

# Dressing proteins with functional materials

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## Dressing proteins with functional materials

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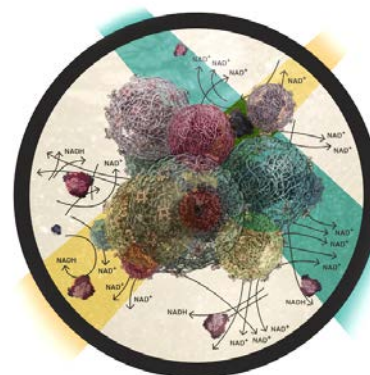
In this talk, I will show how we can combine proteins with artificial materials to give rise to biohybrids with tailored functionalities. One part of the presentation will deal with the application of proteins as templates and protecting scaffolds of unstable inorganic nanomaterials. This approach has been successfully utilized for the stabilization of metal nanoclusters. Interestingly, we have observed that the properties of the nanoclusters and their catalytic performance rely on the sequence of the protein used as template. Only few mutations on the polypeptidic chain triggered significant changes in the nanoclusters. These biohybrids, also named as nanozymes, show enzyme-like kinetics and higher stability than natural enzymes.

In a second part of the talk, I will go into the use of polymeric networks as flexible and porous scaffolds, which significantly improves the stability and robustness of biocatalysts under those conditions in which free enzyme systems are denatured [1,2]. Particularly, I will focus this presentation on the possibilities that protein encapsulation has for the design of advanced multifunctional hybrid biomaterials for sensing and catalysis. In our case, the fabrication of the enzyme-polymer hybrids entails the chemical engineering of the surface of the proteins throughout the deposition of a thin polymeric mantel of ca. 3-5 nm. Hence, the polymer, a porous functional hydrogel, wraps the enzyme, giving rise to small nanogels (ca. 10-15 nm) that are usually referred to as Single Enzyme Nanogels (SENs). The polymeric shell does not show significant diffusional issues and improves the stability of the enzyme under harsh conditions (e.g., high temperature or the presence of organic solvents).

The composition of the polymeric shell can be tailored to anchor functional units such as fluorescent reporters or metalorganic catalysts. The convenient allocation of these small molecules in the confined surroundings of the enzyme permits the design of efficient one-pot cascade reactions. We recently reported how this approach can be used for the development of highly sensitive chemobiosensors [3] and to broaden the catalytic profile of enzymes [4-5].

### References:

- [1] Beloqui et al., *Small*, 2016, 13, 1716-1722
- [2] Beloqui et al., *Chem. Sci.*, 2018, 9, 1006-1013
- [3] D. Sánchez-deAlcázar et al., *ACS Appl. Mat. Inter.*, 2022, 14, 24, 27589-27598
- [4] Rodríguez-Abetxuko et al., *Adv. Funct. Mat.*, 2020, 30, 2002990
- [5] Rodríguez-Abetxuko et al., *Angew. Chem. Int. Ed.*, 2022, 134, e202206926



**Figure.** Schematic representation of the functionalized SENs applied for the chemoenzymatic recycling of enzyme cofactors that will be discussed along the presentation<sup>[5]</sup>

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