STUDY OF HYBRID COMPOSITES MADE ON THE BASIS OF NANOCELLULOSE

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Introduction

Cellulose materials composed of the nanoscale fibrils, so called nanocellulose (NC), draw great attention as they are lightweight, electrically conductive, nontoxic, and optically transparent in the crystalline form. Due to the presence of 3 hydroxyl groups in each elementary unit of the cellulose macromolecule, the NC is able to form hydrogen and chemical bonds with molecules of other substances.. Knowledge of the mechanisms of NC bonding to the surface of various materials is of great importance for the development of new materials based on NC.

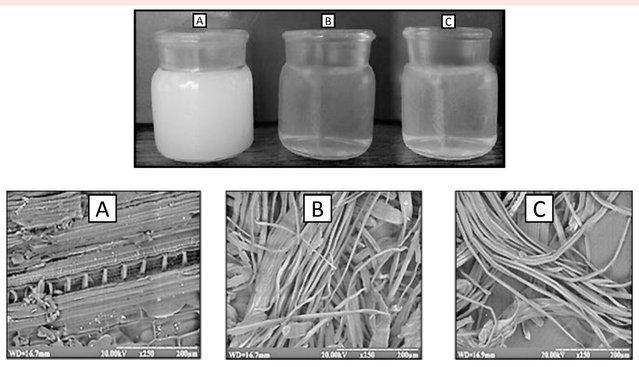
In this work we studied the solid films made from NC (prepared from *Miscanthus x Giganteus*), NC mixed with additives of microcrystalline cellulose (MCC) or graphene oxide (GO) micro/nanoparticles.

Samples and Methods

The hydrolysis of organosolvent pulp from Miscanthus was carried out with a solution of sulfuric acid with a concentration of 43% at 60 °C for 60 min. By washing the NC solution with distilled water and centrifugation (4000 rpm) followed by dialysis, a neutral pH was reached. Ultrasonic treatment of NC with a concentration of 0.6% was carried out on an UZDN-A ultrasonic disintegrator (SELMI, Ukraine) with a radiation frequency of 22 kHz for 60 min. Preparation of NC / NC-MCC / NC-GO suspensions; treatment in the ultrasonic bath, application of drops on a glass slide / quartz, drying the layer: This was an algorithm for obtaining a film layer, which was repeated to obtain a multilayer structure. Non-destructive techniques such as XRD, scanning electron microscopy, as well as optical microscopy, optical absorption and luminescence have been used to characterize the morphology, structure, and properties of NC and its composites.

Results

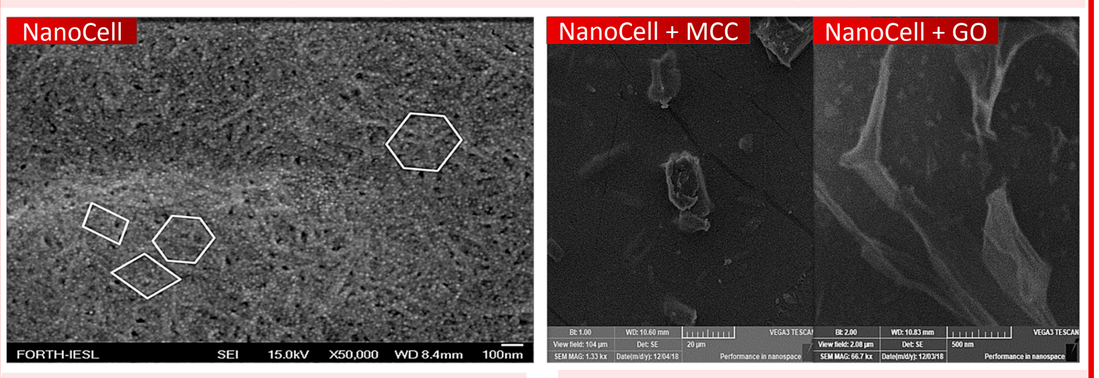
Morphology of Miscanthus



NC concentration of **6** g/l and its water solutions with concentration of the NC of **3** g/l and **0.15** g/l were used in the study. The density of mentioned solutions measured at temperature 25 °C was **1.00033**; **0.99933** and **0.99876** g/l, respectively.

The view of nanocellulose suspense “before” (a) and “after” ultrasound treatment (b); sample b after three months of storage (c). Below are SEM images of samples of the miscanthus stalks (a), organosolvent miscanthus pulp before (b) and after alkaline treatment (c)

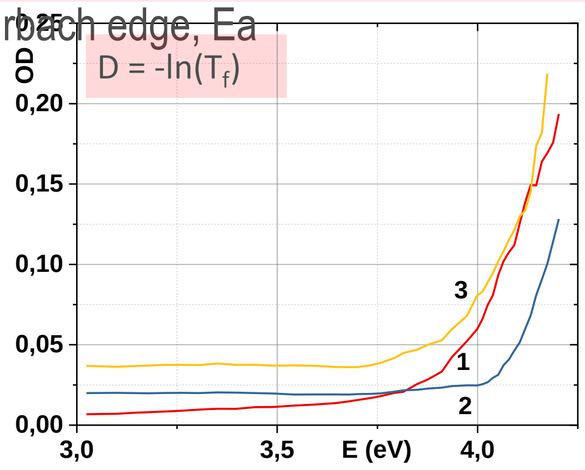
Morphology of the films (SEM images)



Nanofibrils are capable to be self-organized. Their length is of about 200 and diameter of 10 - 15 nm.

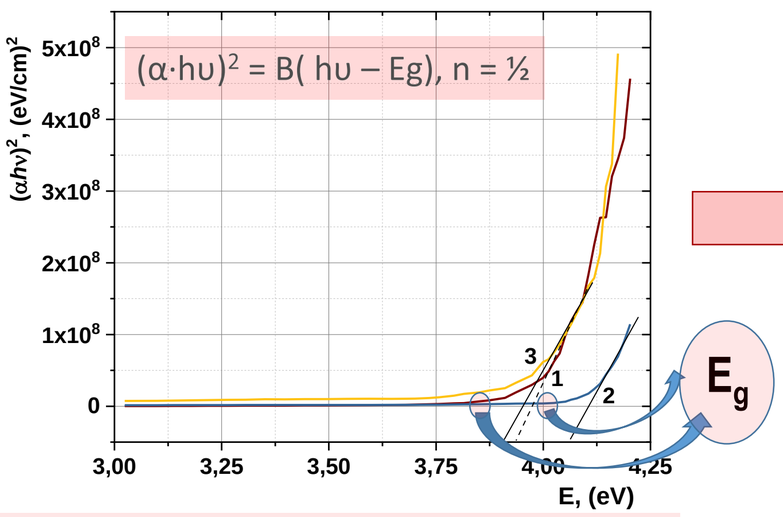
Dimensions of MCC and GO inclusions lie in the range of 1 - 20 microns.

Optical properties: Absorption Urbach edge, Ea



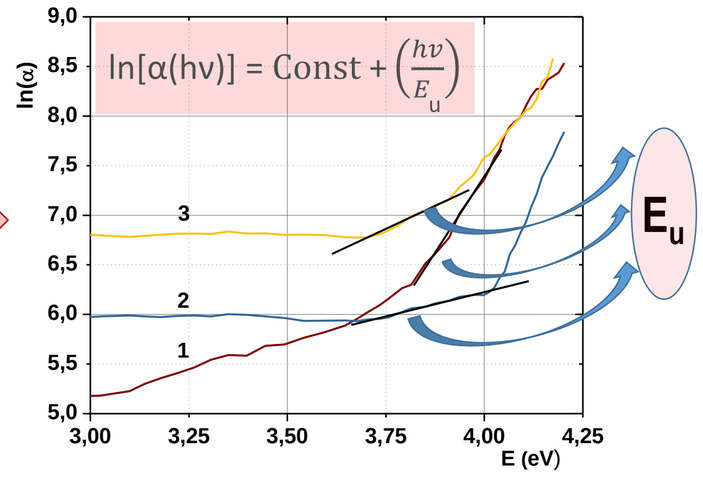
Optical density spectra of NC film (1) and «NC-MCC» (2), «NC – GO» (3) composites

Optical band gap, Eg



Tauc - spectra of the NC film (1), «NC-MCC» (2), and «NC – GO» composites (3)

Optical band gap, Eg

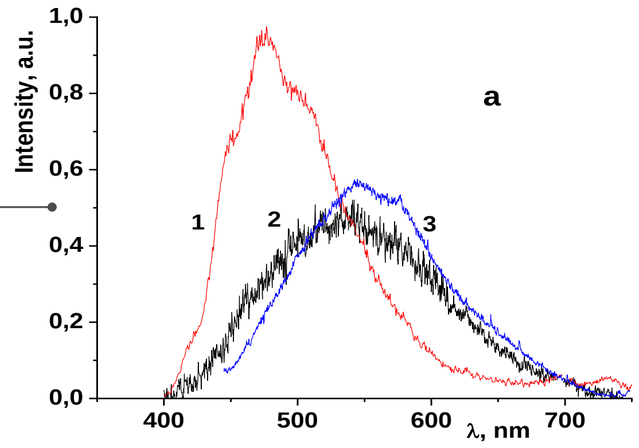


Logarithm of absorption coefficient spectra of the NC (1), «NC-MCC» (2),
and «NC-GO» (3) composites. Lines approximating the Urbach range are shown

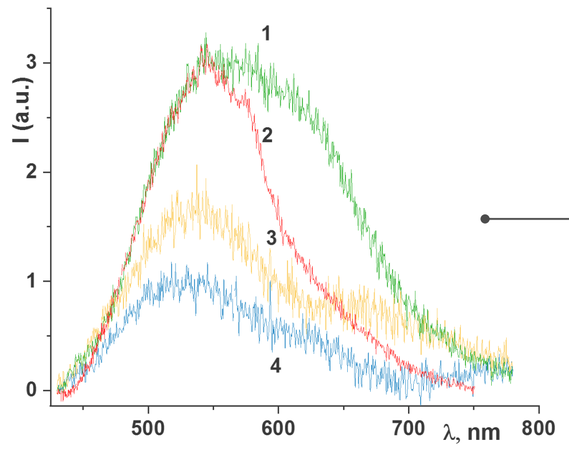
Optical properties: Photoluminescence of the nanocellulose and composites

The PL spectra of the NC water

The spectral components are caused by various chromphor molecules located on the surface of cellulose



The PL spectra dependence on the excitation wavelength. Starting suspense is excited at λex = 325 (1), 360 (2), and 405 nm (3)



Luminescence spectra of NC-OG films (1), MCC starting tablet (2), NC-MCC (3) and NC (4); T = 300 K; λ_{ex} = 405 nm

The PL spectra demonstrate their dependence on the composition of the films

The spectral components correspond to the known PL spectra of the MCC and GO fillers

Conclusions

1. Cellulose nanofibrils deposited in the form of the film on a glass substrate are capable to self-organization.
2. Microcrystalline cellulose and graphene oxide affect the optical band gap (Eg): Eg = 4.02, 4.10, and 3.90 eV for "pure" nanocellulose, "NC - MCC" and "nanocellulose - GO“ composites, respectively.
3. Data on the length of the distribution of localized states in the band gap show the effect of incorporated additives on the structure (amorphousness and defect) of the crystal lattice of nanocellulose. The Urbach energy (Eu) = 0.16, 0.11, and 0.2 for the "NC, NC- GO”, and NC - MCC“, respectively.
4. The obtained optical and electronic characteristics are important for forecasting and designing future, photovoltaic devices using materials made on the basis of nanocellulose.

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