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The Role of Acid Concentration on Band Gap Shrinkage in Cellulose Nanocrystals Fabricated from Water Hyacinth

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ABSTRACT

In this study, the fingerprint of the acid concentration during the hydrolysis process on the optical band gap of cellulose nanocrystals (CNCs) has been systematically studied. The CNCs have been prepared using hydrochloric acid at a hydrolysis temperature of 50°C and at a constant hydrolysis time of 4 hours but with varying hydrochloric cid concentrations of 5%, 10% and 15%. The crystalline structure and phase identification of the CNCs have been studied using XRD technique. UV-Vis Spectroscopy has been done and the optical band gap energy calculated by performing the Tauc's plot. From the study, the grain size has been found to decrease with acid concentration while the band gap energy has been found to increase with increasing acid concentration. Further, the optical band gaps of the CNCs have been found to decrease with the increase in crystallite size. This shrinkage of the band gap has been attributed to the increased impurity concentration leading to the narrowing of the band gap due to the emerging of the impurity band formed by the overlapped impurity states.

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Introduction

Cellulose is one of the most versatile and widely found biopolymers in nature that has found applications in varied areas such as in building technology, as energy source, a component of clothing and for storing and sharing knowledge and culture. Today, cellulose materials are used in a wide range of applications, and the paper and pulp industry constitutes a significant share of the economic output in many countries. Cellulose in nanometers or Nano cellulose has a size range from 10 nm to 350 nm. Nano cellulose has a higher surface area than cellulose, so it can be one of the alternative solutions to make cellulose more easily modified and dissolved in water [1-3].

The acid hydrolysis of cellulose fibers has been found to yield highly ordered rod-like cellulose nanocrystals (CNCs) which are also called nanocrystalline cellulose [4]. The intriguing ability of cellulose nanocrystals (CNCs) to self-organize into a chiral nematic (cholesteric) liquid crystal phase with a helical arrangement has attracted significant interest, resulting in much research effort. This is because the arrangement gives dried CNC films a photonic band gap. The CNC films thus acquire attractive optical properties, creating possibilities for use in applications such as security papers and mirrorless lasing. CNCs are highly crystalline with a width of 2 to 20 nm and a length that runs up to several micrometers [5]. CNCs have been shown to have high mechanical properties along the longitudinal direction with an estimated modulus of elasticity of 138 GPa [6]. Further, it has

been shown that the coefficient of thermal expansion of CNCs is less than 1×10^{-7} °C^{-1} along the longitudinal direction which is as small as that of quartz [7]. These excellent features make cellulose micro fibrils and nanofibers promising materials as the reinforcement in nanocomposites. Various methods can be used to obtain Nano-cellulose, such as acid hydrolysis, ultrasonic technique, and enzymatic hydrolysis [8-11]. The method that most widely used is acid hydrolysis [12]. This method is easy and fast to produce Nano cellulose that has better properties.

Band-gap narrowing effects play an important role in bipolar devices with heavily doped regions [13]. The mechanism for band gap narrowing has been explained by the shifting of the valance band maximum and conduction band minimum of the material. The mechanism for band gap narrowing of doped samples is different in the Nano and micron cases. Crystal size of the samples thus plays a very important part in the band gap change of materials. Potential fluctuations due to the random distribution of the impurities also lead to a broadening of the impurity band. The ionization level of the impurities is consequently reduced. Eventually the impurity band overlaps the conduction band or valence band, effectively narrowing the band gap.

Experimental
Materials
The materials used in this study were water hyacinth stalks and stems obtained from Lake Victoria. The chemicals and reagents used in this work were sodium hydroxide (NaOH), toluene and ethanol for pretreatment process and hydrochloric acid (HCl) for the acid hydrolysis procedure.

Methods

The CNCs were prepared using HCl acid hydrolysis process at a constant temperature of 50°C. With varied acid concentrations of 5%, 10% and 15%, the hydrolysis time was kept at 4hrs. The crystalline structure and phase identification of the cellulose composites were investigated by a PANalytical X'Pert PRO diffractometer using a Cu Kα radiation (λ = 1.54 Å) with a current of 40 mA and an anode voltage of 45 kV. The absorbance spectra were collected using Chary60 Shimadzu UV-Vis spectrophotometer transmission in the 200-500 nm range at the wavelength interval of 0.2 nm.

Results

Figure 1 shows the X-ray diffraction patterns of cellulose nanocrystals in hydrochloric acid of 5%, 10%, 15% concentration and hydrolysis done at temperatures of 50°C for 4 hours.
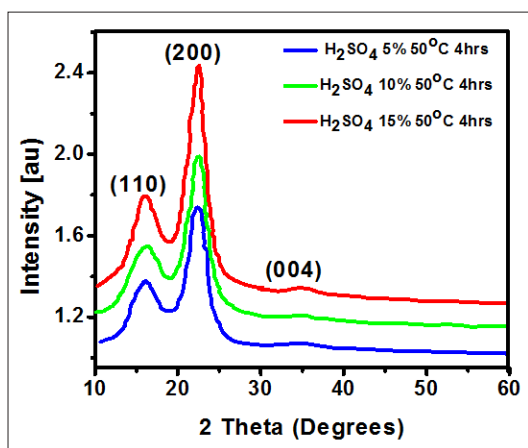

Figure 1: X-ray diffraction patterns of samples prepared at 5%, 10%, 15% concentration and hydrolysis done at temperatures of 50°C for 4 hours.

The grain sizes of the CNCs prepared at different hydrolysis temperatures were calculated by using the Scherrer equation (1).

$$\text{Crystal size} = \frac{0.94\,\lambda}{\beta_{1/2}\,\cos\theta} \quad \text{...............(1)}$$

Where λ is the radiation wavelength, θ is the diffraction angle, and $\beta_{1/2}$ is the corrected angular width (in radians) at half maximum intensity. The results of crystal size are shown in Table 1.

Table 1: The relationship between the acid concentration (%), the diffraction angle θ, the corrected angular width $\beta_{1/2}$ at half maximum intensity (in radians) and the grain size (nm)

Acid Concentration (%)	2Θ (degrees)	$\beta_{1/2}$ (radians)	Grain size (nm)
5	22.5	0.32	4.61
10	22.5	0.38	3.88
15	22.5	0.42	3.51

The table shows that the grain size (crystallite size) increased with decrease in acid concentration.

Figure 2 shows the absorbance spectra and the Tauc's plot of CNCs prepared using H_2SO_4 at 50°C for 4hrs with varying acid concentrations of 5%, 10% and 15% (b).
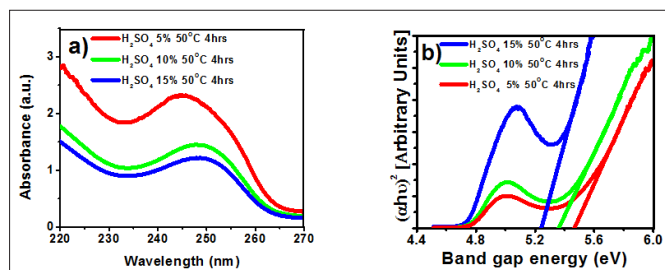

Figure 2: The Absorbance spectra (a) and the *Tauc's* plot (b) of CNC samples prepared using H_2SO_4 at 50°C for 4hrs with varying acid concentrations of 5%, 10% and 15%

From the tauc graph in Figure 2 (b), the band gap energy for CNC samples prepared in HCl at hydrolysis temperature of 50°C at a constant hydrolysis time of 4 hrs but with varying acid concentration of 5%, 10% and 15% were found to be 5.098 eV, 5.358 eV and 5.468 eV respectively as depicted in Table 2.

Table 2: The relationship between the acid concentration (%), the grain size (nm) and the band gap energy (eV)

Acid Concentration (%)	Grain size (nm)	Band gap energy (eV)
5	4.61	5.098
10	3.88	5.358
15	3.51	5.468

This shows an inverse proportionality in the grain size with the increase of concentration of the hydrolysis acid. The inverse proportionality was also observed between the grain size and the band gap energy as depicted in Figure 3.
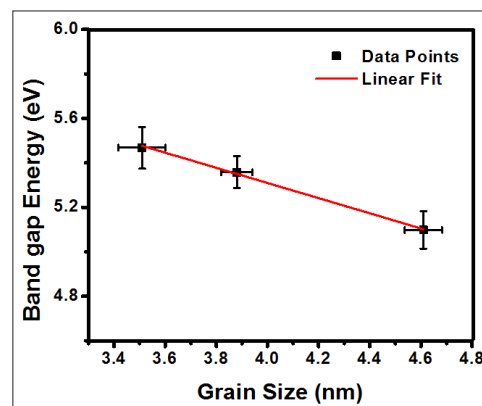

Figure 3: Graph of band gap energy (eV) versus grain size (nm) showing a nearly inverse dependence

Discussion

At increasing the acid concentration, the process was accompanied by reduction of the sizes of particles with simultaneous depolymerization of cellulose macromolecules. The intermolecular bonds between CNCs start rupturing and the particles move to the hydrolyzing solution hence reduction in grain size. The grain size was found to reduce with increase in HCl concentration. This can be explained by the fact that during the cellulose HCl hydrolysis, cellulose in amorphous region got hydrolyzed. As the hydrochloric acid concentration increased, cellulose crystalline regions were gradually swelled and more cellulose in crystalline regions reacted with the acid. Also, cellulose in amorphous regions got hydrolyzed and completely removed by the acid hydrolysis

[14]. As a result, high crystallinity CNCs particles with reduced grain sizes formed.

Interestingly, the band gap energy was found to increase with decrease in the grain size. This increase suggests increase in impurity concentration in spite of the increase of the overall crystallinity of the CNCs. If the crystallite size is large, there are more atoms and thus more bonding and antibonding atomic orbitals overlap that makes the gap between the band gap (valance and conduction band) to decrease.

Conclusion
From the study, an increase in acid concentration has been found to lead to decrease in the grain (crystallite) whereas the band gap energy has been found to increase with increasing acid concentration. The optical band gaps of the CNCs have been found to decrease with the increase in crystallite size. This shrinkage of the band gap has been attributed to the increased impurity concentration leading to the narrowing of the band gap due to the emerging of the impurity band formed by the overlapped impurity states.

Acknowledgement

Conflict of Interest
The authors have no any conflict of interest to declare.

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