ChemISTry ColloquiA

From Molecular Complexes to Catalyst-Functionalized Polymersomes for Photocatalytic Applications: Towards Compartmentalized Artificial Photosynthesis

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The sustainable synthesis of fuels and chemicals using sunlight as driving force and simple readily available feedstock such as H_2O and waste CO_2 provides a potential feasible pathway to mitigate increasing CO_2 emissions and transitioning toward a greener chemical industry. In this context, natural photosynthesis is a source of inspiration and has led to the evolving and multidisciplinary field of artificial photosynthesis (AP).[1-4] Over the last years, we have worked with several systems, ranging from homogeneous, heterogenous, biocatalysts and hybrid materials, to study different half reactions involved in AP. This has given us a broad perspective of the field and the different approaches to study this process and develop more efficient photocatalytic systems.

In this regard, when designing bioinspired photocatalytic platforms for AP, the role of natural membranes is sometimes overlooked. Our research group is currently working towards studying this key structural factor of natural photosynthesis.[4] We are working in the development of polymeric microphotoreactors functionalized with (photo)catalysts to produce solar fuels and chemicals. Our ultimate goal is to drive the electrons from the oxidation of water to the reduction of CO_2-to-Carbon-based fuels and chemicals in aqueous media using solar energy as driving force.[5] My group has developed a novel family of asymmetric porphyrin and phthalocyanine complexes bearing Co, Ni, and Fe as first row transition metal centers for photocatalytic CO_2 reduction in combination with Ir- and Cu-based photosensitizers and organic photosensitizers, under visible light irradiation (447 nm) in aqueous-organic mixtures in presence of a sacrificial electron donor.[5] The Co and Fe phthalocyanine complexes show a remarkable photocatalytic activity and selectivity for photocatalytic CO_2 reduction to CO in homogeneous conditions, even with 10% of water. In contrast, the porphyrin complexes show remarkable activity and selectivity for methane production. Moreover, to further explore the applicability and increase the stability of these systems, we have anchored both the CO_2 reduction catalyst and photosensitizer onto the membrane of polymersomes, developing the first polymersome for compartmentalized photocatalytic CO_2 reduction.[5] The effect of anchoring and the nature of the photosensitizer used allows to tune the selectivity of the photocatalytic reaction to obtain only CO_2 reduction derived products in water, suppressing the normally competing hydrogen evolution reaction. Mechanistic studies are ongoing to rationalize these differences in reactivity between homogeneous and heterogenized systems.

1. C. Das Neves Gomes, et al. *Angew. Chem. Int. Ed.* **2012**, *51*, 187-190.
2. E. Boutin, et al. *Chem. Soc. Rev.* **2020**, *49*, 5772-5809.
3. A. Pannwitz, et al. *Chem. Soc. Rev.* **2021**, *50*, 4833-4855.
4. L. Velasco-Garcia, C. Casadevall. **2023**, *Commun. Chem.* 6:263
5. L. Velasco-Garcia, K. Nassif, A. Bekaliyev, E. J. Espinoza-Suarez, C. Casadevall, *Unpublished results.*

Carla Casadevall is an Assistant Professor (Ramón y Cajal fellow) at the Universitat Rovira i Virigli (URV) and the Institute of Chemical Research of Catalonia (ICIQ) (Tarrgona, Spain). Her group works on the development of catalyst-functionalized polymeric microreactors for the production of solar fuels and chemicals within the fields of artificial photosynthesis and photoredox catalysis. She obtained a BSc in chemistry (2013) and a MSc (2014) in Advanced Catalysis and Molecular Modelling at the University of Girona (Spain). Then she moved to ICIQ to do a PhD (2015-2019) working on homogeneous systems for artificial photosynthesis and photoredox catalysis. During that time, she performed 4 PhD international internships: KTH Royal Institute of Technology (Sweden), Arizona State University (USA), University of Groningen (Netherlands) and MPI-CEC (Germany). After obtaining her PhD she joined the University of Cambridge (UK) in September 2019 as a BBSRC postdoctoral researcher, where she received a prestigious Marie Marie Skłodowska–Curie Individual Fellow (2020-2022) working on biohybrid systems for artificial photosynthesis. In October 2022 she came back to Spain and started her independent career at the URV and ICIQ with a "La Caixa Junior Leader Incoming Fellowship" and recently with a Ramón y Cajal, her current position.