

Energy Materials by Molecular Design: Knitting the Catalytic Pattern of Artificial Photosynthesis

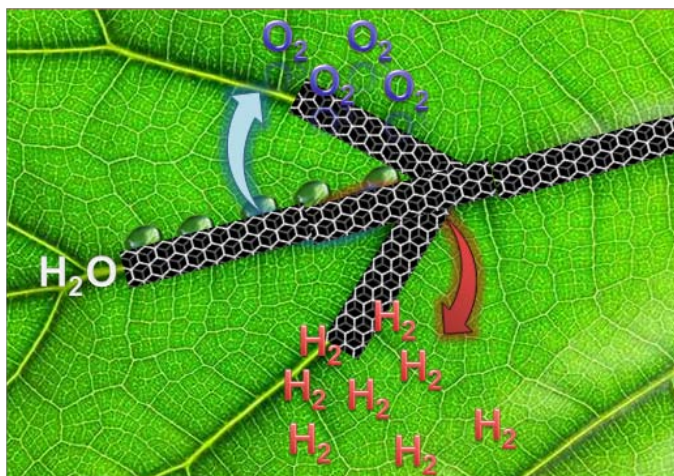
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Bio-energy is renewed daily by catalytic water splitting, at the heart of the photosynthetic machinery, embedded in leaves. In contrast, the artificial process for the continuous extraction of O₂ and H₂, as alternative solar fuels, is an urgent concern of fundamental and applied energy research. The pitfall stems from the thermodynamic and kinetic barrier of the water oxidation stage, causing a major energy loss after the light collection events. Lowering the activation barrier of such “dark” phase translates into new catalyst-mediated pathways, with an overall energy cost close to the thermodynamic requirement ($E^0 = 1.23$ V). This task, together with the long-term stability issue, is pivotal for the “artificial leaf” project, and calls for a tailored merging of molecular water oxidation catalysis (WOC) and nano-materials research. The synergy expected from these two disciplines targets the “all-around” shaping of the WOC functional environment at the nanoscale and supported on a functional surface. [1, 2]

The molecular engineering of a WOC texture, based on functionalized graphene nano-sheets will be discussed herein which integrates the tetra-ruthenate polyoxometalate {Ru₄(μ-O)₄(μ-OH)₂(H₂O)₄[μ-SiW₁₀O₃₆]₂}¹⁰⁻ (**Ru₄POM**), as the inorganic mimic of the natural photosynthetic Mn₄ cluster.[1, 2]



References. [1] (a) Sartorel, A., Miro', P., Salvadori, E., Romain, S., Carraro, M., Scorrano, G., Di Valentin, M. Llobet, A., Bo, C., Bonchio M. (2009): *J. Am. Chem. Soc.* **131**, 16051–16053; (b) Piccinin, S., Sartorel, A., Aquilanti, G., Goldoni, A., Bonchio, M., Fabris, S. (2013): *PNAS* advanced article. [2] (a) Prato, M., Bonchio, M. et al. (2010):, *Nature Chem.*, **2**, 826–831. (b) Paolucci, F., Prato, M., Bonchio, M. et al. (2013): *ACS Nano*, **7**, 811–817.