Artificial Photosynthesis Challenges: Water Splitting at Nanostructured Interfaces

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Solar-powered water oxidation can be exploited for hydrogen generation by direct photocatalytic water splitting. A recent breakthrough in the field of artificial photosynthesis is the discovery of innovative oxygen evolving catalysts taken from the pool of the nano-sized, water soluble, molecular metal oxides, the so-called polyoxometalates (POMs). These catalysts provide a unique mimicry of the oxygen evolving centre in photosynthetic II enzyme (PSII), sharing a common functional-motif, i.e., a redox-active tetranuclear $\{M_4(m\text{-}O)_4\}$ core, and effecting H_2O oxidation to O_2 with unprecedented efficiency. In this scenario, the tetra-ruthenium based POM $[Ru^{IV}_4(m\text{-}OH)_2(m\text{-}O)_4(H_2O)_4(g\text{-}SiW_{10}O_{36})_2]^{10-}$, **$Ru_4(SiW_{10})_2$**, displays fast kinetics, exceptionally light-driven performance and electrocatalytic activity powered by carbon nanotubes.[1-2]

Research in the field of artificial photosynthesis for the conversion of water to fuel has recently come to the awakening turning-point that a key issue is the design of efficient catalytic routines that can operate with energy and rates commensurate with the solar flux at ground level. A factual solution to this need implies the mastering of the electron transfer distance, junctions and potential gradients at the molecular level and within a nano-structured environment. Our vision points to a careful choice/design of the nano-structured support, and to a precise positioning of the catalytic domain on such templates, by tailored synthetic protocols. This is a key point to access single-site catalysis approaching the homogeneous behavior.

We report herein a combined synthetic, spectroscopic and mechanistic study on the use of POM catalysts for water oxidation and their combined use with visible light sensitizers and carbon nanostructures CNT. The outcome is a hybrid nanomaterial with unperturbed CNT electrical properties, in close contact with a unique multi-electron catalyst enabling electrocatalytic water splitting with high efficiency at low overpotentials.

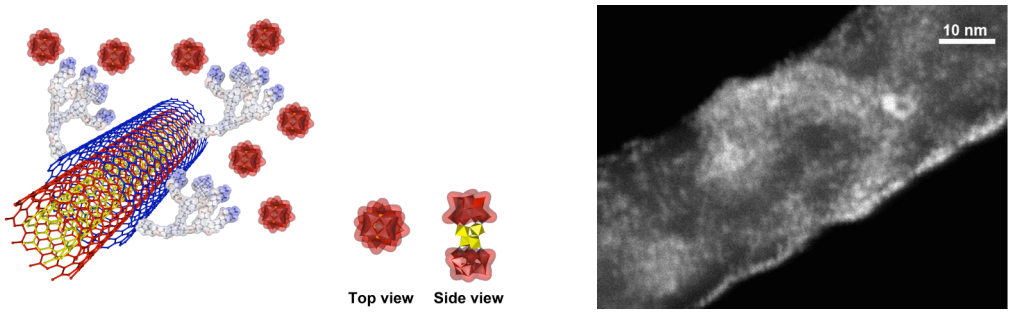

Figure 1. Electrostatic capture of polyanionic **$Ru_4(SiW_{10})_2$** (polyhedric structure) by functionalized MWCNT with attached PAMAM dendrons. STEM images of the resulting nano-hybrids, brighter contrast domains are ascribed to the POM catalyst.

References

[1] a) A. Sartorel, M. Carraro, G. Scorrano, R. De Zorzi, S. Geremia, N. D. McDaniel, S. Bernhard, M. Bonchio. *J. Am. Chem. Soc*. 130, (2008), 5006. b) A. Sartorel, P. Miró, E. Salvadori, S. Romain, M. Carraro, G. Scorrano, M. Di Valentin, A. Lloblet, C. Bo, M. Bonchio. *J. Am. Chem. Soc*. 131, (2009), 16051.
[2] a) F. M. Toma, A. Sartorel, M. Iurlo, M. Carraro, P. Parisse, C. Maccato, S. Rapino, B. Rodriguez Gonzalez, H. Amenitsch, T. Da Ros, L. Casalis, A. Goldoni, M. Marcaccio, G. Scorrano, G. Scoles, F. Paolucci, M. Prato, M. Bonchio. *Nat. Chem.* **2**, 826 (2010). b) M. Prato, M. Bonchio et al. *Chem. Sus. Chem.* (2011) in press.