

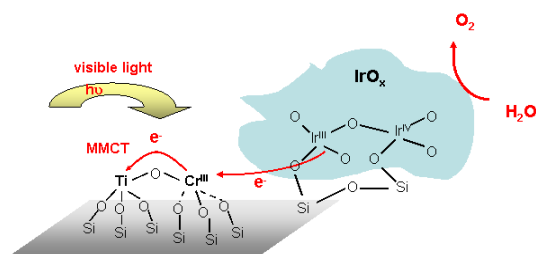
Polynuclear Metal Oxide Photocatalysts on Nanoporous Silica for Visible Light H₂O Oxidation and CO₂ Reduction

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Key words: Mesoporous silica; Binuclear charge transfer chromophore; Visible light; Water oxidation

Presentation Abstract

Conversion of CO₂ to a low alcohol using H₂O as electron source is an attractive goal for sunlight to fuel conversion. To take advantage of the flexibility by which energy flow, charge transport and catalytic transformations can be controlled by discrete molecular structures, we are exploring an inorganic ‘molecular’ approach for assembling artificial photosynthetic systems. The high surface area of nanoporous silica supports afford the high density of photocatalytic sites needed for the chemistry to keep up with the solar flux, while the nanostructured features can be utilized



for spatially separating reducing from oxidizing sites. Photocatalytic units consist of an oxo-bridged binuclear metal-to-metal charge-transfer group (MMCT), which is coupled to a multi-electron transfer catalyst. In some cases, the binuclear charge-transfer unit itself can act as redox site. We have developed mild synthetic methods for assembling and anchoring oxo-bridged binuclear MMCT units

on silica mesopores with high selectivity. The selectivity is based on acidity differences between metal-OH groups and surface silanols (assembly of TiOCo^{II}, TiOCe^{III}, ZrOCu^I, TiOMn^{II}), or on selective redox reactivity (TiOCr^{III}).¹⁻⁴ Structures of these all-organic units were determined by EXAFS, XANES, FT-Raman, FT-IR, EPR and optical spectroscopy. The MMCT groups serve as visible light electron pumps with adjustable redox potential that depends on the selected donor/acceptor metal and oxidation state. When coupling the TiOCr^{III} unit to an Ir oxide nanocluster inside the silica nanopore of MCM-41 silica material, water oxidation was observed upon irradiation of an aqueous suspension with visible light.⁴ Use of an organometallic di-μ-oxo Mn complex as model catalyst allowed us to monitor spectroscopically the state of the transition metal core at a level of detail not readily attainable with metal oxide nanoclusters. Visible light-induced electron transfer from the Mn core to a single Cr charge-transfer center anchored on the silica nanopore surface was observed.⁵ Similarly, CO₂ splitting to CO was achieved by exciting the MMCT transition of ZrOCu^I units of ZrCu^I-MCM-41 loaded with gaseous CO₂. The flexibility of the assembly of the photocatalytic units opens up opportunities for the efficient coupling of water oxidation with CO₂ reduction sites in the nanoporous scaffold.

References

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