Biohybrid Bacterial Microcompartment Shells as Nanoreactors for Photocatalytic Hydrogen Evolution

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Bacterial microcompartments (BMCs) are protein shells that encapsulate enzymes and substrates of specific metabolic pathways to augment catalytic turnover through means of confinement. Compartmentalization of reaction pathways is a ubiquitous phenomenon in biological systems, but more difficult to achieve through synthetic means. As such, in this study we have engineered biohybrid BMC shells loaded with abiotic compounds to leverage the chemistries of synthetic molecules and tune their reactivities within biological microenvironments. We encapsulated the benchmark photosensitizer, $Ru(bpy)_3$, and the molecular catalyst, chloro(pyridine)cobaloxime, to facilitate photocatalytic hydrogen evolution in confinement. The $Ru(bpy)_3$/cobaloxime loaded shells were able to successfully generate H_2, albeit at a lower turnover number (TON) and turnover frequency (TOF) than the bulk multimolecular reaction without protein. Remarkably, when $Ru(bpy)_3$ was added to solution outside of the loaded shells the TOF increased dramatically, surpassing that of the bulk reaction 4-fold. Since $Ru(bpy)_3$ outside the shell should theoretically be incapable of direct electron transfer to cobaloxime located on the inside, our results suggest an electron transport process through the ~30 Å thick shell wall, perhaps via tyrosine-mediated proton coupled electron transfer. These results highlight the potential of BMC shells as nanoreactors for energy-conserving chemistries with applications in photocatalysis, electrocatalysis, and biomaterials.

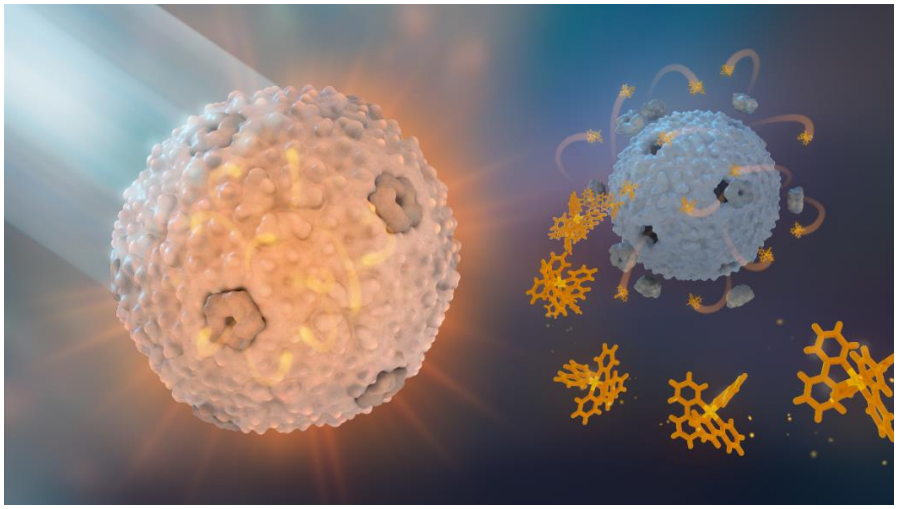

Figure. 1. Scheme showing BMC shell loaded with photosensitizers and illuminated with blue light.