



NANOtechnology

Emerging Applications of Cellulose-based Green Magnetic Nanocomposites

By Tao Wang, Zhiyong Cai, Lei Liu, Ilker S. Bayer, and Abhijit Biswas, *Contributing Editors*

The term “nanocomposites” was coined in early 1980’s to designate a class of heterogeneous materials composed of two or more solid phases with at least one dimension less than 100 nm. The constituent solid phases can be virtually any material including amorphous, crystalline or semicrystalline phases. Research in this area has greatly impacted on our society and everyday life both scientifically and technologically, and this trend will no doubt accelerate as we migrate to an increasingly complicated technological world. The underlying rationale for these enormous advances stems from the general belief that by integrating different materials and manipulating the internal structures on the nanoscale, we will be able to generate many exciting novel materials with tailored and improved properties as well as new synergistic properties that are impossible to achieve in any of the parent constituent materials. Indeed, the past decades witnessed this idea turn into a reality.

In the middle of 1990’s, cellulose, an abundant biopolymer, joined this family of materials as a reinforcement component in polymer matrix composites. This utilization of cellulose, due to its ubiquity, renewability, cost-effectiveness and unique properties, will also have great positive impact on the environment and the development of sustainable technologies. Over the years, steady advances have led to a new class of biodegradable and environmental friendly bionanocomposites with remarkable improvement in material properties as compared to the polymer matrices of conventional macro-composite materials. These improvements are attributed to the excellent properties of cellulose fibers including high modulus, high tensile strength and good barrier properties as well as ease for chemical surface modification.

In recent years, a new type of nanocomposite – cellulose based hybrid nanocomposites, which adopts cellulose nanofibers as

matrices, has been intensively developed. Among these materials, hybrid nanocomposites consisting of cellulosic fibers and magnetic nanoparticles have recently attracted much attention due to their potential novel applications in biomedicine [1, 2], textonics [3], security papermaking and packaging [4]. The incorporation of the magnetic nanoparticles, e.g. Fe_3O_4 magnetites, which possess controllable collective magnetic properties, enables new functionalities that are impossible with each component alone. In contrast to other studies, recent work aims to develop nanocomposites where both matrices and particles are in true nanoscale such that higher mechanical, physical and chemical properties imparted from nanocelluloses can be retained while offering magnetic capabilities as mentioned above. Here, we will briefly describe the synthesis processes of cellulose nanofibers and magnetic nanoparticles as well as recent developments and potential applications.

Cellulose is biopolymer existing in woods, plants and some bacteria. Their nanoscale fibers can be extracted using mechanical, chemical or enzyme treatments, and are typically in the size range of ~ 20 nm in diameter and up to several micrometers in lengths. The crystalline cellulose possesses high mechanical properties such as high modulus, high strength and low density. A typical acid hydrolysis process for obtaining cellulose nanofibers is schematically illustrated in **Figure 1** [5]. To begin, microcrystalline cellulose (MCC) is derived from a natural source (e.g. wood) and mixed with deionized water. A concentrated acid (sulfuric or chloric) is gradually added to the mixed suspension that is kept in an ice bath to reach the desired acid concentration. Then, the solution is heated with agitation followed by repeated wash and centrifugation, dialysis and sonication. This process effectively breaks down the MCC into nanometer-sized fibers or whiskers, for example, the fibers

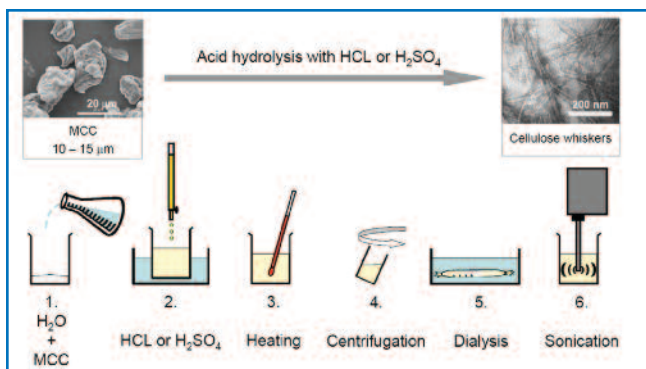


Figure 1. A schematic of typical acid hydrolysis process for obtaining cellulose nanofibers [Source: <http://www.forestprod.org/woodfiber07oksman.pdf>].

with diameter of 10 nm and length 200–400 nm as shown in the figure. These fibers permit a very stable colloidal water suspension that is further processed to form networks as matrices in the nanocomposite.

In the composite material system, another important component that constitutes as fillers or dispersoids is magnetic nanoparticles. Due to their unique properties in magnetic response, chemical stability, low cost and biocompatibility, magnetite nanoparticles have attracted extensive attention for a broad range of applications during the last decade. As a result, many different synthesis pathways have been designed and implemented in order to obtain particles with controlled sizes and properties. Magnetite can be synthesized either from aqueous or organic solutions via a series of chemical precipitation reactions to form magnetic metal oxides such as Fe_3O_4 and Fe_2O_3 . Moreover, the average particle sizes can well-controlled by varying reaction conditions, e.g. reactant type and concentration [6]. The ability to control particle sizes is particularly important to the behavior of magnetic composites because of the existence of critical domain size. Magnetic properties, e.g. ferromagnetic or paramagnetic, largely depends on the particle sizes in addition to their inter spacings. For example, many medical and biological applications require that the mean particle sizes of magnetic iron oxides are within the single domain range (< 20 nm) to maintain uniform physical properties and distribution. **Figure 2** shows an example of synthesized magnetite Fe_3O_4 nanoparticles from an aqueous solution made from iron (II) salt (FeSO_4) in a basic media (NaOH) and in the presence of a mild oxidant (KNO_3) [6]. It can be clearly seen that the mean particle size is reduced from 169 to 76 to 33 nm as the concentration of excess OH^- is increased from 0.2 to 2 to 20 mM, respectively. Such a procedure, in most cases, can take place either independently of the nanocellulose matrix followed by subsequent mixing or filling (ex-situ) or in the presence of the nanocellulose matrix in the solution to form magnetic nanocomposites (in-situ synthesis of nanocomposites).

Nanoparticles dispersed in a cellulose matrix afford one of the important classes of nanocomposites. Embedding nanoparticles in such a nanostructured network possibly reduces particle aggregation and also provides a pathway to control morphological, structural and consequently magnetic properties of the

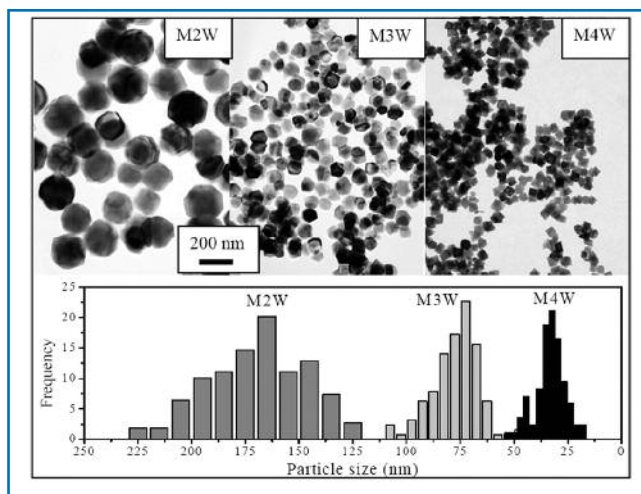


Figure 2. TEM images and histograms of Fe_3O_4 nanoparticles produced at three different Fe (II) concentrations; $[\text{OH}^-]_{\text{ex}} = 0.2$ mM (M2W), 2 mM (M3W), and 20 mM (M4W) [Credit: Andres, et al. *Journal of Physics D-Applied Physics*, 41(13), 2008].

material. Therefore, the volume fraction of the magnetic particles and the structural and textural properties of the matrix are also factors that determine the overall magnetic performance. Furthermore, the interaction between particle surface and parent matrix plays a fundamental role as is the case in any composite material system, to maintain the materials' integrity. To fabricate nanocomposites, the cellulose fibers and magnetic nanoparticles are brought together via processes that mainly include lumen-loading [4,7] and in-situ synthesis [2,8]. The former physically fills the lumen of fibers with particles, which often results in a heterogeneous composite with deleterious particle dispersion, aggregation and therefore inferior performance. In contrast, the latter co-deposits both matrices and particles simultaneously from a premixed precursor and thus offers more homogeneous and uniform composites.

In ex-situ methods to fabricate such a nanocomposite, one common procedure is integrating pre-synthesized Fe_3O_4 particles into the lumens of disintegrated cellulose fibers with the aid of certain retention agent [4,7]. After impregnation with an agitation and washing step to remove unwanted particles, the pulp is pressed to form nanocomposite paper. This approach allows filler particles to be introduced exclusively into the lumen of the fibers while leaving the external surfaces free of filler. The filler is protected by the cell wall from dislodgement during paper-making and the particles do not interfere with interfiber bonding. In addition, the resultant material showed relatively higher saturation magnetization and coercivity. However, the particles are spatially aggregated presumably due to the effect of the magnetic dipole within the short range. This represents a phenomenon commonly encountered in particle nanocomposites. Moreover, this morphology also lower the mechanical properties, such as tensile strength and results in brittle material as compared to the host matrix.

To circumvent these problems, a research team in New Zealand prepared the hybrid nanocomposites using a different route [8]. In their process, magnetic cellulose fibers were generated by coat-

ing bleached Kraft fibers from the Monterey pine (*Pinus radiata*) with 12–26 nm magnetite nanoparticles in an aqueous suspension via a series of agitation, filtration, washing and sonication steps. One significant finding, as both their X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD) analyses revealed, was that a new bonding phase α -FeOOH was formed at the interface between the Fe_3O_4 particles and cellulose fibers. The formation of such a bridge is crucial to the integrity of heterogeneous hybrid materials in processing and practical applications. In the meanwhile, it allows the inherent properties of the fiber, e.g. tensile strength and flexibility, to be retained while enabling the magnetic properties to the matrix material. In addition, mapping chemical composition with energy dispersive X-ray spectroscopy (EDS) indicated that the surface of the fibers were completely and uniformly encapsulated by the nanoparticles. This flexible nanomagnetic material has much potential in engineering a variety of new concepts and applications, such as in security papermaking and packaging, information storage, electromagnetic shielding, magnetographic printing and magnetic filtering.

In recent research aiming at a biomedical application, an innovative approach, that allows for a more controlled nanostructured morphology and geometrical shape, was developed by a Chinese group. In their study [2], cellulose drops in a precooled aqueous solution of sodium hydroxide and urea were utilized to first form regenerated cellulose microspheres (RCS) using sol-gel process. These porous beads were then used as template microreactors permitting in situ co-precipitation of Fe_3O_4 nanoparticles into the cellulose pores of RCS in a solution mixture of FeCl_4 and FeCl_2 to finally form magnetic Fe_3O_4 /cellulose microspheres (MRCS). This process is able to create MRCS about 6 μm in diameter with embedded 20 nm nanoparticles. Transmission electron microscopy (TEM) clearly shows that embedded Fe_3O_4 nanoparticles were dispersed uniformly inside MRCS matrix at certain spacings. These ideal nanostructures ensure that the micron-sized cellulose beads maintain the superparamagnetic property as indicated by observed very small hysteresis loop and low coercivity with a vibrating sample magnetometer (VSM). It is worth noting that superparamagnetic or paramagnetic property is one of the most desirable features in current miniaturized bead-based high-throughput biomedical and biological screening and diagnostics. Such beads can be magnetized and attracted to that field in the presence of an external magnetic field; however, they will not retain any magnetization when the external field is removed and can flow with the carrier medium like non-magnetic beads. Therefore, a large variety of novel lab-on-a-chip devices are designed and implemented because of the ability for fully manipulating with above-mentioned on/off characteristics [2]. **Figure 3** summarizes the characterization of the materials at varied Fe_3O_4 contents. As an embodiment, the authors successfully demonstrated the magnetic-induced transference for improving targeting protein delivery and release using these nanocomposite beads.

Very recently, an interesting advance in the development of cellulose nanofibril template materials may further enable nanocomposites to have tunable properties and open up many

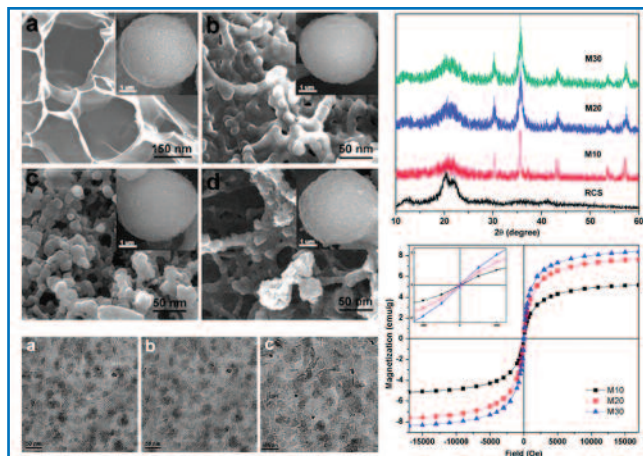


Figure 3. Summary of the RCA and MRCS characterization **Upper left:** SEM images showing surface morphology and magnetic cellulose microspheres at Fe_3O_4 contents of (a) 0, (b) 10.2%, (c) 13.9% and (d) 19.6%. **Lower left:** TEM images of magnetic microspheres at Fe_3O_4 contents of (a) 10.2%, (b) 13.9% and (c) 19.6%. **Upper right:** XRD patterns of RCS, MRCS at particle contents of 10.2% (M10), 13.9% (M20) and 19.6% (M30). **Lower right:** Magnetic hysteresis curves of magnetic microspheres at particle contents of 10.2% (M10), 13.9% (M20) and 19.6% (M30) [Credit: Luo, et al. *Journal of Materials Chemistry*, 19(21):3538–3545, 2009].

new multifunctional utilities [9]. A group of researchers from Sweden, Morocco, Spain and Finland developed a simple yet useful approach to exploit nanofiber scaffolds as a template for in-situ chemical reactions to form Co nanoparticles. They used freeze-dried bacterial cellulose nanofiber to generate a tunable multifunctional nanocomposite. The approach allowed magnetic hydrogels that are highly porous, flexible and responsive to the external magnetic field to be generated. Moreover, by pressing the aerogel under pressure, another form, a very stiff and highly magnetic nanoparticle content nanopaper, can be readily obtained. **Figure 4** shows cellulose magnetic nanocom-

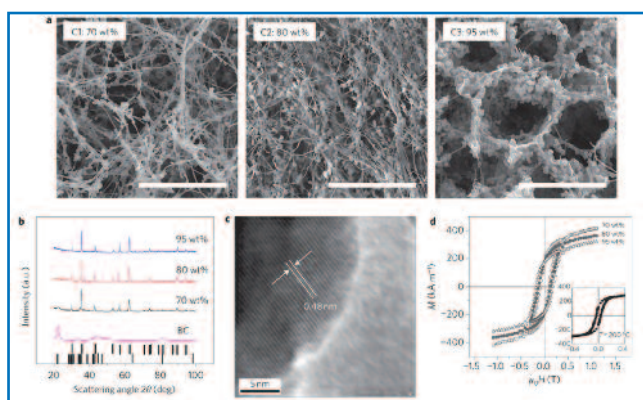


Figure 4. Cellulose magnetic nanocomposite aerogels at varied loadings of cobalt ferrite nanoparticles. (a), SEM images (from left to right): sample C1 (70 wt% of particles), sample C2 (80 wt% of particles) and sample C3 (95 wt% of particles). Scale bars, 4 μm . (b), XRD patterns for the different C1, C2 and C3 compositions. (c), HRTEM image of a single particle from sample C3, and (d), Magnetic hysteresis loops of cobalt-ferrite-based aerogels. Inset: hysteresis loop of cobalt ferrite-based C2 at $T/4200$ 8C. [Credit: Salazar-Alvarez, et al. *Nature Nanotechnology*, 5:584–588, 2010].

posite aerogels at varied loadings of cobalt ferrite nanoparticles and characterization. These initial successes of versatile functionalities suggested many potential applications ranging from novel microfluidics devices to electronic actuators to security documentation.

In spite of these rapid progresses, the green magnetic nanomaterials field is largely new, as evidenced by few studies on the fundamental issues, such as interfacial interaction of the cellulose matrices and inorganic nanoparticles [8], as well as manipulation of the nanostructured components, as compared to a rather large body of research in conventional polymer/cellulose nanocomposite materials. One major hurdle is the lack of understanding to the interfacial behavior between nanocellulose fiber and inorganic particles. The heterogeneous dispersion of the nanoparticles is also detrimental to the integrity of the resulting composites and therefore limits mechanical loading, adhesion, and local magnetic performances. To overcome such problems, a quick but not simple solution may be the use of core/shell nanoparticles since both core/shell (e.g. made from polymers or silica) and shell/cellulose interactions were relatively well studied for many systems. For example, several chemical modification mechanisms using coupling agents, such as organosilanes [10], and aminopropyl-triethoxysilane (APTES), have been explored to modify the interfacial behaviors of the dispersions and matrices. Since both surfaces of the cellulosic fiber and the silica shell present hydroxyl groups, it is expected that the issue can be addressed by investigating and establishing an optimal partial silanization protocol to not only achieve strong covalent or other interfacial bonding strategies but to improve particle dispersion as well. However, precautions have to be taken as this may complicate the fabrication process and alter the properties of the final nanocomposite materials.

The cellulose/magnetic nanoparticle composite technology holds great promise in offering both multiple functionalities and economical. Not only is cellulose abundant, renewable, biodegradable, but the production process is also simple, so it is very likely to become an economically viable technology, in addition to having profound benefits to sustainable technology and also to our environment. With the versatile properties and a large variety of potential applications revealed in early developments, these new materials have the potential to impact many advanced multifunctional areas such as electromagnetically driven printing, "smart" magnetic biochips, novel localized drug delivery and other applications yet to be envisioned. Furthermore, this research area is expected to grow rapidly, and dramatic improvements in materials' functions will be achieved in the years to come, especially in furthering advanced applications as well as the pursuit of environmentally friendly green technologies worldwide.

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About our guest contributing editors:

Tao Wang, Ph.D., is a research assistant professor at the Center for Nano Science and Technology (NDnano) and Department of Electrical Engineering at the University of Notre Dame. He has previously conducted research at Louisiana State University and RWTH Aachen, Germany and has also worked as a microsystems engineer at Mezzo Technologies, Inc. His research interests focus on nanomaterials, integrated lab-on-a-chip systems with optical or magnetic manipulation, and MEMS devices. T. Wang received his Ph.D. degree in materials science at the University of Wisconsin - Madison Center for Nanotechnology.

Zhiyong Cai, Ph.D., P.E. is a Project Leader of Engineered Composite Science at USDA Forest Products Laboratory and Adjunct Professor at University of Tennessee. He received his BS in Physics from East China Normal University, MS in Wood Science from Nanjing Forestry University, and Ph.D. in Wood Science and Engineering from Purdue University. He is responsible for developing new and improved composites from wood and other non-wood fiber sources using thermoset, thermoplastic, inorganic and other naturally-derived binders. He is also interested in new applications of nano-cellulose composites.

Lei Liu, Ph.D., received the B.S. and M.S. degrees in electrical engineering from Nanjing University, Nanjing, China, in 1998 and 2001, respectively, and the Ph.D. degree in electrical engineering from the University of Virginia, Charlottesville, VA, in 2007. From 2007 to 2009, he was a Post-Doctoral Research Associate with the Department of Electrical and Computer Engineering, University of Virginia. In September 2009, he joined the faculty of the University of Notre Dame, as a Research Assistant Professor of electrical engineering. He is also a research faculty fellow with the Advanced Diagnostics and Therapeutics Initiative (AD&T) of the University of Notre Dame. His research interests include millimeter- and sub-millimeter-wave device and circuit design, modeling, and testing, quasi-optical techniques, terahertz detectors for imaging and spectroscopy, novel microwave materials and devices, superconducting electronics, microfabrication and processing.

Comments and criticisms may be sent to:
abiswas@nd.edu or ibayer1@uiuc.edu