



Review

Coupling metal oxide nanoparticle catalysts for water oxidation to molecular light absorbers

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ABSTRACT

Water oxidation, as a mandatory reaction of solar fuels conversion systems, requires the use of light absorbers with electronic properties that are well matched with those of the multi-electron catalyst in order to achieve high efficiency. Molecular light absorbers offer flexibility in fine tuning of orbital energetics, and metal oxide nanoparticles have emerged as robust oxygen evolving catalysts. Hence, these material choices offer a promising approach for the development of photocatalytic systems for water oxidation. However, efficient charge transfer coupling of molecular light absorbers and metal oxide nanoparticle catalysts has proven a challenge. Recent new approaches toward the efficient coupling of these components based on synthetic design improvements combined with direct spectroscopic observation and kinetic evaluation of charge transfer processes are discussed.

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1. Introduction

Efficient water oxidation driven by sunlight is an essential reaction for any solar fuel conversion system because it provides the electrons and protons needed for converting carbon dioxide to a liquid transportation fuel. The necessity of using water as donor stems from the requirement that a solar fuels technology on the terawatt scale be completely cyclic, with no major side products accumulating at the fuels generation or consumption stage. Because carbon dioxide and water are always the end products of spent fuel, electrons and protons need to be taken from water in order for the fuels generation–utilization process to be cyclic. Metal oxides of late first row transition elements Co, Mn, Fe, Ni, and some multi-metal variants have recently emerged as water oxidation catalysts with sufficiently high activity for incorporation into solar fuel conversion systems. These oxides are attractive because of robustness and Earth abundance, which are essential for scalability. Breakthroughs in nanostructuring of these metal oxides have led to dramatic enhancement of the number of catalytic surface sites per geometrical area [1–14] resulting in nanoparticulate or nanostructured metal oxide catalysts that operate at sufficiently high rates to keep up with the photon flux impinging on the catalyst at maximum solar intensity ($1500 \text{ photons s}^{-1} \text{ nm}^{-2}$) [15], a key requirement for an efficient artificial photosystem.

For efficient coupling of metal oxide catalysts, molecular light absorbers offer a distinct advantage over semiconductor light absorbers in terms of the fine tuning of the redox properties. This allows the precise matching of the redox potential of the sensitizer and the catalyst for maximum conversion of solar photon energy into chemical energy of the reduced fuel product and evolving oxygen. Furthermore, the light absorber–catalyst contact can be designed and controlled at the atomic level by covalent anchoring methods or specific electrostatic interactions, while solid–solid interfaces of semiconductor light absorbers and metal oxide catalysts typically cannot. Efficient coupling is important for achieving high quantum yield of charge transfer from light absorber to catalyst.

A particular challenge of light-driven multi-electron catalysis is matching of the rate of photon absorption by the chromophore with the speed of multi-electron catalysis in order to maximize the productive use of absorbed light. While average turnover frequencies per exposed surface metal of oxide catalysts for water oxidation are on the order of $10^{-2} \text{ O}_2 \text{ s}^{-1}$ [1,16–18], the very high density of sites per geometrical area of a nanostructured catalyst offers productive use of every charge generated by an absorbed photon even at high solar flux because there is a sufficient number of sites at disposal to start a fresh catalytic cycle. However, a persistent challenge for molecular light absorber–metal oxide catalyst systems, particularly for the water oxidation half reaction, is to achieve high thermodynamic and quantum efficiency for charge transfer between the light absorber and the catalyst. In this article, we will review recent progress toward efficient coupling of molec-

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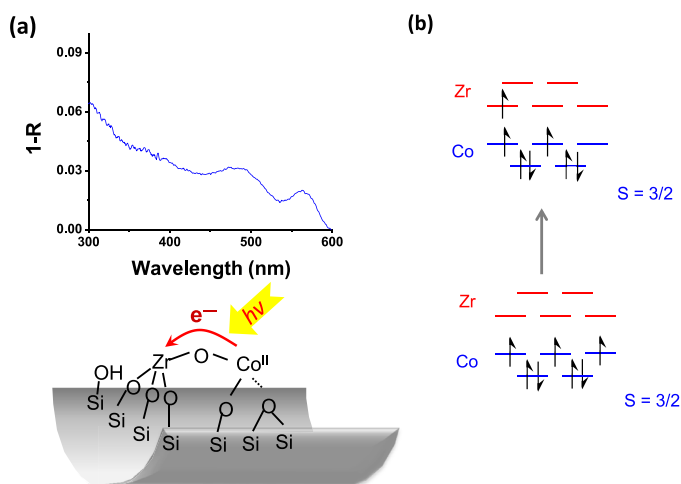


Fig. 1. ZrOCo metal-to-metal charge-transfer unit covalently anchored on silica mesopore surface (SBA-15). (a) Optical absorption of binuclear ZrOCo unit measured by diffuse reflectance spectroscopy. The absorption of Co was subtracted using the spectrum of monometallic Co-SBA-15. From Ref. [19], with permission. (b) Orbital occupancy change upon optical MMCT excitation.

ular light absorber-metal oxide nanoparticle catalyst assemblies for visible light-driven water oxidation.

2. All-inorganic binuclear light absorber-metal oxide nanoparticle catalyst systems

Oxo-bridged hetero binuclear units anchored on silica are molecularly defined visible light absorbers that can be coupled to nanoparticle water oxidation catalysts by selective assembly methods. These all-inorganic binuclear units possess a metal-to-metal charge-transfer absorption (MMCT) extending from the UV deep into the visible spectral region, as shown for a ZrOCo^{II} unit anchored on a mesopore silica surface in Fig. 1(a) [19,20]. Absorption of a photon by the MMCT transition results in electron transfer from a HOMO of the Co^{II} donor to the LUMO of the Zr^{IV} acceptor (Fig. 1b). Transient Co^{III} so produced has sufficient oxidation power to drive a water oxidation catalyst. Recent syntheses of a dozen different hetero binuclear units featuring Earth abundant transition and some group IIIA–VIA metals [21] provide a wide range of light absorbers with flexible choice of redox potential of the donor center. This allows matching of the redox potential of the light absorber with that of the water oxidation catalyst. For systems studied thus far by transient optical spectroscopy, such as TiOMn^{II} and TiOCu^I, excited MMCT lifetimes extend to microseconds, which should be adequate for driving multi-electron catalysts for water oxidation [22–24].

2.1. Driving Ir oxide nanoparticle catalyst with TiOCr light absorber

In an early example, TiOCr units anchored in the pore surface of mesoporous silica MCM-41 (unidimensional silica structure of 3 nm diameter channels, here with Al as minor substituent (Al/Si = 0.04) for stable anchoring of Cr centers) were coupled to Ir oxide nanoclusters of 2 nm diameter using a chemical deposition method based on the redox properties of Cr centers and organometallic Ir precursor [25]. Ir oxide nanoparticles in the form of aqueous colloids or nanoclusters supported on mesoporous silica or anodes are known as efficient water oxidation catalysts [26–28]. The coupling was achieved by spontaneous redox reaction of Ir^{III}(acac)₃ precursor (acac = acetylacetonate) in solution at room temperature with Cr centers of TiOCr^{IV} units in MCM-41, resulting in the formation of TiOCr^{III} with adjacent Ir^{IV}(acac)₂ as manifested by FT-IR, FT-Raman

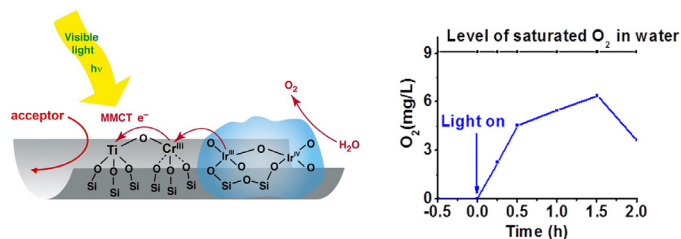


Fig. 2. TiOCr^{III}-IrO_x photocatalytic unit for water oxidation. Electrochemical monitoring of O₂ evolution upon illumination of the Ti^{IV}OCr^{III} → Ti^{III}OCr^{IV} MMCT transition at 458 nm. The sample is an aqueous suspension of MCM-41 mesoporous silica particles containing TiOCr^{III}-IrO_x units. The electron on transient Ti^{III} is transferred to sacrificial persulfate acceptor. From Ref. [25], with permission.

and UV–vis spectroscopic monitoring [25]. The loss of acac ligand upon oxidation of the precursor to Ir^{IV} observed in the infrared and optical spectra created a nucleus for growth of Ir oxide nanocluster upon mild calcination at 350 °C. While the proximity of the TiOCr^{III} charge transfer light absorber and the IrO_x clusters cannot be directly demonstrated spectroscopically (the bridge mode of a Cr–O–Ir linkage was detected by FT-Raman at 808 cm⁻¹ when starting with single Cr centers, however) [29], photochemical studies discussed in the following established that the catalyst cluster is positioned in electron transfer distance from the Cr donor center of the TiOCr unit. The proximity of the IrO_x cluster is most probably due to the fact that the ligand-deficient Ir center that serves as nucleus for growth is generated in charge transfer distance from the Cr center (nanometer or less).

Excitation of the Ti^{IV}OCr^{III} → Ti^{III}OCr^{IV} absorption of TiOCr-IrO_x units in mesoporous silica particles suspended in close to neutral aqueous solution with 458 nm light resulted in water oxidation to O₂, which was monitored in solution by an O₂-sensitive Clark electrode, [25]. As a half reaction, the system required a sacrificial electron acceptor such as persulfate which reoxidized transient Ti^{III}, as shown in Fig. 2. The observation of visible light driven water oxidation by excitation of the Ti^{III}OCr^{IV}-IrO_x state is consistent with the estimated redox potential of 2 V for transient Cr^{IV}. From the remarkably high quantum yield of 13%, efficient electron transfer coupling of the Cr donor center with the Ir oxide catalyst is inferred. The result was confirmed by the observation of Ti^{III} by EPR spectroscopy that accumulates during photocatalysis when the persulfate acceptor was omitted, indicating that hole transfer from transient Ti^{III}OCr^{IV} to the Ir oxide catalyst cluster competes successfully with back electron transfer of Ti^{III}. Once the Cr center captured an electron from IrO_x, Ti^{III} has no open electron transfer path and is rendered sufficiently long lived for detection by EPR spectroscopy. The TiOCr-IrO_x system was the first example of an all-inorganic assembly consisting of a molecularly defined single photon, single charge transfer pump driving a multi-electron catalyst for water oxidation.

2.2. Coupling water oxidation to carbon dioxide reduction at ZrOCo-Ir oxide unit

By expanding the approach of redox reaction with precursor metal complexes for the spatially controlled positioning of Ir oxide catalyst clusters to light-driven instead of dark processes, it became feasible to assemble a ZrOCo^{II}-IrO_x unit that not only affords photo-induced water oxidation, but converts CO₂ to CO by reduction at transient Zr^{III} formed upon MMCT excitation. Carbon dioxide reduction was previously demonstrated for ZrOCo^{II} units anchored in mesoporous silica SBA-15 (unidimensional channels of 8 nm pore diameter) loaded with 1 atm of CO₂ gas upon illumination of the MMCT transition in the presence of an amine as sacrificial donor [19]. Hence, ZrOCo^{II}-IrO_x units were shown to close the photosynthetic cycle of CO₂ reduction by H₂O [20]. In

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