

Bio-inspired Nano-Architectures for Artificial Photosynthesis

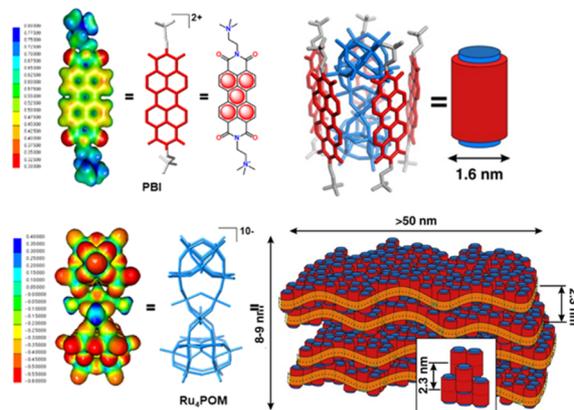
Life, as we know it, is perpetually fuelled by light-activated redox processes based on small and ubiquitous molecules as H_2O and CO_2 . Photocatalytic H_2O oxidation evolves oxygen that is necessary for our aerobic life. On the reduction end, photosynthetic CO_2 fixation has the potential to win over the anthropogenic carbon emissions (ca. 120 Pg yr^{-1} vs. 7 Pg yr^{-1} ; $1 \text{ Pg} = 1 \text{ petagram} = 1 \text{ billion tonnes} = 10^{15} \text{ grams}$). In both cases, making oxygen and reducing CO_2 is exceptionally difficult. Indeed, to overcome kinetic and thermodynamic limitations, natural photosynthesis adopts a combined strategy of spatial organization and separation of functions with cascade multi-redox catalysis.

The PhD project will address the design of bio-inspired, integrated light-antennas and multi-redox catalysts, specifically designed to mimic the photosynthetic function, by using totally synthetic components, assembled into hierarchical nano-architectures.

In particular

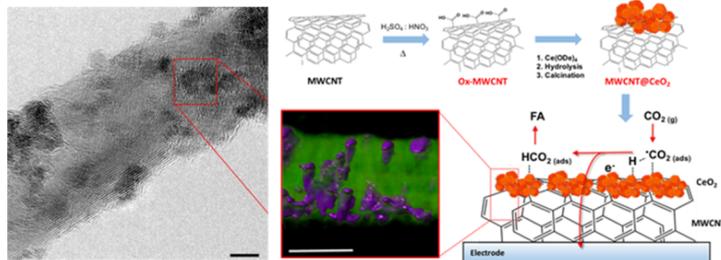
(i) The self-assembly of multi-perylenebisimide chromophores (PBI) will be investigated in the presence of nano-dimensional polyoxometalate catalysts (POMs) that perform water oxidation at low overpotential and neutral pH, in close analogy with the oxygen evolving center of the natural PSII enzyme (PSII-OEC). The stoichiometry and geometry of the resulting photo-complex will be dictated by non-covalent, interactions based on electrostatic and hydrophobic forces. The expected photophysical and electronic properties include: (i) a favorable light harvesting efficiency using “green” photons ($\lambda > 500 \text{ nm}$), (ii) exciton accumulation and negligible excimeric loss; (iii) a robust amphiphilic structure that promotes hierarchical aggregation into ordered 2D-paracrystalline domains, thus mimicking the natural photosynthetic membrane. The structural properties investigated by X-ray diffraction and scattering analysis as well as by electron and atomic force microscopy, will be correlated with the photocatalytic performance both in solution and on photoelectrodes.

The dynamics and electronic properties of the hybrid supramolecular matrix will be addressed by a computational study with the aim to highlight the impact of the multi-chromophore arrangement on the exciton-based energy transfer, facilitating a more efficient delivery of harvested light energy to the catalytic charge-separation sites. Exciton formation in natural photosynthetic systems is instrumental to minimize energy losses due to electron-phonon coupling and disorders in soft protein matrices. The modularity of the building blocks, the simplicity of the non-covalent chemistry and the biomimetic appeal of the supramolecular architectures, will offer a unique opportunity for innovation in Artificial Photosynthesis.



(ii) The combination of multiwalled carbon nanotubes (MWCNTs) with undoped CeO_2 nanoparticles (NPs) will be investigated for the direct electrocatalytic reduction of CO_2 to formic acid (FA) at acidic pH (HNO_3 0.1 M). Converging evidence identifies non-stoichiometric $\text{CeIV/III/O}_2\text{-x}$ reduced sites as essential for selective CO_2 reduction (CO_2RR). The MWCNT-mediated electrochemical reduction of the CeO_2 NPs offers a definite advantage with respect to generally adopted thermochemical cycles ($800\text{-}1500 \text{ }^\circ\text{C}$), or deep hydrogenation pre-treatments for the activation of CeO_2 -based electrocatalysts.

Density Functional Theory (DFT) calculations will be used to investigate the mechanism of CO_2 electro-hydrogenation with the aim to address the size, density and dynamics of oxygen vacancy clusters with respect to the kinetics and selectivity of CO_2 reduction. The impact of the nanocarbon scaffolds on the electronic properties of CeO_2 as well on the electrocatalytic properties of the resulting hybrid composite will be studied, focussing on the mobility and clustering of the oxygen vacancies. This latter aspect is pivotal for the catalytic reaction via CO_2 adsorption and multi-site activation, thus lowering the overpotential of the reduction process. The mechanism of CO_2RR on the MWCNT@CeO_2 nano-hybrids will be investigated.



References

M. Bonchio, M. Prato M. et al. “Efficient water oxidation at carbon nanotube–polyoxometalate electrocatalytic interfaces” *Nature Chemistry* 2, 826–831 (2010); M. Bonchio, M. Prato et al. “Hierarchical organization of perylene bisimides and polyoxometalates for photo-assisted water oxidation”. *Nature Chemistry* 11, 146–153 (2019); M. Bonchio, P. Fornasiero, M. Prato et al.

"Pd@TiO₂/carbon nanohorn electrocatalysts: reversible CO₂ hydrogenation to formic acid" *Energy Environ. Sci.*, 11, 1571-1580 (2018).