Ph.D. Thesis offer

Regioselective modification of cellulose nanocrystals: advanced characterization by DNP-NMR and innovative 2D and 3D assemblies

Thesis project

Cellulose nanocrystals (CNCs) are biosourced colloidal rods that are very interesting building blocks for the design of innovative materials thanks to their inherent properties (renewable origin, biocompatibility, self-organization and mechanical properties). A special feature of these nano-objects, which has only scarcely been exploited yet, is their ability to be locally derivatized (either their lateral surface or their extremity can be targeted). The goal of the project is first to take advantage of this property and achieve a dual and localized grafting of both stimuli-sensitive polymer chains and gold or silver nanoparticles on CNCs. Such dual derivatization will enable the generation of novel assemblies triggered by the application of the stimulus, while the nanoparticles will confer optical, antimicrobial, catalytic, or sensing properties. This strategy raises synthesis and characterization challenges that will fully benefit from the complementary expertise of CERMAV and MEM labs where the Ph.D. project will take place. The project will be based on the regioselective derivatization of CNCs and the control of their assembling, and on the use of the DNP-NMR spectroscopy developed at MEM that stands as the unique experimental tool capable not only of quantitatively detecting the inherently low end-grafting (conventional techniques are not sensitive enough) but also of characterizing the details of the surface chemistry such as the precise location and conformation of the grafts. This task devoted to chemical derivatization will be followed by the structural characterization of the hybrid objects and their 2D/3D assemblies, which will be performed using complementary microscopy (TEM, cryo-TEM, AFM), scattering (X-ray and neutron), and spectroscopic (ellipsometry, SPR) techniques. Finally, the functional properties of the systems will be investigated to assess their potential applications in the fields of catalytic degradation or contaminant sensing through enhanced opto-electronic properties.

It is therefore a multidisciplinary and multi-scale project combining aspects of heterogeneous chemistry, physical chemistry of biosourced colloids, DNP-NMR spectroscopy, and integrating the evaluation of functional properties. The studies will benefit from a particularly rich instrumental and technical environment and from the support of external collaborators.

Host laboratories

This thesis project corresponds to a collaboration between two laboratories in Grenoble and will be carried out within the following teams:

- the Structure and Properties of Glycomaterials team of the Centre de Recherches sur les Macromolécules Végétales (CERMAV, UPR CNRS 5301) located on the Grenoble university campus, which is internationally recognized in the field of biosourced materials design based on a multi-scale approach. http://www.cermav.cnrs.fr

- the Magnetic Resonance team of the Modelling and Exploration of Materials Laboratory (MEM, UMR CEA-UGA) located on the scientific polygon, which is at the forefront of the development of dynamic nuclear polarization and solid-state NMR applied to the study of complex functional materials, including bio-based materials. https://www.mem-lab.fr et https://nmr-dnp-grenoble.net

Applicant's profile

The candidate should have a good knowledge of colloid and polymer chemistry and physics, and a strong interest in experimentation and advanced spectroscopic studies. Knowledge and/or experience in the field of bio-based materials and/or NMR would be an asset. The candidate will need to show enthusiasm, initiative and autonomy to develop this project and should appreciate working in a team. Good communication skills and fluency in English are required.

Additional information

Starting date: 01/10/2022
Funding : Grenoble Alpes University grant CBH Graduate School / Labex Arcane
Application deadline: 30/03/2021

Elements to be provided for the application

Please send CV, cover letter, transcripts of M1 and M2 (semester 2) or equivalent, contact details of referees and/or letter(s) of recommendation by email to bruno.jean@cermav.cnrs.fr and gael.depaepe@cea.fr

References

Lin, F.; Cousin, F.; Putaux, J.-L.; Jean, B. Temperature-Controlled Star-Shaped Cellulose Nanocrystal Assemblies Resulting from Asymmetric Polymer Grafting. *ACS Macro Letters* **2019**, 345-351.

Lin, F.; Putaux, J.-L. ; Pignon, F.; Jean, B. Temperature-triggered Formation of a Cellulose II Nanocrystal Network through Regioselective Derivatization. *Nanoscale* **2021**, *13*, 6447-6460

Kumar, A.; Durand, H.; Zeno, E.; Balsollier, C.; Watbled, B.; Sillard, C.; Fort, S.; Baussanne, I.; Belgacem, N.; Lee, D.; Hediger, S.; Demeunynck, M.; Bras, J.; De Paëpe, G. The Surface Chemistry of a Nanocellulose Drug Carrier Unravelled by MAS-DNP. *Chemical Science* **2020**, *11*, 3868-3877.

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