Synthesis of Carbon Nanodots from Cellulose Nanocrystals Oil Palm Empty Fruit by Pyrolysis Method

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Abstract. Biomass such as cellulose is one of the most common abundant organic materials on the Earth. Biomass has carbon chain that could be an excellent choice for the fabrication of carbon materials. Cellulose nanocrystal is nano-sized cellulose and could become the potential source in fabricating carbon nanodots that are affected by pyrolysis temperature. In fact, the size and temperature are essentially important to synthesize the carbon nanodots. This research is contributed to synthesize this material, and to investigate the effect of temperature. The percentage of cellulose nanocrystals and carbon nanodots obtained are less than 50%. Carbon nanodots are synthesized by pyrolysis method and cellulose nanocrystals are fabricated by membrane method. TEM analysis shows that cellulose nanocrystals are nano-sized. Under UV light source, the samples show fluorscencing colours i.e. blue to green. From this research it can be concluded that the temperature affects the characteristics of carbon nanodots produced by pyrolysis method.

Keywords: Carbon Nanodots, Cellulose Nanocrystals, Fluorescent, Pyrolysis

1. Introduction

Cellulose is a high-molecular-weight linear homopolymer, comprising b-D-glucopyranosyl repeating units joined by (1- 4) glycosidic linkages [1]. 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 [2,3,4]. When acid hydrolysis is used, the structure and properties are affected to the source of the original cellulose material and the preparation process [5,6]. Nanocellulose prepared by sulfuric acid hydrolysis carries a number of surface negative charges, leading to stable colloidal suspensions [6,7].

Cellulose nanocrystals or also known as nanocellulose are promising as advanced nanomaterials that are 100-250 in length and 4-10 nm in width. Nanocelluloses 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 [7]. In addition, CNCs exhibit several advantages as precursors for the production of carbon structures including a high fixed carbon
and 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 decomposed thermally to produce specific carbon structures.

Fluorescent carbon nanoparticles or carbon nanodots (C-Dots) have drawn considerable interest due to their stability in photoluminescence property, broad ranges of excitation and emission spectra, great biocompatibility, and low cytotoxicity effects towards biological components [8,9]. C-Dots have important in various applications [10].

The process synthesis of C-Dots include arc-discharge, acid dehydration, electrochemical oxidation, laser ablation, hydrothermal reaction, and combustion (thermal) [11,12,13]. Among these, combustion (thermal) supported methods-known as pyrolysis of carbonaceous materials is a simple, clean and inexpensive synthesis option [14–17]. These CDs were most likely formed during the thermal decomposition of the CNCs due to fragmentation of the cellulose structure into small pieces that carbonize to form the CDs. In addition, during thermal decomposition may react to produce the CDs particles.

Pyrolysis parameters such as type of reactor system, heating temperature, pressure, presence of catalysts, and heating duration affect the composition of the end-products [16]. The synthesis method involving the pyrolysis of cellulose nanocrystals from oil palm empty fruit in a laboratory furnace is simple and economic. Heating temperatures between 250°C and 400°C were investigated to carbonize them into carbon residues. Experimental parameters, particularly the heating temperature relating to the pyrolysis of starting materials were evaluated to obtain C-Dots with optimum optical property. Please check grammar!!

2. Experimental

2.1 Materials

Oil Palm Empty Fruit, Distilled water, Dialysis membrane, Nitric acid, Sulfate acid, Sodium hydroxide, Sodium hypochlorite 12% and Acetate acid.

2.1.1 Nanocrystals cellulose isolation from Oil Palm Empty Fruit

2.1.1.1 Alkaline Treatment

As many as 50 g powders of Oil Palm Empty Fruit were put in beaker glass, distilled water is added until the powder submersed then stirred for 2 hours at 50°C and filtered, and this procedure was repeated once more. The residue was dispersed in 500ml of 2% NaOH solution and stirred for 2 hours at 80°C and washed until filtrate was neutral and this alkaline treatment was repeated once more and the fibers were dried at 50°C for 24 hours.

2.1.1.2 Bleaching Treatment

The bleaching treatment was conducted by using sodium chlorite solution and 8 to 10 drops of glacial acetate acid while being heated at 60°C to 70°C, so that the lignin content was removed in this process. The mixture was stirred at frequent intervals for 1 hour, and it was filtered quantitatively and washed with cold water. The bleached pulps were treated with 250 mL of 0.05 N nitric acid solution and stirred for 1 hour at 70°C filtered. After being washed extensively with distilled water to reach pH 7, heating was conducted for 1 hour using NaOH 17.5%. Then the samples were filtered and washed to have pH 7, followed by bleaching treatment using NaOCl 5%, then dried to produce alpha cellulose.

2.1.2 Preparation of Nanocrystals by Hydrolysis Method

As many as 1 g alpha cellulose dispersed in 25 mL of 45% sulphuric acid for 45 minutes at 45°C then cooled and added 45 mL of distilled water and left one night until suspension is formed. The suspension was centrifuged at 10000 rpm for 25 minutes and ultra-sonicated for 10 minutes for well dispersion of nanomaterials preventing agglomeration. Then, inserted into dialysis membrane then stirred for 4 days in 100 ml of distilled water then evaporated at 70°C to produce nanocrystal cellulose. TEM analysis was performed to analyze nanocrystal cellulose.

2.1.3 Preparation of Carbon Nanodots

The pyrolysis treatment was applied to produce C-Dots. As many as 200 mg nanocrystal cellulose was placed into laboratory furnace with various heating temperature i.e. 250°C, 300°C, and 400°C. After being treated, the
samples were dissolved with distilled water and performed under UV light to investigate the fluorescence properties.

2.2 Methods
2.2.1 Characterization with TEM
The samples were dripped by ammonium molybdate 2%, and then the solution were trapped in resin. And then the solution was cut with micro cutting to obtain single nanocrystals. Cellulose morphology analysis was carried out using a JEOL 1400 with an acceleration voltage of 120 kV.

2.2.2 Characterization with UV Light
The samples were dissolved with distilled water to be placed under UV light. And then fluorescent color were observed.

3. Results and Discussion
TEM analysis was used to determine surface morphology, and this analysis was done to enlarge objects in small sizes. TEM results obtained from cellulose nanocrystals is displayed in Figure 1. The morphology of nanocrystal was rod-like forms, which was arranged variously, like needles.

![Figure 1. TEM Nanocrystal](image)

After receiving the TEM photographic image, we performed the analysis the particle size distribution by ImageJ application. Based on calculations performed, it was obtained the diameter size of cellulose nanocrystals range between 8.3 nm with particle size distribution shown in figure 2.

![Figure 2. Particle Size Distribution of Cellulose Nanocrystals](image)
The pyrolysis method was performed in three temperatures, i.e. 250°C, 300°C and 400°C. Based on the results, the temperatures that were applied affected the fluorescent properties of each samples of C-dots. Physical characteristics of C-Dots under day light showed colorless transparent, while the samples placed under UV light showed green-to-blue fluorescence at temperature shown in Figure 3. The fluorescence characteristics showed that the C-dots have successfully been synthesized from nanocrystals cellulose as precursor.

Figure 3. Fluorescence of CDots under day light (a)250°C, (b)300°C, (c)400°C, under UV light (d) 250°C, (e) 300°C, and (f) 400°C

4 Conclusions
This work has successfully demonstrated the conversion of cellulose nanocrystals from oil palm empty fruit into fluorescing C-Dots via simple thermal pyrolysis method without any surface passivation. The obtained materials from different pyrolysis temperature show different fluorescent and morphology. From this research, it can be concluded that heating temperature affects the fluorescence. If the temperature is higher than the efficiency of quantum, the fluorescence properties decrease. So, the higher the temperature affects the greater of outside conversion resulting in reduced quantum efficiency.

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