Supporting Information

On the mineralization of nanocellulose to produce functional hybrid materials

Luis Valencia[a*], Rishab Handa[b], Susanna Monti[c], Alma Berenice Jasso-Salcedo[d], Dimitrios Georgouvelas[e], Ilse Magaña[d], Ramón Díaz de León[d], Krassimir P. Velikov[f,g,h], Aji P. Mathew[e] and Sugam Kumar[i*]

[a] *Biofiber Tech Sweden AB, Birger Jarlsgatan 57 C, SE -113 56 Stockholm*

[b] *Experimental Physics, Saarland University, 66123, Saarbrucken, Germany*

[c] *CNR-ICCOM–Institute of Chemistry of Organometallic Compounds, via Moruzzi 1,56124 Pisa, Italy*

[d] *Research Center for Applied Chemistry, Enrique Reyna Hermosillo, No.140, Col. San José de los Cerritos, Saltillo 25294, Mexico*

[e] *Department of Materials and Environmental Chemistry, Stockholm University, Frescativägen 8, 10691, Stockholm, Sweden*

[f] *Soft Condensed Matter & Biophysics, Debye Institute for Nanomaterials Science, Utrecht University, Princetonplein 1, 3584 CC Utrecht, the Netherlands*

[g] *Unilever Innovation Centre Wageningen, Bronland 14, 6708 WH*

[h] *Institute of Physics, University of Amsterdam, Science Park 904, 1098 XH Amsterdam, the Netherlands*

[i] *Solid-State Physics Division, Bhabha Atomic Research Centre, Mumbai, 400 085, India*

*Authors to whom correspond: luisalex_val@hotmail.com; sugam@barc.gov.in

Table S1. Summary of the different characterization techniques utilized to evaluate nanocellulose-based hybrid materials. (References designated as R (e.g. R1 to R20) are given below this table in SI, while rest of the references are present in main manuscript).

Class	Different Techniques	Information obtained	Ref.	Selected example	Advantages/limitations
Spectroscopic techniques	Raman Spectroscopy	Chemical structure of a material, phase, and polymorphism, vibrational energy modes,	124,126, R1,R2	Ref. R2 shows that the hybrid of Ag nanoparticle-decorated bacterial nanocellulose can be used as a 3D flexible substrate for surface-enhanced Raman scattering (SERS)	**Advantages:** Fast, non-destructive, highly specific, no sample preparation required, suitable for several organic and inorganic materials, not interfered by water. **Limitations:** The possibility of fluorescence interference. Laser-induced degradation is possible for sensitive samples. Not suitable for metals and alloys.
	Infrared Spectroscopy (FTIR)	Information about the different functional groups present in cellulose and the modification in them upon hybridization	99,166,177,178,180,182,183, R3-R5	In ref. 99, FTIR spectroscopy confirmed the formation of leaf-like zeolitic imidazolate frameworks (ZIF-L) in nanocellulose foams and interactions therein.	**Advantages:** Fast, non-destructive, highly specific, no sample preparation required. **Limitations**: Some materials absorb Infrared radiation. Difficult to differentiate among functional groups with characteristic peaks in the same spectral range.
	Nuclear Magnetic Resonance Spectroscopy (NMR)	Detail information about the functional groups, topology, three-dimensional structure of molecules as well as dynamics, reaction rate, and environment of molecules	126,R1	In ref. R1, boron–CNF interactions and the chemistry of CNF–Boric acid–sepiolite hybrids were examined by solid-state ^{11}B MAS NMR spectroscopy.	**Advantages:** Non-destructive, highly specific, no sample preparation required. **Limitations**: Determining the structure of high molecular weight molecules is problematic. Only nuclei having magnetic moments can be analyzed. Long times required per analysis.

	X-ray Photoelectron Spectroscopy (XPS)	Elemental composition, and electronic state of all elements in a material (surface chemistry of the material)	124, 159,180,183,R6,R7	In ref. 180, XPS spectra of CNF-MOF have been investigated for evaluating the interactions between the two components.	**Advantages:** Highly sensitive to elements and their valance states, effective for a variety of organic and inorganic materials, sensitive to all elements (except hydrogen and helium) with high sensitivity. **Limitations:** Very surface sensitive, so avoid surface contamination at all cost. Not sensitive to hydrogen and helium. Compatibility of the samples with high vacuum environment is needed
	Energy dispersive X-Ray Spectroscopy (EDS/EDAX/EDX)	Elemental composition	88,99,173,176-178	In ref. 99, the homogenous distribution of the in-situ growth ZIF-L in a gelatin/NC hybrid foam has been demonstrated using EDS mapping.	**Advantages:** Relatively quick elemental analysis and mapping. Sensitive to elements with atomic numbers as low as C, spectra are easily interpretable **Limitations:** Not sensitive to very low Z elements like H, He, Li. Only atomic information, not molecular, limited sensitivity ~ concentrations of the order of 0.1%.
	Extended X-Ray Absorption Fine Structure (EXAFS) and X-ray Absorption Near-Edge Structure (XANES) Spectroscopy	Chemical composition, coordination environment, the identity of neighboring atoms, their distance from the excited atom.	R2	In ref. R2, XANES measurements could confirm the oxidation state of silver nanoparticles in CNC-AgNp hybrids whereas EXAFS could reveal bulk atomic structure (e.g., bond length, interatomic distance) of the AgNP.	**Advantages:** Extremely specific, highly local providing, distribution of atoms only within the first 1-2 shells surrounding the absorber. **Limitations:** Requirement of high intense broad-band x-radiation source (synchrotron), EXAFS pattern will be a superposition of two distinct atoms of the absorber type.
	Photoluminescence Spectroscopy	Photoluminescence response of the hybrids, information about the defect states, band	R8	In ref R8, The trap levels were identified in	**Advantages:** Fast, in-situ measurement.

		gap in semiconducting nanoparticles		hierarchical TiO2 superstructures, formed by mineralization of Cellulose.	**Limitation:** Not generally a quantitative technique, complex data analysis, not all molecules produce fluorescence/luminescence.
	UV-visible Spectroscopy	Evidencing the formation of metallic nanoparticles in the cellulose matrix, measuring the transmittance of hybrid films	[59,63,163,180,280,R5,R9]	In ref. 63, UV-Vis spectra of the plasmonic nanopaper of cellulose-silver nanoparticles are reported.	**Advantages:** Non-destructive, fast, in-situ, particle quantification, sensitive to shape/size of the nanoparticles also, easy to use, minimal processing, inexpensive. **Limitations:** Data interpretation becomes tricky if many species present in the sample absorb light.
	Circular dichroism spectroscopy	Cholesteric liquid crystalline phases of the CNC and modifications in it on hybridization	[61,R9]	In ref. 61, chirality transfer from the host mesoporous CNC film to gold nanoparticles was investigated by circular dichroism studies	**Advantages**: Ease of measurements, small amount required, sample recovery possible. Possible to monitor changes (e.g., conformation, stability, binding) in dif. Environments. **Limitations**: Only qualitative analysis of data. Does not provide atomic-level structure analysis.
Microscopy	Scanning Electron Microscopy (SEM)	Surface structure and morphology, particle size and shape	[88,91,92,99,108,163,R3,R5,R6]	Ref. 99 shows the distribution of MOF on CNF and the impact of charge density on the morphology of the hybrid using SEM	**Advantages:** High-resolution images of a sample surface provide structural parameters as well as morphology. **Limitations:** Need to coat non-conductive samples (e.g., cellulose) vacuum environment, sample preparation is required, possibility of artifacts.
	Transmission Electron Microscopy (TEM)	Structural parameters (shape, size etc.), morphology, chirality, 3D reconstruction	[58,63,R3]	In ref. 58, tilting in cryo-TEM was used to create 3D tomograms of palladium patches deposited onto CNC.	**Advantages:** Magnification of much higher degree than SEM, direct imaging, possibility of electron diffraction.

					Limitations: Requirement of thin sample layer, not very sensitive to the low Z materials, possibility of sample destruction (biological) vacuum environment, sample preparation is required, the possibility of artifacts.
	Atomic Force Microscopy (AFM)	Topographical characterization of surfaces and high-resolution imaging of soft matter and biological samples.	49,167, 130,131, R10,R11	In ref 49, AFM was used to elucidate the in-situ growth of metal oxide nanoparticles on TOCNF thin films.	**Advantages:** A great alternative for beam-sensitive materials (like most soft matter). 3D imaging is possible, can be used in vacuum as well as in air and liquid. Provides details of the surface, able to perform force measurements between particle-particles and particle-surface. **Limitations:** Scanning speed is significantly slower than other advanced microscopes, such as SEM. Small scan image size.
	Confocal microscopy	3D images of surface textures and objects. Selective staining using fluorophores allows visualizing structures of interest within a specimen.	R10,R12, R13	In ref R13, the nanocellulose-titania hybrids have been examined for cell transplantation support material, by studying cell viability using confocal laser scanning microscope.	**Advantages:** Very low and controllable depth of field, elimination of background away from the focal plane, and ability to collect serial optical sections. Higher contrast and definition, compared to wide-field techniques. **Limitation:** Limited number of excitation wavelengths of commonly available lasers, high-intensity laser can destruct the biological samples.
	Tomography	Internal structures (3D imaging) of hybrid materials, using either x-rays or neutrons, or electrons	133,R14	In ref. 133, synchrotron X-ray tomography has been used to study the three-dimensional structure of cellulose -silica hybrid aerogel.	**Advantages**: Can provide 3D information. **Limitation:** not suitable for all elements (e.g. x-ray tomography is not sensitive for low Z

				In ref. R14, Internal mesopores could be identified in calcined SiO2-CNC-polymer hybrids using 3D electron tomographic reconstruction	elements and neutron tomography can not be carried out for the elements, (which can undergo nuclear reaction on interaction with neutrons)
Macroscopic properties	Rheology	Rheological properties (storage modulus, loss modulus, viscosity) display the mechanical and flowability properties of gels, hydrogels, elastomers, emulsions, etc.	45, 88,126,R5 ,R15	In ref. R15, viscoelastic solid behavior of hybrid inks of TOCNF-MOF is studied	**Advantages**: easy to measure, provide information in real-time, extremely sensitive, exchangeable geometries to analyse diverse types of samples. **Disadvantages**: The high sensitivity can bring misleading conclusions. Difficult to analyze complex systems.
	Zeta-potential measurements	Stability provides an idea of the surface charge in terms of zeta-potential. Can be useful to optimize the formulations of suspensions, formation of films and to predict interactions with surfaces	130, 167,176,1 82,202,R1 6	In ref R16, electrophoretic mobility, as well as electrolytic conductivity of the dispersed silver nanoparticles in the CNF, have been determined by zeta potential measurements, employing laser doppler electrophoresis.	**Advantages:** easy to measure, no sample preparation required, in-situ, non-destructive. **Limitations:** Does not provide exactly the surface charge. Difficult to interpret the results in the presence of multiple charged species. Not always possible for solid samples.
	BET measurement	Measurement of surface area, porosity. Useful on vapor, CO_2, and other gases adsorption properties.	99,163,17 6,177,179 ,180,183, R3,R4,R6	In ref. 179, the porosity of the hybrid aerogels, prepared by in-situ growth of MOF nanoparticles on bacterial cellulose has been probed through N_2 sorption	**Advantages:** Small amounts of sample, non-destructive analysis. **Limitation:** Drying and degassing of samples collapses 3D structures, risk of underestimated nanocellulose gas uptake.

	Thermogravimetric Analysis	Thermal stability, amount of the inorganic material in the cellulose matrix, gas sorption/desorption by weight.	110,112,176, R5	In ref 110, TGA was used to i) prove the zeolite loadings in nanocellulose-based foams, and ii) perform cyclic absorption measurements of CO_2, and measure the selectivity towards nitrogen.	**Advantages:** mostly all the solid samples can be analyzed with minimal or no specific sample preparation, high accuracy, and precision of balance. **Limitation:** Data interpretation is not always straightforward, non-homogenous samples cannot be tested, difficult to interpret the results for the mixture of samples.
	Quartz crystal microbalance with dissipation	In-situ adsorption on a substrate, amount of adsorbed material, and the details of the adsorbed layer.	49,130,131,R11,R12	In ref 49, in-situ formation of small nanoclusters of metal oxides in nanocellulose has been detected by QCMD.	**Advantage:** provides in-situ information, fast, highly sensitive providing adsorbed mass in the range ng percm^2 **Limitations:** data modeling can be difficult particularly in the case of non-homogeneous deposition, the thickness of the film is also restricted. Restricted to liquid and non-harsh solvents.
Scattering techniques	X-ray diffraction	Crystalline structure of the CNC/embedded nanoparticles	166,177,178,180,182	In ref. 178, XRD has been used to confirm the crystal structure of MOF synthesized on the TOCNF template.	**Advantages:** Easy identification of unknown materials to determine composition with few samples and straightforward analysis. Also elucidates the oxidation state and more information. **Limitation**: only crystallizable samples can be measured. Non-dynamic method.
	Dynamic light scattering	Hydrodynamic size, diffusion coefficients	R17	In ref R17, The mean hydrodynamic diameter, polydispersity index, and particles size distributions have been determined in	**Advantages**: In-situ, non-destructive, fast **Limitations:** highly sensitive to impurities like dust.

				cellulose-silver nanoparticle hybrids using DLS.	
	Small-angle X-ray scattering	Size, size distribution, shape, morphology of the hybrids	49,126,128,R18	In ref. 49, the growth of metal oxide nanoparticles in nanocellulose has been observed by in-situ SAXS.	**Advantages:** measures samples in native condition, fast, sensitive to shapes/morphology, provides a statistically better picture than microscopy techniques. **Limitations:** data modeling is difficult (provides data in Fourier space), can damage the sample particularly at synchrotron sources, not good for low Z materials
	Small-angle neutron scattering (SANS)	Size, size distribution, shape, morphology of the hybrids	126,129,R19, R20	In ref. R19, morphological structure of cellulose-based organic-inorganic nanocomposite materials has been examined using SANS.	**Advantages:** Measures samples in native condition, fast, sensitive to shapes/morphology, provides statistically better picture than microscopy techniques, sensitive to low Z materials as well as differentiate between isotopes, unique advantage of contrast variation in multi-component hybrids. **Limitations:** data modelling is difficult (provides data in Fourier space), not possible for neutron absorbing samples.

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