Invited Paper

Nanomanufacturing Metrology for Cellulosic Nanomaterials: an Update

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ABSTRACT

The development of the metrology and standards for advanced manufacturing of cellulosic nanomaterials (or basically, wood-based nanotechnology) is imperative to the success of this rising economic sector. Wood-based nanotechnology is a revolutionary technology that will create new jobs and strengthen America's forest-based economy through industrial development and expansion. It allows this, previously perceived, low-tech industry to leap-frog directly into high-tech products and processes and thus improves its current economic slump. Recent global investments in nanotechnology programs have led to a deeper appreciation of the high performance nature of cellulose nanomaterials. Cellulose, manufactured to the smallest possible-size (~2 nm x ~100 nm), is a high-value material that enables products to be lighter and stronger; have less embodied energy; utilize no catalysts in the manufacturing, are biologically compatible and, come from a readily renewable resource. In addition to the potential for a dramatic impact on the national economy – estimated to be as much as $250 billion worldwide by 2020 – cellulose-based nanotechnology creates a pathway for expanded and new markets utilizing these renewable materials. The installed capacity associated with the US pulp and paper industry represents an opportunity, with investment, to rapidly move to large scale production of nano-based materials. However, effective imaging, characterization and fundamental measurement science for process control and characterization are lacking at the present time. This talk will discuss some of these needed measurements and potential solutions.

Keywords: calibration, cellulose measurements, metrology, scanning electron microscope, SEM, standards, reference material

1.0 INTRODUCTION

"Innovation Invigorates America" and the development of the metrology and standards for advanced manufacturing of cellulosic nanomaterials (CNM) or basically, wood-based nanotechnology is critical to the success of this rising economic sector. Postek et al (1) reported on the initial developments of the imaging and metrology of cellulose nanomaterials and subsequent papers expanded upon that (2, 3) and in 2013 enough research had been done to elicit from the field a compilation of over 100 research projects in cellulose nanomaterials (4), warranting this update.

Wood-based nanotechnology is a revolutionary technology that will create new jobs and strengthen America's

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[2] Certain commercial equipment is identified in this report to adequately describe the experimental procedure. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the equipment identified is necessarily the best available for the purpose.

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forest-based economy through industrial development and expansion. (5). Wood-based nanotechnology allows this, previously perceived, low-tech industry to leap-frog directly into high-tech products and processes and thus improves its current economic slump. Cellulose, manufactured to the smallest possible-size (~2 nm x ~100 nm), is a high-value material that enables products to be lighter and stronger; require less embodied energy; utilize no catalysts in the manufacturing, is biologically compatible and, comes from a readily renewable resource. Research has already shown that cellulisic nanofibrillar material can be aligned hydrodynamically and ultra strong fibers stronger than aluminum and steel per weight can be produced (6).

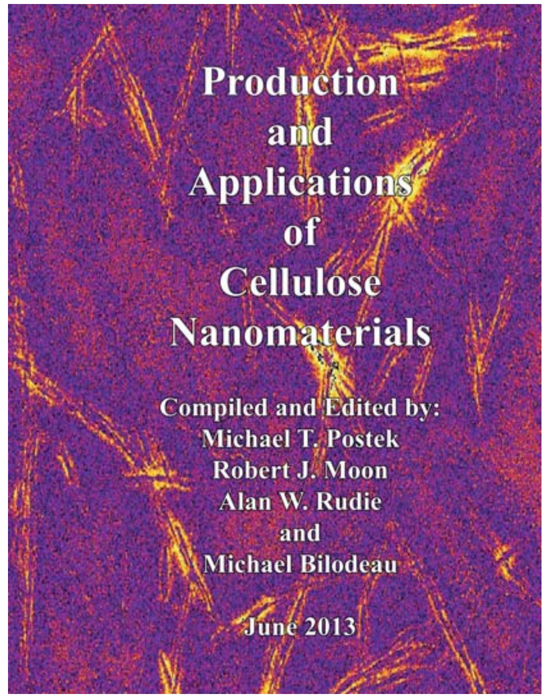
Recent global investments in nanotechnology programs have led to a deeper appreciation of the high performance nature of cellulose nanomaterials. In addition to the potential for a dramatic impact on the US national economy – estimated to be as much as $250 billion worldwide by 2020 – cellulose-based nanotechnology creates a pathway for expanded and new markets utilizing these renewable materials. Utilizing the installed capacity associated with the US pulp and paper industry represents an opportunity, with an appropriate level of investment, to rapidly move to large scale production of cellulose-based materials. It is conservatively estimated, that a wood-based nanotechnology program would have a benefit to cost ratio of 25:1. However, effective imaging, characterization and fundamental measurement science and tools for process control and characterization are lacking at the present time.

2.0 DISCUSSION

Even with the huge potential economic benefits possible, various restructuring in the US Forest Products Industry has consolidated and hence reduced the available support for wood science and technology (7). Fundamental research support, which would evolve this low technology industry sector quickly into a high-technology industrial player, is well below other high tech industries. This is sharp contrast to the US semiconductor industry which historically has invested (up to ~30%) a significant amount of corporate profit each year into research and development for future technology, devices and products. The semiconductor industry leaders know that in order for it to continue to compete it must continually push the technology envelope. A ground swell in the Forest Products Industry is working to change this industry's philosophies and adopt a more dynamic approach, but it has been slow and difficult to enable this realignment.

2.1 The Current "Chasm" of Death or "Catch 23." There has been much discussed and published about the technology "Valley of Death" but there is a different more fundamental type of chasm in play here. The technology valley, where new applications die because of lack of funding in the ramp-up stages, is potentially still somewhere in the future, but it is not there yet. Fundamentally, there is still a great deal to be learned about the *economical* bulk manufacturing of cellulose nanomaterials themselves. Clearly, small and medium batch manufacturing is beginning to show promise, but large-scale manufacturing of CNM has yet to be started in earnest. One thing is for sure is that the current industrial philosophy dictates that there will be no large scale investment in the necessary infrastructure to bulk manufacture CNM until there is a well-documented high-volume application to incorporate the raw material produced (or a solution outside normal channels is found). At the other extreme, the applications developers' philosophy is that they need an unlimited raw CNM material supply before they can invest to develop that "killer-app." Which is the cart and which is the horse? The killer app might be something as straight forward as CNM for cement additives, drilling fluids or thin film electronics. If just one of these applications hits, the current entire worldwide supply of CNM would be inadequate, and to satisfy the demand and ramp-up would take time. But, once that ramp-up takes hold, all CNM research will benefit from abundant low-cost CNM material.

In addition to the polarization of the suppliers and users, a technology chasm, of its own, has developed in between these two poles. This chasm is the uncertainty of what is required to meet the characterization and quality control needed by either or both sides of the valley. Production quality control instrumentation for bulk CNM manufacturing does not exist and more importantly it is not clear today what tools should be developed. Again, unlike the semiconductor industry which has set forth its needs and goals via the SIA Roadmap for semiconductors (which helps to clearly direct instrument manufacturers to be prepared with needed production tools) no such document is available for the CNM manufacturing. Therefore, progress is slowed because the tools and expertise are not being developed in parallel. This is a new concept because until now most new technology was more dependent on evolving established infrastructure which could be modified to meet the need as it emerged. In this instance none really esists.



2.2 Nanometrology of Cellulose Nanomaterials. Many nanomaterials are of great interest for many applications, so there is no single imaging, characterization or metrology method that fits all applications, at this time. CNMs are extremely difficult materials to image and characterize because of their extremely small size and the fact that they are low atomic number materials (mostly carbon, oxygen and hydrogen). Some guidance on instrument choices can be obtained from work previously done on carbon nanotubes (CNT) such as work by Belin and Epron (8), but, many new techniques must be developed.

CNM are biological in origin hence, they must be considered to behave similar in nature to the ultrastructure of other woody cellular plant structures. Clearly there is a large data base available on handling and sample preparation of these materials (such as ref. 9). But, this also means that upon drying, these materials may shrivel up and deform like any other biological material. Therefore, more careful specimen preparation techniques must be explored which preserve the physical characteristics desired.

In a recent publication: **"Production and Applications of Cellulose Nanomaterials"** over 100 projects in CNM were compiled from across the World (4). This publication was an open call for short descriptions of work, at that time, currently being done on CNM. All appropriate work submitted was included (following extensive review), therefore, this was the first publication to provide a comprehensive snapshot of research and the methodologies being used at the time when these data were obtained.

"Production and Applications of Cellulose Nanomaterials" can be mined for a great deal of information regarding the research ongoing in CNM. Of interest here, are data found in Tables 1 and 2. These tables are compilations of the imaging and characterization methods used by the researchers in their submissions to that book. Understandably, many of these methods closely parallel those used for similar CNT research. Table 1 shows the top 9 methods used by the authors in their research in CNM (in the order of their use) with SEM, TEM, and AFM, being the three most commonly used methods. There were no top 10 methods since from the 9th method onward, the additional methods found in Table 2 were only sparsely used. This demonstrates that: "*if all you have is a hammer everything is a nail*," or said another and more appropriate way for this research: "*if you have*

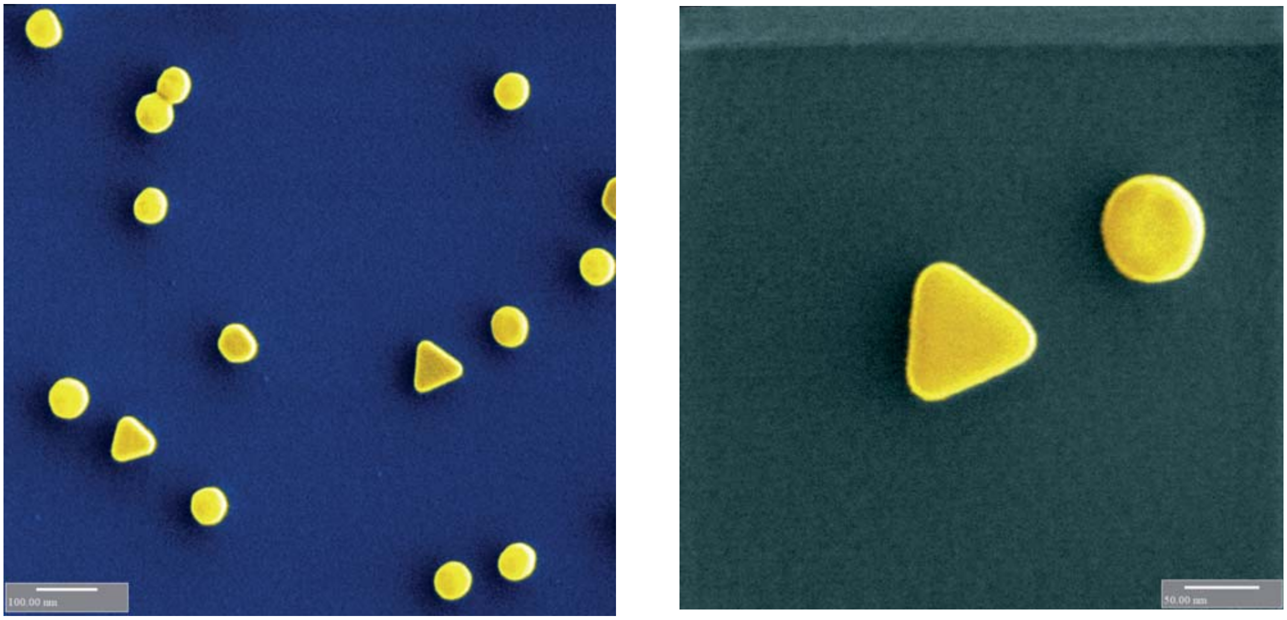


Figure 1. *Helium ion micrograph of 60 nm gold nanoparticles showing agglomeration and particle size and shape variation. (Micrograph courtesy of Andras Valdar)*

a nail lots of things can be hammers." More importantly where Tables 1 and 2 are concerned, these represent all research or laboratory grade instruments; none of the instruments used were high throughput manufacturing grade instruments.

2.3 Methods Divergence, Modeling and Hybrid Metrology. Clearly, Tables 1 and 2 demonstrate that a large number of instruments can be used in the imaging and characterization of CNM and a similar array has been used for research with CNT. This leads to an important point that has plagued metrology of nanomaterials for some time. This is a methods divergence issue. Different metrology instruments measuring the same material can yield different measurements [the same instrument using different operating conditions can also report different measurements]. Some of the reasons for divergence in the scanning electron microscope have been discussed by Postek et al. (2, 3, 4). This is epitomized by Stefaniak et al. (10), and Linsinger et al. (11) who recently described the metrological challenges associated with the development of nanoscale reference materials (RM) for particle size since the measurement of nanoparticle size is highly method dependent. Hence, while most lists of nano-object properties included particle "size," few define what is meant by size (or how that size was determined). This means that one laboratory measuring a nanoparticle by an SEM and another measuring the same type of material by optics will, very likely, report different size measurements. The dependency of a property on the chosen analytical method can be illustrated with NIST RM 8011 (10 nm nominal), as shown in Table 3. RM 8011 is composed of gold nanoparticles in an aqueous suspension. For this RM, NIST assigned different values of "size" for atomic force microscopy (AFM), scanning electron microscopy (SEM), transmission electron microscopy (TEM), differential mobility analysis (DMA), dynamic light scattering (DLS) and small-angle X-ray scattering (SAXS) techniques. The RM 8011 assigned size values ranged from (8.5 ± 0.3) nm (AFM) to (13.5 ± 0.1) nm (DLS) due to methods divergence.

2.3.1 Methods Divergence. Reference materials are highly studied, so it can be concluded from the work on RM 8011, and others, that the apparent differences in size values obtained by different techniques for the aforementioned RMs result from the fact that (a) not all primary nanoparticles in a population are identical (i.e., with few exceptions, there is always a distribution with respect to dimensions and sometimes shape). This is

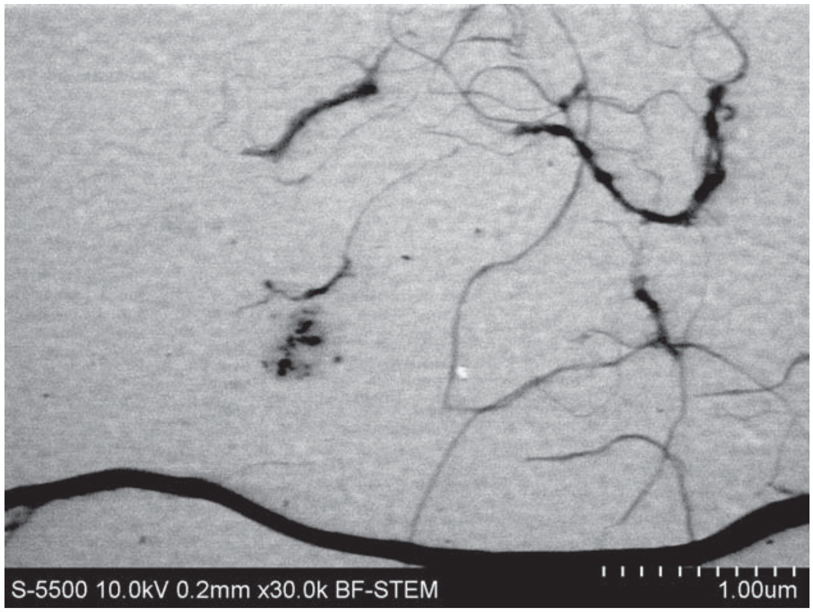


Figure 2. *High resolution scanning transmission electron micrograph of nanocellulose fibers*

clearly shown in Figure 1 for 60 nm gold nanoparticles, (b) most nanoparticle populations contain some agglomerates (which will impact the mean size and potentially skew results) and (c) measurement techniques (as stated above) vary with respect to the way in which they "sense" the dimensional properties of particles and under what conditions these measurements are conducted. For example, microscope-based methods and other counting methods generally produce number-weighted distributions, while light scattering techniques generate intensity-weighted distributions. Furthermore, methods may differ with respect to whether they produce an ensemble average (as in DLS) or a highly localized, single particle measurement (as in SEM, TEM, or AFM), or they may simply measure different aspects of the nanoparticle dimensions (e.g., height above a flat substrate, equivalent spherical diameter, radius of gyration or hydrodynamic size). The different values may in fact reflect real differences in the "size" of the nanoparticle measured or measurement of the perceived particle "sensed" by the instrument. Sample preparation can also introduce biases into the assessment of size, and such artefacts are difficult to separate in many cases (12). All of these factors should be understood before meaningful decisions are made regarding quality control.

Other potential sources for variance between measurement methods can be attributed to measurement artefacts or technical limitations. For example, in optical microscopy, illumination source and diffraction are fundamental factors that must be considered; electron beam/sample interactions, signal origination and collection provide measurement limitations in particle beam microscopy (electron and ion beams), and tip/probe/sample interactions are limiting factors in probe microscopy (e.g., atomic force microscopy). Hence, it is critical that the investigator understands the technical characteristics and the measurement processes being used, because instruments may measure a given sample in vastly different ways resulting in the "methods divergence." A clear understanding of the numerous factors that comprise and contribute to imaging and measurement uncertainty in a scanning electron microscope or any measurement tool is essential, and true dimensional accuracy can only be achieved through modelling of the entire measurement process (13). Physics based models are being developed for optical, scanning probe and scanning particle beam instrumentation, but have generally not been fully applied to nano-object characterization. While modelling may be too involved or unnecessary for some applications, in order to claim accuracy for any dimensional measurement it is essential to account for all significant contributors to potential methods divergence. Modeling also helps in understanding why measurements between tools differ.

2.4 The Challenge. This is a complicated issue since there are so many factors involved and the actual challenge will eventually come down to economically determining the most effective method to qualify a "boat load" of CNM. That method has not yet surfaced, but its basic characteristics can begin to be identified. This instrument must be a ***"bullet proof black box"*** providing the least amount of operator intervention possible. An in-line qualification tool needs to be:

1) Fully automated
2) Highly sensitive to process change
3) Highly precise
4) Capable of extremely high throughput

Clearly, instruments possessing these qualities exist for other industrial environments. For example, in the semiconductor industry, the critical dimension scanning electron microscope (CD-SEM) is currently extensively used in wafer fabrication facilities across the World. These instruments meet all of the above criteria, but the semiconductor wafers process stream is vastly different than any CNM process stream is, or will be. For one thing CNM are highly hydrated materials which would not fare well in a vacuum environment without special handling – thus decreasing throughput. That is not to say that the CD-SEM concept might be applied, if sufficient resources were applied to the research and development of an appropriate variable pressure SEM instrument. That technology exists, but has not been applied to large production environments - yet.

A more direct route to in-line quality control is to consider an optical technique which could also meet the needs without disrupting the process stream. Sacui et al. (14) compared a number of characterization methods and concluded that the fluorescence and Raman microscopy data may be useful for monitoring purity during CNC/CNF processing. Therefore, they could be utilized as the "black-box" instrument and the primary instrument possessing the needed qualities while being backed up by an ensemble of other instruments, as required by the industrial user and qualifications needed, to have the product accepted by the customer. For this instrument the main qualities are sensitivity to process change, precision and throughput. Accuracy may not be required. The semiconductor industry is beginning to apply a similar concept where the strengths of several tools are utilized to their best benefit for the industrial process and then the data is modeled and statistically analyzed. This concept is referred to as hybrid metrology and has begun to show good success in process fabs across the World.

It is clear though, that any CNM production metrology instrument will require significant R&D in order to make it useful for the specialized CNM manufacturing. Therefore, the sooner the instrument manufacturers are brought on board the quicker the instruments will become available.

2.5 Public Private Partnering. Historically, support for advanced manufacturing metrology research at the nanoscale has come from specific industries or consortia such as the Semiconductor Research Corporation or International SEMATECH, which are aimed at solving the short-term problems specifically for the semiconductor industry. It is clear that such strong, focused leadership will be required to develop the tools and methodologies needed for advanced manufacturing of CNM at the nanoscale. A consortium-type organization similar to International SEMATECH, initially co-funded by government and industry, could serve as a focal point and champion for the development of the needed roadmaping and could help to accelerate the needed development in instrumentation and metrology, as well as other fields. But, the industry must see this as a great opportunity to open new markets and to create a new business model. To successfully develop this CNM roadmap, industry will need to come together to identify common goals, similar to what ITRS did. To accomplish this, topics of mutual need, such as metrology, which are “precompetitive” in nature (work where companies are not concerned that their competitors have equal access to the results), are perfect topics for discussion since the generic information can be taken back to the respective companies and modified as needed for specific proprietary processes.

3.0 CONCLUSION

The US is currently not the leader in cellulosic nanomaterial manufacturing. But, that can change. The National Nanotechnology Initiative (NNI) has recognized this by including these materials in its Signature Initiatives. New metrology and characterization ,ethods are needed to fully support the growing diversity and demands of measurements required for cellulose-based advanced manufacturing, innovation, and research. In many ways, these materials are much more difficult to work with and to characterize than previous materials (e.g., carbon nanotubes). Physical measurements and standards provide the tools, information and traceability to national standards that these customers need to enable advanced manufacturing, to develop and test new materials, to enable innovation, to compete in a global economy, develop quality assurance metrics and to ensure compliance with regulations. If this is not developed in a timely manner, the gap between customer needs will grow wider as product development cycles continue to accelerate.

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Table 1 **Top Methods for Imaging and Characterizing Cellulose Nanomaterials**
• **Scanning Electron Microscopy (SEM**
• **Transmission Electron Microscopy (TEM)**
• **Atomic Force Microscopy (AFM)**
• **Thermo Gravimetrical Analysis (TGA)**
• **X-ray Diffraction (XRD)**
• **Raman Spectroscopy (RS)**
• **Fourier Transform Infrared (FTIR) Spectroscopy**
• **UV/Vis Spectroscopy (UV/Vis)**
• **X-ray Photoelectron Spectroscopy (XPS)**

Table 2 **Additional Methods for Imaging and Characterizing Cellulose Nanomaterials**
• Dynamic Light Scattering (DLS)
• Nuclear Magnetic Resonance (NMR)
• Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES)
• Dynamic Mechanical Analysis (DMA)
• Optics/Digital Image Correlation (DIC)
• Förster Resonance Energy Transfer (FRET)
• Laser Scanning Confocal Microscopy (LSCM)
• Helium Ion Microscope (HIM)

Table 3
Reference Values Mean Size and Expanded Uncertainty
Average Particle Size (Diameter, in nm)
(from: Documentation from NIST RM 8011)

Technique	Analyte Form	Particle Size (nm)
AFM	Dry, deposited on substrate	8.5 ± 0.3
SEM	Dry, deposited on substrate	9.9 ± 0.1
TEM	Dry, deposited on substrate	8.9 ± 0.1
DMA	Dry, aerosol	11.3 ± 01
DLS	Liquid suspension	13.5 ± 0.1
SAXS	Liquid suspension	9.1 ± 1.8