Title	Sustainable smart materials for autonomous soft robots

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International Secondment	
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# months (min.3)	4

Project description (2 page max):

The design and development of smart materials, which display adaptive functions and reconfigure dynamically in their environment, is a grand challenge toward the development of next generation soft robotic systems. Despite the progress, it remains challenging to design and develop soft materials with adaptable, time-dependent properties and to leverage these properties in order to perform autonomous operations. By embracing the concepts learned in the study of stimuli-responsive hydrogels with transient mechanical properties,[1,2] this project aims at developing sustainable smart hydrogels for autonomous actuation and robotics applications.

The research activity will be focused on the development of methods for the preparation of hydrogels based on cellulose derivatives, including carboxymethyl cellulose (CMC) and cellulose nanocrystals (CNC), crosslinked by redox-responsive Fe^{3+} ions. Indeed, Fe^{3+} ions can form strong metal–ligand coordination bonds with the cellulose chains and promote the formation of stable highly cross-linked hydrogels.[3,4] The assembly mechanisms of the Fe^{3+}-coordinated cellulose hydrogels as function of the cross-linker density will be investigated and the structural and energetic aspects will be modeled based on molecular dynamics simulations that we have recently developed.[4] Coarse-grained models will be employed to gain insight into the self-assembly process of the Fe^{3+}-cellulose coordination complexes and optimize the mechanical properties of the materials. The mechanical properties of the Fe^{3+}-coordinated hydrogels generated by different concentrations of Fe^{3+} will be evaluated by rheometry and microindentation (evaluation of Young's module) and further characterized by scanning electron microscope (SEM). The coordination of Fe^{3+} with the cellulose chains will be investigated by UV-vis spectroscopy, while the redox properties of the hydrogels will be characterized using electrochemical methods. The reduction of the higher-stiffness Fe^{3+}-cellulose hydrogel to low stiffness Fe^{2+}-cellulose hydrogel will be carried out by using different chemical agents and photochemically. The investigation will then focus on the aerobic reoxidation of the Fe^{2+}-cellulose hydrogel in order to establish transient stiffness functions of the hydrogel. The thermodynamic efficiency of these dissi-

pative processes will be evaluated by adapting nonequilibrium thermodynamic theories originally developed for light-powered molecular motors.
The outcomes from this initial phase of the project will enable the design and development of an autonomous robotic gel device, which will be triggered by light. To achieve this, we will fabricate centimeter-sized rod-shaped bilayer devices by layering the Fe^{3+}-cellulose-based hydrogel onto a substrate composed of bis-acrylamide-cross-linked hydrogel. Light-triggered bending of the bilayer gel device will be investigated, alongside the autonomous transient actuation of the bilayer hydrogel device under aerobic conditions. The potential applications of these hydrogel devices will be assessed for autonomous micromanipulation. Light-driven directional movement of the hydrogel devices will be also investigated by fabricating the bilayer hydrogel in an asymmetric structure. This configuration will be optimized to enable directional crawling motion of the hydrogel device. Part of these investigations will take place during an international secondment at The Hebrew University of Jerusalem, providing the PhD student with hands-on experience in operating light-triggered soft robotic devices.
Finally, this project will enable the transition from classical static materials to more life-like materials capable of adaptive, autonomous behavior, providing new opportunities for autonomous soft robotic applications.

References:

1) R. Baretta, M. Frasconi "Electrically powered dissipative hydrogel networks reveal transient stiffness properties for out-of equilibrium operations" *J. Am. Chem. Soc.* **2024**, *146*, 7408–7418.
2) R. Baretta, G. Davidson-Rozenfeld, V. Gutkin, M. Frasconi, I. Willner "Chemical and photochemical-driven dissipative Fe^{3+}/Fe^{2+}-ion cross-linked carboxymethyl cellulose gels operating under aerobic conditions: applications for transient controlled release and mechanical actuation" *J. Am. Chem. Soc.* **2024**, in press.
3) V. Gabrielli, R. Baretta, R. Pilot, A. Ferrarini, M. Frasconi "Insights into the gelation mechanism of metal-coordinated hydrogels by paramagnetic NMR spectroscopy and molecular dynamics" *Macromolecules* **2022**, *55*, 450−461.
4) V. Gabrielli, A. Ferrarini, M. Frasconi "A study across scales to unveil microstructural regimes in the multivalent metal driven self-assembly of cellulose nanocrystals" *Nanoscale* **2023**, *15*, 13384.