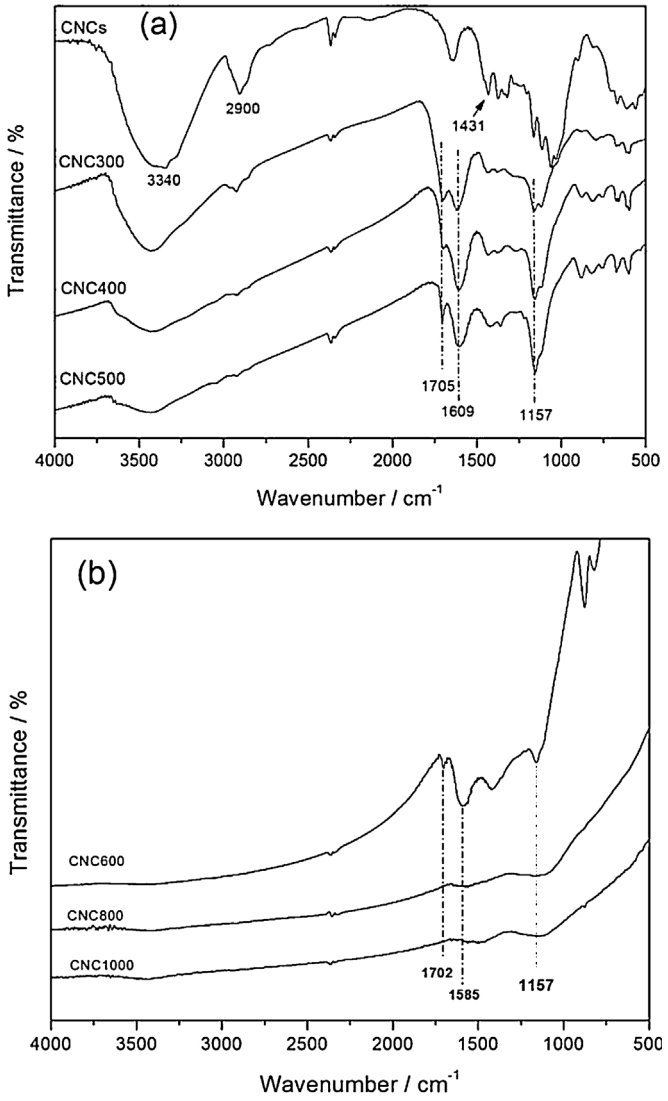

Fig. 2. FTIR spectra of CNCs, CNC300, CNC400, CNC500 (a) and CNC600, CNC800, CNC1000 (b).

aqueous suspension of CNCs (~1% m/v) was freeze-dried to obtain a powder consisting of cellulose nanoparticles.

2.2. Pyrolysis of cellulose nanocrystals

The pyrolysis of the freeze-dried CNCs was carried out in a tubular furnace under a nitrogen flow of 50 mL min^{-1} with a heating rate of 10 °C min^{-1}. A systematic study was performed at 300–1000 °C, producing carbons materials (i.e., CNC300, CNC400, CNC500, CNC600, CNC700, CNC800, CNC900 and CNC1000, respectively). After pyrolysis, the obtained carbon materials were characterized as obtained or after dispersion (in different solvents) and centrifugation.

2.3. Characterization methods

Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) images were recorded using a FEI Tecnai G2-Spirit with an acceleration voltage of 120 kV. The CNCs were deposited from an aqueous suspension onto a carbon-Formvar-coated copper TEM grid. The CNC samples were stained with a uranyl acetate solution to enhance the microscopy