PROGRAMMED ASSEMBLY OF PHOTO- AND THERMORESPONSIVE PROTOCELLS INTO PROTOCELLULAR MATERIALS CAPABLE OF PHOTO-MECHANO-CHEMICAL TRANSDUCTION

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Bottom-up synthetic biology is an emerging research field whose objectives is to design and fabricate existing biological systems from inanimate molecules, materials, and chemical reactions. One of the key biological systems that bottom-up synthetic biology is trying to re-design and fabricate is the living cell. This research led to the concept of "protocell" and "protocellular material" (PCMs). A protocell is a micro-compartmentalised system capable of imitating at least one of the key features of a living cell (*e.g.*, enzyme catalysis, communication based on diffusible chemical signals, information storage). A protocellular materials is instead a free-standing and covalently interconnected networks of communicating protocells that can display synergistic functions.

While thus far efforts have been placed in the development of methods to fabricate PCMs with complex 3D architectures and demonstrate their chemical communication properties, in this contribution we show our efforts in moving beyond the state-of-the-art and develop the first PCMs capable of photo-mechano-chemical transduction. These are PCMs capable of converting a light stimulus into complex mechanical movements that in turn can influence the biocatalysis hosted within the protocell units composing the material itself. In order to achieve this, we have designed and assembled a covalent and thermoresponsive poly(*N*-isopropylacrylamide) (P(NIPAM)) polymer network directly inside the lumen of the protocells composing the PCM, where we also placed poly(ethylene oxide) (PEG) stabilised gold nanoparticles (AuNPs), amyloglucosidase (AGx), and glucose oxidase (GOx). By exploiting the photo-thermal effect of AuNPs and the thermoresponsive properties of the PNIPAM network in a synergistic manner, we were able to achieve reversible light-induced contractions of the PCM. Most importantly, the contraction caused the material to become hydrophobic. This made the contracted protocell membranes impermeable to small hydrophilic substrate molecules for enzyme catalysis, and effectively shut off the hosted enzyme cascade.

The fabrication of tissue-like materials with increasingly advanced biomimetic properties will not only help us to understand the physicochemical basis of the emerging behaviours of living tissues, but will also find important applications in tissue engineering, pharmacokinetics, mechanobiology, personalised therapy, in the development of micro-bioreactors and soft robotics.

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