International Journal of Engineering Research and Development
e-ISSN: 2278-067X, p-ISSN: 2278-800X, www.ijerd.com
Volume 10, Issue 8 (August 2014), PP.01-07

Nanostructured Paper for Flexible Energy

[1]Venkata Veera Lohit.M, [2]M.V.Tharun Kumar Reddy, Jonnalagadda Gayatri[3]
[1,2,3]Department of Electronics and communication engineering, SCSVMV University, Kanchipuram, Mobile Ph. +919498025217,

Abstract: Cellulose is one of the most abundant organic materials on earth, and cellulose paper is ubiquitous in our daily life. Re-engineering cellulose fibers at the nanoscale will allow this renewable material to be applied to advanced energy storage systems and optoelectronic devices. In this article, we examine the recent development of Nano fibrillated cellulose and discuss how the integration of other nanomaterial's leads to a wide range of applications. The unique properties of Nano fibrillated cellulose enable multi-scaling structuring of the functional composites, which can be tailored to develop new concepts of energy and electronic devices. Tapping into the nanostructured materials offered by nature can offer many opportunities that will take nanotechnology research to a new level.

Keywords: Cellulose, Conductive paper, CNT, NFC, Nano cellulose paper, Nano fibrils, Silicon electrode, Ultra capacitors

I. INTRODUCTION

For thousands of years, cellulose paper has been a major medium for displaying and transmitting information in many parts of world. Its chemical and mechanical stability under unmatched by other materials used in large abundance. Cellulose, the major component of paper, can be obtained from plants and represent one of the most abundant organic materials on earth.

In the past decade, research on nanostructures of cellulose has increased dramatically due to the potential applications in electronics, biosensors, and energy storage devices. Large scale, energy-efficient production of nano fibrillated cellulose (NFC) has recently become possible by employing various physical chemical and enzymatic pretreatment methods before the homogenization step. In parallel, the development of nanostructured inorganic materials in the form of nanocrystls, nanowires and nanotubes provides a list of functional inks for integration into paper.

Cellulose by itself is usually limited in functionalities. However, three-dimensional (3D) hierarchical structures formed by cellulose fibers at different length sacks, combined with the ability to accommodate their functional materials, open up many opportunities for applications in electrical, electromechanical, and optical devices.

The focus of this article is to progress in the development of energy and electronics devices fabricated using wood fiber cellulose as the building block in conjunction with other nanomaterials. The first part of this article will focus on the hierarchical structure of wood cellulose, as well as the fabrication and properties of paper. In particular, regular cellulose fibers with a diameter of ~20 μm and nano cellulose fibers with a diameter of ~20 nm will be discussed in detail. The second part will focus on the recent development of conductive paper for energy devices, particularly for ultracpacitors and batteries. The last part will focus on the development of transparent nano cellulose paper and its potential applications in electronics and optoelectronic devices.

II. CELLULOSE: THE BUILDING BLOCK

The cell wall of wood has a fascinating 3D hierarchical structure designed to maximize the stability and durability of the trees. The wood fiber is made up of the crystalline cellulose nanofibrilis (around 40 wt% of the wood), random amorphous hemicellulose (around 25 wt% of the wood), and organic "glue" lignin (around 30 wt% of the wood) that cross-link different polysaccharide in wood to form a strong and durable structure. At the molecular scale, the cellulose polymer molecules have a linear chain structures consisting of glucose repeating units with many hydroxyl groups. They pack into cellulose crystals with dimensions of a few A, which in turn are organized into nano fibrils with a diameter around 4nm and a length over 1μm. These nan fibrils aggregate into bundles with cross-sectional dimensions of around 20nm × $20nm^2$, which further combine to form a cylindrical wood fiber with a length of 1-3 mm, a diameter of 20-50 μm, and a fiber wall thickness of about 4μm (Figure 1a). In its natural state, the delignified fiber wall has a specific surface area around $100m^2/g$, The fiber wall collapse during drying, and the specific surface areas decreases to around $1m^2/g$. The rich

structural motifs of wood fiber cellulose are different scales make them attractive for 3D structural manipulation.

To design the next generation high performance fibril- based paper regular fibers with ~20µm diameter need to be disintegrated into NFC(Figure 1b).Turbak et al. first reported the production of NFC, with diameter of 2-3 nm and a length of 1-2 µm, by using high pressure mechanical disintegration of wood pulp. Excess energy consumption in the homogeneous process was one of the major drawbacks that limited practical applications of this material. It was later shown that the introduction of charged functional groups by carboxymethylation prior to mechanical disintegration enhanced the swelling of the fiber wall, and hence decreased the energy consumption of the fiber disintegration process. The new approach can decrease energy consumption by approximately ten times when comparing to the traditional Methods that do not employ the pretreatment.

III. ENERGY STORED WITH CONDUCTIVE PAPER

The 3D hierarchical structure of cellulose paper is very interesting for an energy storage system that involves liquid electrolytes, since the interconnected porosity allows fast access of ionic species to the electrode surfaces. In order to render electrical conductivity in cellulose paper, conducting materials such as conductive metal oxide, graphene, carbon nanotubes (CNTs), metal nanowires, and conductive polymers can be integrated (**Figure 2**). The conductive materials can be introduced into paper at different length scales, from molecular mixing with a cellulose polymer to surface coating on photocopy paper.

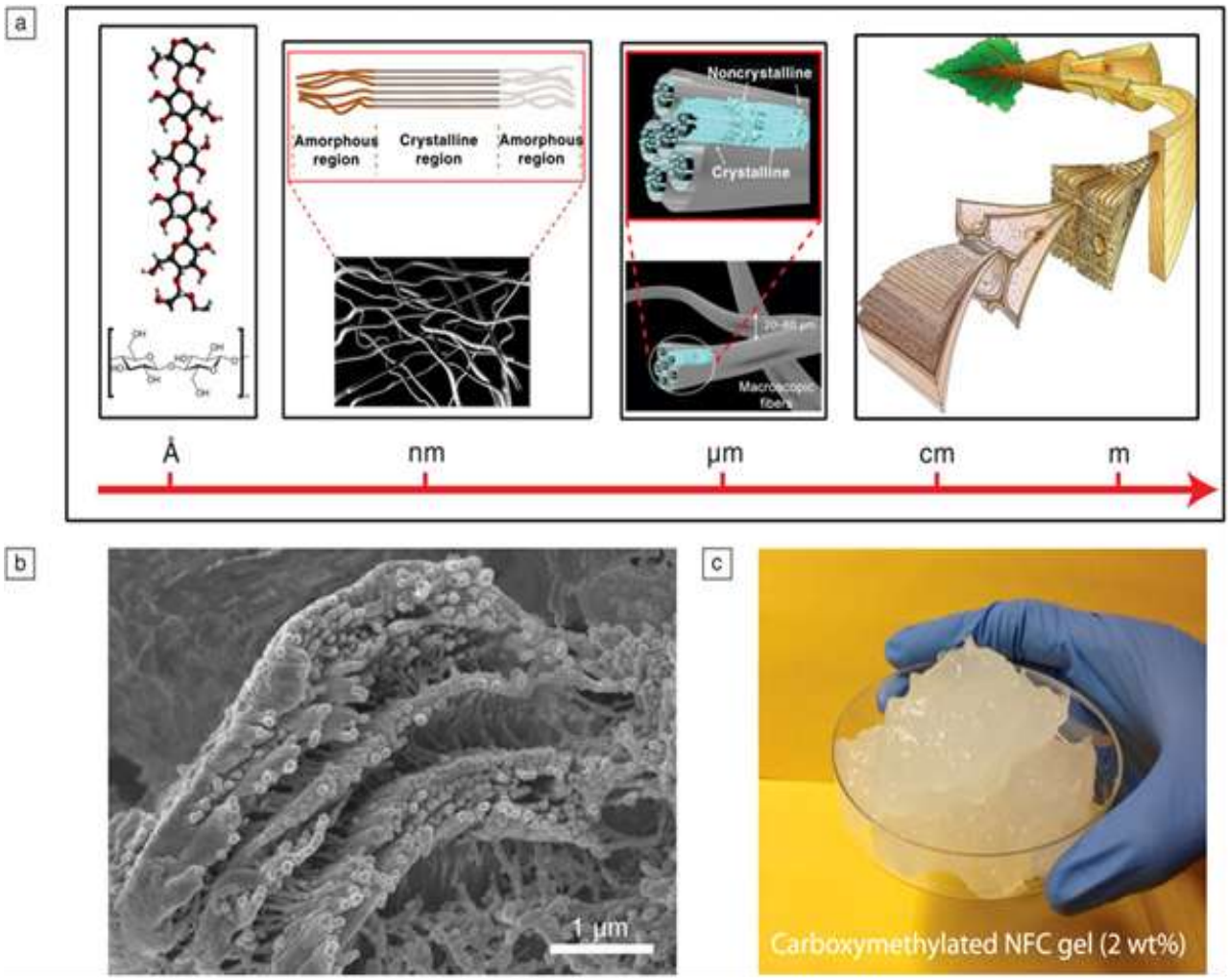

Figure 1. Structure of cellulose fiber. (a) Schematic to show the hierarchical structure of cellulose from the wood cell wall to micro fibrillated fiber to nano fibrillated fiber to a cellulose molecule. Image courtesy of Mark Harrington. © 1996 University of Canterbury. (b) Nano cellulose fibrils (with a square cross-section of around 20 × 20 nm^2) within the open wet fiber wall, where the lamellar organization of fibrils in the fiber wall is obvious © 2011 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim. (c)

Photograph of nano fibrillated cellulose (NFC) gel at 2 wt% in water.

CNTs are particularly versatile in binding with cellulose. Ajayam and coworkers developed a method to dissolve unmodified cellulose fibers in a room temperature ionic liquid, 1-buty1, 3-methylimidazolium chloride ([bmIm][CI]). The cellulose solution was then coated onto vertically grown CNTs to form the conductive paper, which can be used as an electrode for super capacitors and lithium-ion batteries (Figure 3a).

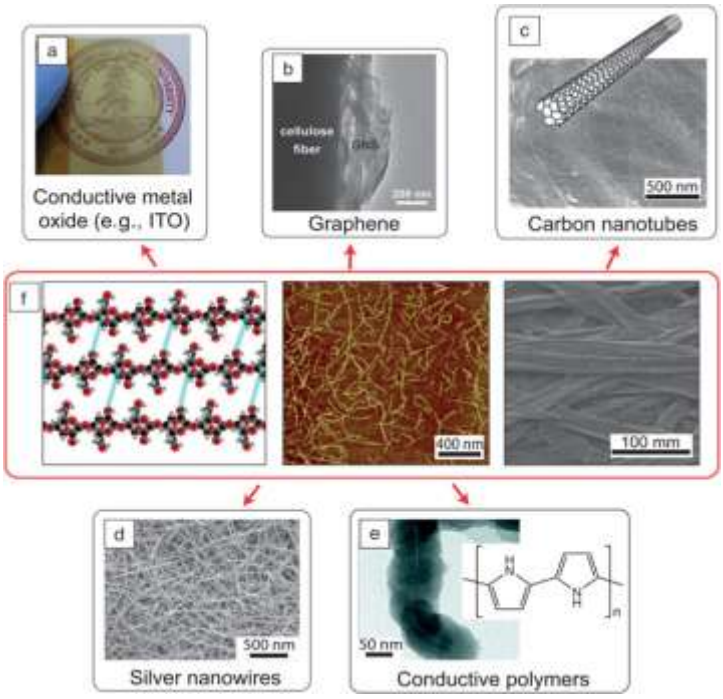

Figure 2. Diagram showing conductive materials, such as (a) tin doped indium oxide (ITO) © 2013 Royal Society of Chemistry. (b) Graphene © 2011 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim. (c) Carbon nanotubes and (d) silver nanowires © 2009 National Academy of Sciences. (e) Conductive polymers©2009 American Chemical Society, can be integrated into cellulose at different scales (f), ranging from the molecular level to nanofibrilis, and the microfiber level.

At the nanofibrilis scale, the similarity in dimensions of the nanocellulose fibers and CNTs allows uniform mixing of the two materials resulting in highly conductive porous composite suitable for high surface area electrodes (Figure 3b). Conductive

Polymers are also widely used to coat nanocellulose fibers, Polypyrrole has been found to wet cellulose very well, and polymerization of pyroles on the surface of cellulose fibers. Coating of cellulose fibers aerogel was demonstrated by using a polyniline-dodeeyl benzene sulfonic acid doped solution in toluene. The use of an organic solvent allows the high porosity of the aerogel to be preserved.

Alternatively simple Meyer rod coating of CNT ink onto commercially available photo copy paper was shown to be highly effective in producing conductive paper with a sheet resistance of around 10 ohm/sq. (Figure 3c). (The Meyer rod is a stainless steel rod that is wound tightly with wires of a certain diameter. The rod is usually used for conformal coating of solution based materials on a flat substrate.)

The high conductivity was attributed to the strong solvent absorption properties of the porous paper structure and the conform; coating of flexible CNTs on the cellulose fibers to form continuous electrical conduction pathways, This fabrication method is also applicable to coating nanowires such as silver ink onto cellulose paper. Filtration methods were used to deposit graphene on filter paper to produce conductive paper for ultra-capacitors.

Conductive paper made from cellulose fibers and CNTs demonstrate excellent mechanical properties, In the case of CNT coated photocopy paper, the sheet resistance increased only slightly (<5%) after the conductive paper was bent to a 2mm radius 100 times. In contrast, conductive paper fabricated with a metal evaporation coating does not with stand bending very well, and the sheet resistance in this case increased by 50% after three bending cycles to a radius of 2mm. The graphene cellulose paper was shown to with stand high tensile stress up to 8.6 Mpa. The increase in resistance was relatively small (<5%) when the change in strain was around 2%.

Due to hydrophilicity of cellulose fibers, conductive paper has been widely used as electrodes for ultra-capacitors with aqueous electrolytes. Unmodified CNTs and graphene are hydrophobic, and their application in ultra-capacitors have been hindered by poor electrolyte wetting. By using cellulose as a substrate for the carbon matrix, aqueous electrolyte contact. For lithium ion battery applications, the use of conductive cellulose paper offers new opportunities in fabricating highly flexible electrodes and battery systems.

The unique structure of conductive cellulose paper made from ionic liquid and CNTs (Figure 3a) allows the working electrode and separator to be combined in a single sheet of paper. A simple symmetrical ultra-capacitor was built by combining two such electrodes and using KOH as an electrolyte. For fabricating lithium ion batteries, lithium ion battery exhibited a specific capacity of around 110 mAh/g.

Mixing CNTs directly with NFC allows for better tuning of the 3D structure of the composite. Upon freeze drying the mixture a highly conductive cellulose aerogel can be fabricated (Figure 3b). Further deposition of silicon onto the nanofibrilis cellulose using plasma-enhanced chemical vapor deposition can produce a highly flexible silicon electrode, which has stable cycling at around 1500mAh/g for more than 100 cycles.NaCL- based ion exchange batteries were demonstrated using polypyrrole coated nano cellulose fibers as electrodes. Since polypyrrole can absorb and expel chloride ions during the oxidation/reduction process, the reversible proce4ss is utilized to store energy. The batteries have reasonable capacity of around 25-33mAh/g.

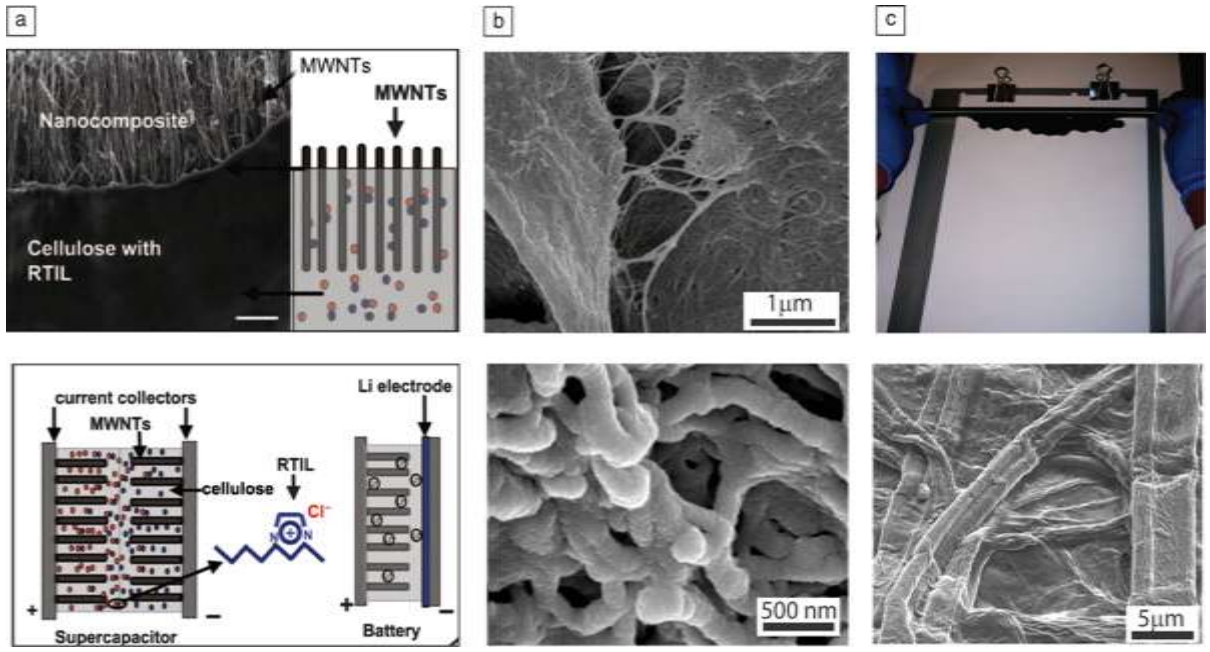

Figure 3: Fabrication of the nanocomposite paper for super capacitor and battery applications. (a) Room-temperature ionic liquid (RTIL) derived cellulose/carbon nanotubes (CNTs) composite with the cross-sectional SEM image showing multi-walled nanotubes (MWNTs) protruding from the thin films. (Scale bar is 2 μm.) The schematic displays the partial exposure of MWNT (top) and the structures of the ultracapacitor and lithium-ion batteries fabricated using the conductive paper (bottom) © 2007 National Academy of Sciences. (b) Nanofibrilis cellulose/CNT thin film derived from filtration of the solution mixture (top) and after coating of silicon by chemical vapor deposition (bottom) © 2013 Elsevier.) (c) Meyer-rod coating of CNTs solution onto photocopy paper and the corresponding SEM image showing the micron-sized fibers (bottom). © 2009 National Academy of Sciences.

Coating CNTs directly on commercial photocopy paper offers a simpler approach for producing a highly conductive paper substrate. The high porosity of the paper allows rapid absorption of the conductive paper substrate. The high priority if the paper allows rapid absorption of the conductive inks. Conductive paper coated with $Li_4Ti_5O_{12}$ and $LiMn_2O_4$ demonstrated stable performance for more than 50 cycles. Although full cell performance still needs to be improved, the paper based electrodes provide a high mechanical flexibility. The CNT coated photocopy paper also showed excellent performance as an ultra-capacitor electrode (Figure 4a), with a specific capacitance of 200F/g and stable cycling of over 40,000 cycles (Figure 4b). The graphene cellulose paper electrode also demonstrated a high specific capacitance of 200 F/g and retained >99% capacitance over 5000 cycles. In other simple approach, ultracapcitors were fabricated by a simple pencil drawing of graphite onto both sides of cellulose paper. In an aqueous electrolyte, the device showed good areal

capacitance of around 2.3 mF cm^{-2} and up to 15,000 cycles of charge/discharge, with more than 90% capacitance retention. The relatively good electrochemical stability of paper, combined with the low cost and good compatibility with other nanomaterials, provide a new opportunities in applying the renewable material to advanced energy storage systems.

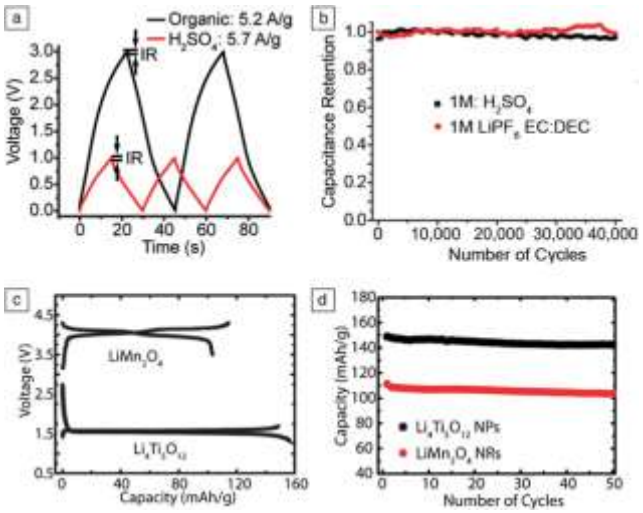

Figure 4. (a) Galvanostatic charging/discharging curves of carbon nanotube (CNT)/paper ultracapacitor with organic electrolytes and sulfuric acid. (b) Capacitance retention of the ultracapacitor in different electrolytes. (c) Galvanostatic charging/discharging of $LiMn_2O_4$ and $Li_4Ti_5O_{12}$ electrodes using the photocopy paper/CNT composite as a current collector. (d) Cycling performance of the $LiMn_2O_4$ and $Li_4Ti_5O_{12}$ electrodes © 2009 National Academy of Sciences.

IV. TRANSPARENT NANOCELLULOSE PAPER FOR ELECTRONIC AND OPTOELECTRONIC DEVICES

The use of nanocellulose paper as a "green" substrate for electronic and optoelectronic devices has attracted board attention. Commercial paper has a relatively rough surface and weak mechanical properties, which can be problematic for electronic devices fabrication. The porosity and thus the refractive index variation inside the paper substrate opaque. Re-engineering paper substrates using NFC as the building blocks can address the previously mentioned problems. To prepare nanocellulose paper from NFC, a simple vacuum filtration method can be used, followed by oven drying ,pressing, or freezing, transparent, mechanically strong and has an extremely low coefficient of thermal expansion. Yano et al. demonstrated the fabrication of transparent nanocellulose paper, which showed optical transmittance up to 70% (figure 5a).

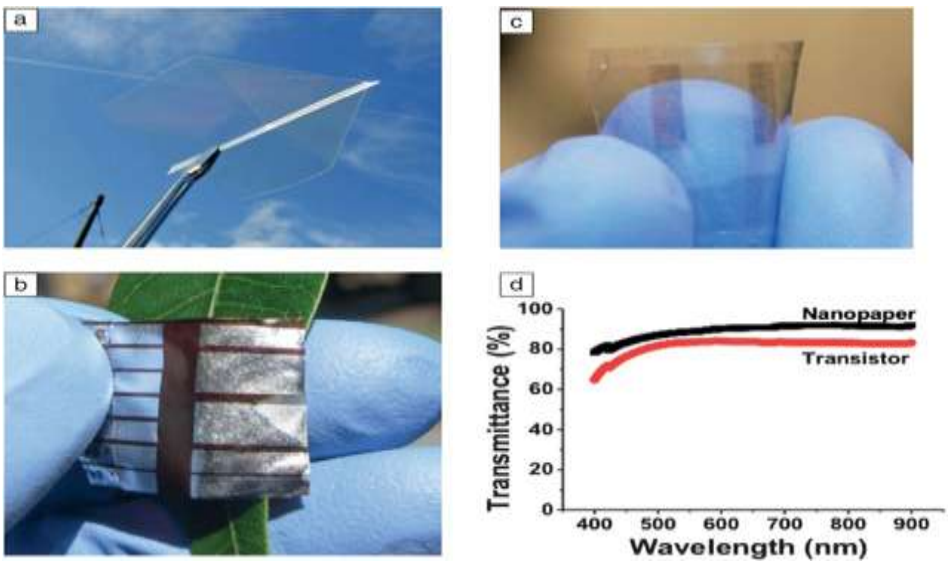

Figure 5. (a) Transparent nanocellulose paper made of cellulose nanofibers © 2009 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim. (b) An organic photovoltaics device on transparent nanocellulose paper © 2013 Royal Society of Chemistry. (c) A picture of a transparent and flexible nanocellulose paper transistor. (d) Comparison of the optical transmittance of nanopaper and a nanopaper transistor © 2013 American Chemical Society.

Using TEMPO oxidized NFC, nanopaper with higher transmittance (84-89%) can be obtained (Figure 5d). The optical transmittance of nano paper can be tailored by varying the diameters of the NFC nanofibers. Meanwhile, nanocellulose paper is generally as light weighted as regular paper but with a much higher young's modulus. Figure 6 shows an ash by plot of specific modulus and strength. Since nano cellulose paper has no binder or any other

Additives, it belongs to the "D" zone of the CN neat film, where the specific stiffness and strength can go up to 20GPa (gcm-3)-1 and 300 Mpa (g cm-3)-1, respectively. Sehaqui et al. showed that elastic modulus of nano cellulose paper can reach 33GPa after fiber alignment.

The excellent optical transmittance and mechanical strength of nanopaper, together with the roll to roll printing process, will allow the next generation flexible electronics and optoelectronics devices to be integrated on the renewable material. Electronic and optic electronic devices based on transparent nanocellulose paper and printing techniques have been recently demonstrated. Figure 5c shows a picture of a fully transparent organic field-effect transistor fabricated on nano cellulose paper. The transmittance of the devices s 83.5% at 550nm (Figure 5d). The transistor also shows excellent mechanical properties, with only around a 10% decrease in mobility when the device was bent in directions parallel or vertical to the conduction channel. Organic photovoltaics on transparent nanocellulose paper has also been demonstrated. (Figure 5b). Other important devices such as integrated transparent sensors and 3D devices, may also fabricated on nanocellulose paper. As potential replacement for plastic substrates, nanocellulose paper holds great promise to fabricating fully integrated flexible electronics and displays with unique properties, and at the same time is compatible with high throughout process such as roll-to-roll printing.

V. CONCLUSION

In this article, we have reviewed recent progress in the application of nanocellulose paper for flexible energy storage and electronic devices. Broadly speaking, there are three major building blocks that can be derived from cellulose: regular fiber with an average diameter of 20μm, nanocellulose fibers with a diameter of ~20nm, and molecular scales of cellulose molecules.

Conductive paper made from cellulose fibers of 20μm in diameter can function in a new type of current collector that enables high-performance paper ultra-capacitors and li-ion batteries. Another emerging area is the development of nanocellulose paper, which is made of nanometers, such nanocellulose paper is highly transparent, smooth, and mechanically strong, allowing applications in a range of flexible energy and electronics devices. Proof-of-concept devices such as transistors and organic photovoltaics have been demonstrated. The combination of cellulose fibers and nanofabrication techniques heralds a new era of green electronics that can be manufactured using high throughput printing technology.

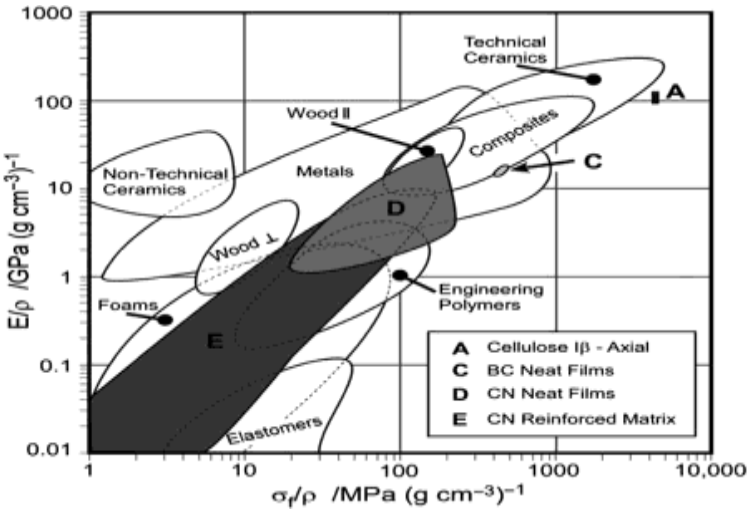

Figure 6. Ashby plot of specific modulus (E/ρ) versus specific strength (σf/ρ) © 2011 Royal Society of Chemistry.

REFERENCES

[1] D. Klemm, F. Kramer, S. Moritz, T. Lindström, M. Ankerfors, D. Gray, A. Dorris, Angew. Chem. Int. Ed.**50**, 5438 (2011).

[2] R.J. Moon, A. Martini, J. Nairn, J. Simonsen, J.Youngblood, Chem. Soc. Rev. **40**, 3941 (2011).

[3] D. Tobjörk, R. Österbacka, Adv. Mater. (Weinheim, Ger.)**23**, 1935 (2011).

[4] L. Nyholm, G. Nyström, A. Mihranyan, M. Strømme, Adv. Mater. (Weinheim, Ger.) **23**, 3751 (2011).

[5] Russo, B.Y. Ahn, J.J. Adams, E.B. Duoss, J.T.Bernhard, J.A. Lewis, Adv. Mater. (Weinheim, Ger.) **23**, 3426 (2011).

[6] L. Hu, J.W. Choi, Y. Yang, S. Jeong, F. La Mantia, L.-F. Cui, Y. Cui, Proc. Natl. Acad. Sci. U.S.A. **106**, 21490 (2009).

[7] C.Q. Peng, Y.S. Thio, R.A. Gerhardt, Nanotechnology 19, 1 (2008).

[8] Z. Weng, Y. Su, D.-W. Wang, F. Li, J. Du, H.-M. Cheng, Adv. Energy Mater. **1**, 917 (2011).

[9] Y.-L. Tai, Z.-G. Yang, J. Mater. Chem. **21**, 5938 (2011).

[10] Sjostrom, Wood Chemistry-Fundamentals and Applications (Academic Press, San Diego, 1993).

[11] G.Annergren,L.Wågberg,inFundamentalsof Papermaking Materials, Transactions of the Fundamental Research Symposium, C.F. Baker, Ed. (Pira International, Cambridge, UK, 1997).

[12] A.F. Turbak, F.W. Snyder, K.R. Sandberg, J. Appl. Polym. Sci. Appl. Polym. Symp. **37**, 815 (1983).

[13] L. Wågberg, L. Winter, L. Ödberg, T. Lindström, Colloids Surf. **27**, 163 (1987).

[14] A.B. Fall, S.B. Lindström, O. Sundman, L. Ödberg, Wågberg, Langmuir **27**, 11332 (2011).

[15] T. Saito, S. Kimura, Y. Nishiyama, A. Isogai,

a. Biomacromolecules **8**, 2485 (2007).

[16] T. Saito, Y. Nishiyama, J.-L. Putaux, M. Vignon, A. Isogai, Biomacromolecules, **7**, 1687 (2006).

[17] L. Hu, G. Zheng, J. Yao, N. Liu, B. Weil, Y. Cui, M. Eskilsson, E. Karabulut, L. Wågberg, Z. Ruan, S. Fan, J.T. Bloking, M.D. McGehee, and Energy Environ. Sci. **6**, 513 (2013).

[18] G. Nystrom, A. Razaq, M. Strømme, L. Nyholm, A. Mihranyan, Nano Lett. **9**, 3635 (2009).

[19] V.L. Pushparaj, M.M. Shaijumon, A. Kumar, S. Murugesan, L. Ci, R. Vajtai, R.J. Linhardt, O. Nalamasu, P.M. Ajayan, Proc. Natl. Acad. Sci. U.S.A. **104**, 13574 (2007).

[20] L. Hu, N. Liu, M. Eskilsson, G. Zheng, J. McDonough, L. Wågberg, Y. Cui,Nano Energy **2**, 138 (2013).

[21] D.O. Carlsson, G. Nystrom, Q. Zhou, L.A. Berglund, L. Nyholm, M. Stromme, J. Mater. Chem. **22**, 19014 (2012).

[22] M. Paakko, J. Vapaavuori, R. Silvennoinen, H. Kosonen, M. Ankerfors, T. Lindstrom, L.A. Berglund, O. Ikkala, Soft Matter **4**, 2492 (2008).

[23] G. Zheng, L. Hu, H. Wu, X. Xie, Y. Cui, and Energy Environ. Sci. **4**, 3368 (2011).

[24] M. Nogi, S. Iwamoto, A.N. Nakagaito, H. Yano, Adv. Mater. (Weinheim, Ger.)**21**, 1595 (2009).

[25] A.N. Nakagaito, M. Nogi, H. Yano, MRS Bull. **35**, 214 (2010).

[26] R.T. Olsson, M.A.S. Azizi Samir, G. Salazar Alvarez, L. Belova, V. Strom, L.A. Berglund, O. Ikkala, J. Nogues, U.W. Gedde, Nat. Nanotechnology. **5**, 584 (2010).

[27] H. Sehaqui, A. Liu, Q. Zhou, L.A. Berglund, Biomacromolecules **11**, 2195 (2010).

[28] H. Sehaqui, N. Ezekiel Mushi, S. Morimune, M. Salajkova, T. Nishino, L.A. Berglund, ACS Appl. Mater. Interfaces **4**, 1043 (2012).

[29] J. Huang, H. Zhu, Y. Chen, C. Preston, K. Rohrbach, J. Cumings, L. Hu, ACS Nano, doi: 10.1021/nn304407r (2012).

[30] H. Zhu, S. Parvinian, C. Preston, O. Vaaland, Z. Ruan, L. Hu, L. Hu, Nanoscale(2013), doi: 10.1039/C3NR00520H.