Environmental Engineering and Management Journal March 2011, Vol.10, No. 3, 463-466
http://omicron.ch.tuiasi.ro/EEMJ/

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Book Review

THE NANOSCIENCE AND TECHNOLOGY OF RENEWABLE BIOMATERIALS

Lucian A. Lucia and Orlando J. Rojas (Eds.)

John Wiley and Sons,
ISBN: 978-1-405-16786-4, 2009, XIV+344 pages.

The accelerating development of science and industry, a continuous necessity of improvement has lead to a growing demand of new products characterized by superior properties at nanoscale level. The structure, properties and behavior of natural and man-made nanostructures has become a challenge for modern society and mankind. The techniques for making and characterizing the nanostructures and putting them together to use has given birth to a new discipline known as nanotechnology.

The nanostructured materials may be viewed as enabling the scientific and technology advancements offering the possibility to obtain cost-effective manufacture of nanomaterials with specific properties and subsequent efficiency. At the same time, nanostructures obtained by chemical synthesis are not enough to cover the diversity of needs and to meet all desired goals. The principles of sustainable development, green chemistry and green engineering have determined a reorientation to natural materials and the nanostructures of natural origin. The application of lignocellulosic materials has become a domain of intense research especially during the last decade.

The increased interest on nanoscience and technological development in agreement with environmental health and safety issues implying the use of biomaterials lead to the necessity of a detailed study of renewable biomaterials andt its nanoscopic power, which would reflect the advancements and new possibilities in this field.

Lucian A. Lucia and Orlando J. Rojas (Department of Forest Biomaterials, North Carolina State University, USA), the editors of **The Nanoscience and Technology of Renewable Biomaterials** present comprehensive and critical studies on the nanoscience and include the latest advances in biomass nanotechnology. The book includes essential parts from science and engineering reviews, is introducing the key aspects from industrial development regarding nanomaterials of different origin and utilization, focusing especially on the present possibilities and future vision for the nanotechnology.

The book is structured into 12 chapters presenting valuable possibilities in science and technology, including a detailed research work conducted for different type of nanoscopic biomaterials (cellulose, hemicelluloses, lignin) for the investigation at nano-level and for the clarifying the methods for production of nanostructures in reliable ways.

The chapter 1 – *A Fundamental Review of the Relationships between Nanotechnology and Lignocellulosic Biomass*, provides a general and well detailed survey containing the information regarding nanotechnology, lignocellulosic biomass and the relationship between them. Simple and concise way of presentation offered by authors (Theodore H. Wegner and E. Philip Jones) helps to understand the importance of nanostructured materials. The basis of nanotechnology and its connection with forest biomass are interconnected involving the principle of sustainability, green chemistry and engineering. Also, the autors are underlining the importance of nanostructured materials produced by photochemical factories using air, sunlight and water. Moreover, the authors are introduicing several nanotechnology-enabled product possibilities toghether with a detailed presentation of nanoscale properties of forest materials. One of the main aim of this chapter is to focus the attention on the new directions in the nano-manufacturing and on the identification of the priority and most productive areas: (1) achieve lighter weight, higher strength materials; (2) produce nanocristalline fibrils from wood; (3) control water interaction with cellulose; (4) produce hyperperformance nanocomposites using nanocristalline cellulose fibrils; (5) capture the photonic and piezoelectric properties of lignocelluloses; and (6) reduce energy usage and capital costs in processing wood to products. It sholud be mentioned that authors are discussing the appropriate actions to mitigate risk to health, safety and the environment that result from the exposure to introduction of nanostructured materials.

Chapter 2 – *Biogenesis of Cellulose Nanofibrils by a Biological Nanomachine*, is dedicated to one of the most important nano-componet of vegetal origin – nanofibrils. After a brief presentation of the structure of cellulose, nanofibrils are introduced as nanomaterials with unique properties, opening a new domain in the research of the surface properties in the chemistry and the study of biological role of cellulose. The review on biogenesis include the process whereby β-1,4-linked glucan chains form long, semi-cristalline fibrils with nano-scale lateral dimensions. The wonderful structure of nanofibrils determine its surface interaction properties, being one of the main factor influencing further deposition of other wall components (lignin, hemicelluloses). FF-TEM (freeze fracture transmission electron microscopy) and identification of CS (cellulose synthase) gene are two basic methods used for the explanation of CSC (cellulose synthesis complex) operation at nanoscale level. As a real mechanistic understanding for the CSC mediating cellulose biogenesis to build the cell wall has not been reported, the authors are discussing several expectations concerning the activity of plant CSC: assemble with genetically determined morphology; stabilize in operational form in the plasma membrane; aquire UDP-glucose substrate; polymerise glucose with β-1,4-linkage; operate so that fibrils emerge outside the plasma membrane; control cellulose chain length and fibril size; possibly control cellulose crystallization; and move in plasma membrane to spin out cellulose fibrils. The comprehensive survey presented in chapter 2 is based on several recent reviews describing the functions of CSC governing the cellulose biogenesis. In this way, the authors are introducing one of the nature's most remarkable biological nanomachines and also set the stage for future manipulation of cellulose properties in plants biomass and, possibly, synthesis of cellulose-free systems.

Chapter 3 – *Tools for the Characterisation of Biomass at the Nanometer Scale*, is discussing different nanoscale measurement methods with an adapted technique in the case of biomass specimens presenting difficulties (softness, hydrophilicity, nonconducting) at nanoscale. Taking in consideration that nanostructure of biomass is varying depending on the amount of water present during the analysis and also on the procedure for water removing, the authors (James F. Beecher, Christofer G. Hunt and J. Y. Zhu) are presenting different methods for the analysis and their limitations depending on: pore structure and accessibility, cellulose crystallinity ans sample preparation. Several microscopic and spectroscopic methods are described depending on the advantages and disadvantages conferred by physico-chemical properties and especially the strategy of specimen preparation. For the last one, two aspects are analysed: drying procedure and preparation of cross-section (microtomming and focused ion-beam cutting). The 'so-called" microscopic methods are represented by the SPM (scanning probe microscopies) methods including AFM (atomic force microscopy) and STM (scan tunneling microscopy), the FBM (focused beam microscopies) methods as SEM (scanning electron microscopy), XPS (X-ray photoelectron spectroscopy) and SIMS (secondary ion mass spectrometry), and also TEM (transmission electron microscopy) methods including ET (electron tomography) and UEM (ultrafast electron microscopy). Even if AFM technique was originally developed to measure nanoscale topography, the authors are presenting this method as the most common technique easy to use and offering information on chemical and material properties. More specialized instruments such as nanoindenters and near-fields scanning optical microscopes are presented as less versatile but providing 'cleaner' information. Finally, are concluding that a correct understanding of natural systems depend not only on the method of specimen preparation and proper choise of analytical technique, but also on a skeptical approach to data.

Chapter 4 – *Tools to Probe Nanoscale Surface Phenomena in Cellulose Thin Films: Applications in the Area of Adsorption and Friction,* is focused on the surfaces and interfaces properties. The authors (Junlong Song, Yan Li, Juan P. Hinestroza and Orlando J. Rojas) are presenting the importance of interfaces in applications involving material functionalization, coatings, colloidal stability. It is suggested that interfacial properties, in many cases, are more important than the nature and the composition of the bulk phases, and ultimately define the molecular behavior of the system. The main subject of the interest is directed to the surface phenomena in cellulose thin films and different applications in the area of the adsorption and friction are described.. In this chapter, the AFM (noncontact mode) is also mentioned as a method for the characterization of cellulose coated substrate, in this way, such homogeneous and flat films of celluloses may serve as useful platform for nanoscale studies that involve SPR (surface plasma resonance), QCM (quartz crystal microbalance) and LFM (lateral force microscopy). Later, in the chapter QCM and SPR are described as tools to monitor the adsorption of molecules on solid surfaces. The authors are presenting some examples regarding the modification of the surface of cellulose thin films via adsorption of polyampholytes and nonionic polymers. Overall, it is concluded that a fundamental understanding of the adsorption and friction behavior can unveil a more complete understanding about boundary lubrication and nanostructuring phenomena on cellulose systems.

Chapter 5 – *Polyelectrolyte Multylayers for Fibre Engineering* (Rikard Lingström, Erik Johansson and Lars Wågberg), begins with general information about polyelectrolyte multilayers (PEM) and direct our attention to a remarkable application of cellulose surface modification: the build up of polyelectrolyte multilayers for further uses, especially to improve the adhesion between surfaces. The PEM method proved to be very useful in different applications, but at nanoscale level, it has a large efficiency in the case of paper fibers in the engeneering of paper surfaces with enchanced interfiber bonding due to nanoscale treatment. However, the presented information is directed from the characterization of the dry properties of PEM to the formation of the layers and joints between PEM-covered surfaces. The authors anticipate a lot of future work devoted to the dry characterization of PEMs formed with different components and under different conditions.

If chapters 2-5 are focusing on cellulose, the next chapters (6-7) are discussing the other important components of the cell wall: hemicelluloses and lignin, analysing it regarding its nanostructure, interaction and potential nano-application.

In chapter 6 – *Hemicelluloses at Interfaces: Some Aspects of the Interactions, adsorbed hemicelluloses are used to analyse the surface and interfacial phenomena*, comes to continue with the previous studies. The authors (Tekla Tammelin, Arja Paananen and Monika Őesterberg) analyze the formation of films by adsorption dissolved hemicelluloses fractions isolated from wood pulp (galactomanan, pure pectin and pure xylan) on cellulose nanofilms. For advanced characterization QCM and AFM experiments were done. The authors are suggesting that although the dependence of the adsorption behavior on ionic strength can largely be explained by electrostatics, the main driving force for the adsorption seem to be of nanoelectrostatic nature. Also, other factors as polymer solubility and preferable polymer contacts need to be considered when explaining the adsorption behavior.

Chapter 7 – *Lignin: Functional Biomaterial with Potential in Surface Chemistry and Nanoscience*, begins with a detailed presentation concerning lignin sysnthesis and structural aspects, continues with isolation methods from wood, pulp and pulping liquors. The characterization of Kraft lignin's solution properties focuses onto important properties from nano-scale view: colloidal behavior, self-aggregation of colloidal particles into larger clusters. In the case of aggregation due to Brownian motion, two well defined limiting regims of kinetics are identified: DLCA (diffusion-limited cluster (colloid)-cluster(colloid) aggregation) and RLCA (reaction-limited cluster (colloid)-cluster (colloid) aggregation) – the universal aggregation processes known to give aggregates of fractal geometry. By comparison of different experimental results, the authors (Shannon M. Notley and Magnus Norgren) manage to present a striking resemblance between fractal clusters of Kraft lignin (KL) imaged using Cryo-TEM and self-aggregated gold colloids. As with all aspects of nanoscience, molecular interactions are of great importance, whether considering lignin as a polymer in solution or in solid state, and hence this chapter discusses the topochemical and interfacial properties of lignin. The reader can notice the remarkable images and useful graphic and schematic representations from this chapter. It is strongly suggested the introduction of lignin in nanoscience and nanotechnology, the multitude of opportunities being available due to its unique structure and properties, large accessible volume and surety of supply can provide many opportunities. At the same, the authors do not hesitate to mention the problematic areas for lignin implementation: a production with a constant molecular structure and free of both organic and inorganic contaminants.

Chapter 8 – *Cellulose and Chitin as Nanoscopic Biomaterials* (Jacob D. Goodrich, Deepanjan Bhattacharya and William T. Winter), presents the general and microscopic characterization as well as preparation of cellulose and chitin (isolated from bagasse and shrimp shells) nanoparticles. Several experimental results from SEM, AFM and TEM analysis are presented (including marvelous images), also NMR and X-ray diffraction come to complete the investigations. The authors suggest that the abundance of hydroxyl groups available on the surface of these materials facilitate their topographical modification, the modified nanoparticles are analysed using XRD, FTIR and Contact angle techniques. The data provided in this chapter is a mere subset of potential that nanoscopic biomaterials such as cellulose and chitin possess in the field of composite materials. There are endless combinations of cellulose and chitin nanoparticles derivatives and thermoplastic composite blends that can be explored.

Chapter 9 – *Bacterial Cellulose and its Polymeric Nanocomposites* (Marie-Pierre G Laborie), demonstrates very elegantly how the smallest organisms amongst us, bacteria, can provide us with a very pure form of cellulose that not only has interest in its own right, but can be easily combined with a number of other biomaterials (xyloglucan, mannan, pectin, lignin). Compatibilization of bacterial cellulose with a wider range of polymers may be afforded by surface grafting of appropriate functional groups or chains to yield new nanocomposites. Besides, more complex nanostructured materials might be developed from bacterial cellulose by functionalizing its surface with molecules such as proteins or other compounds that display interesting self-assembling properties. The last research indicates that the development in the field of BC (bacterial cellulose) nanomaterials will further intensify and new high-value application will be developed.

Chapter 10 – *Cellulose Nanocrystals in Polymer Matrices*, explore the nanoscopic, well ordered cellulose domains of a cellulosic array as part of an effort to describe the inclusion of these crystalline structures into polymeric matrices. John Simonsen and Youssef Habibi have provided a concise overview and account of the general area of cellulose nanocrystals, more specifically on their composites with various polymers and their transport properties.

Chapter 11 – *Development and Application of Naturally Renewable Scaffold Materials for Bone Tissue Engineering* present modern and sophisticated applications for renewable materials. The authors (Seth D. McCullenn, Atiel D. Hanson, Lucian A. Lucia and Elizabeth G. Loboa) explore the engineering of renewable materials for advanced applications such as scaffolds for human tissue growth. In vivo work has focused on examining implanted materials via histology and quantifying radio-opacity compared to bone-controls. These techniques offer merely a glance at what has been achieved and require more detailed investigatory work before worldwide clinical acceptance.

Finally, in chapter 12 – *Template Synthesis of Nanostructured Metals Using Cellulose Nanocrystal*, Yongsoon Shin and Gregory J. Exarhos demonstrate the application of green chemistry principles in the synthesis of metallic nanoparticles on CNXL without additional reducing agents, as well as preparation of porous metal oxides and metal carbide nanorods.

The authors present the latest experiments and interpretations, still detailed reduction pathways of metal ions are still a puzzle, even though surface-initiated reaction is clear. The fundamental investigation for the reduction mechanism is under study. The homogeneous dispersion of monodisperse metal nanoparticles on CNML through the 'green' reducing process can be expected to have a huge impact in the application of clean heterogeneous catalysis.

The detailed information presented in this book results from an intense and productive research activity in the domain of renewable biomaterials directed to new perspectives offered by nanoscience and nanotechnology. Structured and elaborated according to the requirements of contemporary research in nanoscience, the book provides a usefull review of main renewable biomaterials and offers a visualization as a whole of new perspectives in technology and engineering for all those interested in modern research. It is clear that the future generation will assist the change from many relatively crude and unsophisticated technologies to highly efficient and environmentally friendly one based on nano-biomaterials.

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