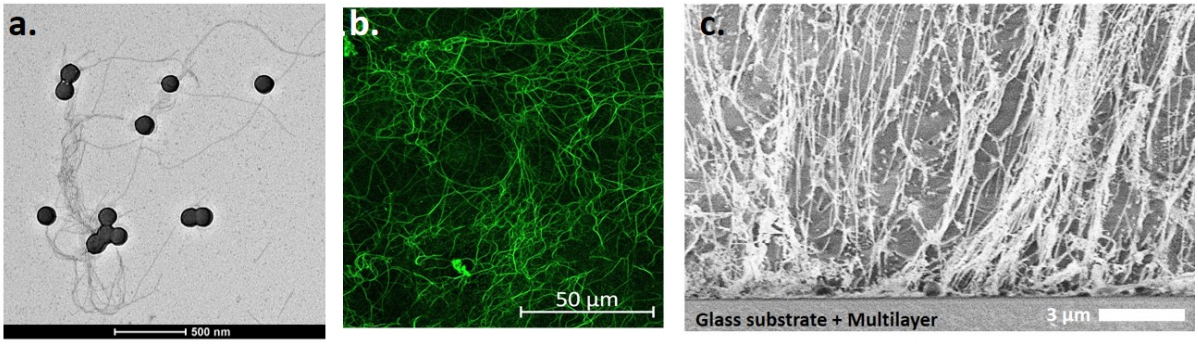
Enzyme-Assisted Self-Assembly: from Catalytic Flow Chemistry to Autocatalytic Hydrogel Growth

Loïc JIERRY

Institut Charles Sadron, UPR22, Strasbourg, France
Ecole Européenne de Chimie, Polymères et Matériaux

Keywords: supramolecular hydrogel, self-assembly, peptide chemistry, enzyme, (auto)catalysis.

Nature controls many biological mechanisms through localized self-assembly processes. (*i*) Cellular adhesion is, for example, initiated by focal adhesions which initiate the formation of actin fibers that play an essential role in cell motility; (*ii*) centrosomes initiate the formation of microtubule spindles that control cellular division. Yet, developing localized molecular self-assembly processes leading to the growth of nanostructures exclusively near a surface, or at an interface, is still a challenge in surface chemistry.[1] In 2004, a new way to initiate the self-assembly of low molecular weight hydrogelators (LMWH) has been reported: an enzyme is used as a trigger able to transform a precursor compound into an efficient LMWH.[2] In the last five years, we have localized different enzymes on various kind of materials (planar substrates, nanoparticles, porous systems) or in a specific environment (host 3D material) to control the self-assembly process in a spatiotemporal way.[3],[4] Based on this approach, we have designed original flow reactors allowing the production of enantiopure chemicals using a catalytically-active hydrogel supported on polymer foams.[4] Very recently, supramolecular hydrogels able to self-sustain their own growth through an autocatalytic way was shown by our group as well.[5] In addition to the description of these recent works, this presentation will also briefly focus on our recent developments about both the understanding of the mechanisms of enzyme-assisted self-assembly, and the formation of reaction-diffusion patterns of peptides self-assembly within enzyme-embedded host materials.



(a) TEM image of self-assembled peptides nanofibers grew from enzyme-coated silica nanoparticles; (b) Fluorescence confocal microscopy image of fibrous self-assembled peptides network generated from enzyme embedded within a host polyethylene glycol gel; (c) Cryo-SEM of self-assembled peptide fibers initiated from enzyme-modified glass substrate.

[1]. Vigier Carrière, C.; Boulmedais, F; Schaaf, P.; Jierry, L. Surface-Assisted Self-Assembly Strategies Leading to Supramolecular Hydrogels. *Angew. Chem., Int. Ed.* **2018**, *57*, 1448 – 1456.
[2]. Yang, Z.; Gu, H.; Fu, D.; Gao, P.; Lam, J. K.; Xu, B. Enzymatic Formation of Supramolecular Hydrogels. *Adv. Mater.* **2004**, *16*, 1440-1444.
[3]. Rodon Fores, J.; Mendez, M. L. M.; Mao, X.; Wagner, D.; Schmutz, M.; Rabineau, M.; Lavalle, P.; Schaaf, P.; Boulmedais, F.; Jierry, L. Localized Supramolecular Peptide Self-Assembly Directed by Enzyme-Induced Protons Gradient. *Angew. Chem., Int. Ed.* **2017**, 56, 15984-15988.
[4]. Rodon Fores, J.; Criado-Gonzalez, M.; Chaumont, A; Carvalho, A.; Blanck, C.; Schmutz, M.; Serra, C.A.; Boulmedais, F.; Schaaf, P.; Jierry, L. Supported Catalytically Active Supramolecular Hydrogels for Continuous Flow Chemistry. *Angew. Chem., Int. Ed.* **2019**, *58*, 18817-18822.
[5]. Rodon Fores, J.; Criado-Gonzalez, M.; Chaumont, A.; Carvalho, A.; Blanck, C.; Schmutz, M.; Boulmedais, F.; Schaaf, P.; Jierry, L. Autonomous Growth of Spatially Localized Supramolecular Hydrogel with Autocatalytic Ability. *Angew. Chem., Int. Ed.* **2020**, doi.org/10.1002/anie.202005377