

Development of Multiheme Cytochromes-Carbon Dots Biohybrids for Solar Chemicals and Fuels Generation

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Inorganic-biological hybrids which combine synthetic light-harvesting nanoparticles and biocatalysts show great potential to harvest solar energy for chemicals and fuels production in a sustainable way.¹⁻³ Inspired by natural photosynthesis, we aim to provide proof-of-principle for whole-cell biohybrid photocatalysis producing value-added chemicals from coupled redox transformations within the Gram-negative bacterium *Shewanella oneidensis* MR-1 (MR-1). A multiheme protein complex MtrCAB provides a direct conduit for bidirectional electron exchange across the MR-1 outer membrane. In this work, we developed a protocol to covalently label MtrC with light-harvesting carbon dots (CDs) to form MtrC-CDs biohybrids. CDs were modified with maleimide functionalities and covalently attached to single Cys MtrC variants through a maleimide-thiol reaction. The MtrC-CDs biohybrids were purified with strep tag resin. UV-vis spectroscopy, fluorescence emission spectroscopy and Native PAGE demonstrated the presence of CDs in the biohybrids. The fluorescence lifetime of biohybrids suggest fast, light induced electron transfer between CDs and MtrC, further confirmed by the reduction of MtrC-CDs upon illumination. The MtrC-CDs biohybrids can potentially be assembled to MR-1 to drive photo-induced electron into the whole cell for solar chemicals and fuels generation.

¹ Cestellos-Blanco, S.; Zhang, H.; Kim, J.M.; Shen, Y.-x.; Yang, P. *Nat Catal* **2020**, 3, 245–255.

² Guo, J.; Suástegui, M.; Sakimoto, K.K.; Moody, V.M.; Xiao, G.; Nocera, D.G.; Joshi, N.S. *Science* **2018**, 362, 813–816.

³ Kornienko, N.; Zhang, J.Z.; Sakimoto, K.K.; Yang, P.; Reisner, E. *Nat. Nanotechnol.* **2018**, 13, 890–89