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 \( \{M_4(m-O)_{12}\} \) core, and effecting \( \text{H}_2\text{O} \) oxidation to \( \text{O}_2 \) with unprecedented efficiency. In this scenario, the tetra-ruthenium based POM \( [\text{Ru}^\text{IV}_4(m-\text{OH})_2(m-O)_{12}(\text{H}_2\text{O})_4(g-\text{SiW}_{10}\text{O}_{36})_2]^{10^-}, \text{Ru}_4(\text{SiW}_{10})_2, \) 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 \( \text{Ru}_4(\text{SiW}_{10})_2 \) (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
