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Visible Light-Driven Water Oxidation by Ir Oxide Clusters Coupled to Single Cr Centers in Mesoporous Silica

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Inert nanoporous oxides such as silica offer opportunities for assembling and coupling photocatalytic components for the direct conversion of water and carbon dioxide to fuel molecules under visible light. In these materials, framework substitution or covalent anchoring of metal centers and polynuclear components, and spatial separation of oxidizing from reducing sites can be explored by virtue of their surface chemistry and compartmentalized structure.[1] A particular challenging task of this or any other approach to artificial photosynthesis is the visible light-driven oxidation of water.[2] Of the small number of established oxygen evolving catalysts, all are driven either electrochemically, by adding strong oxidants directly to the solution, or by generating the oxidant photochemically from a suitable precursor.[2,3] To develop solar to fuel systems by integrating photocatalytic components into nanostructured scaffolds, direct coupling of the catalytic water oxidation site to a built-in visible light-driven electron pump is required.[4] Moreover, the chemical nature of the charge-transfer pump has to be such that it can be coupled to a reducing site in the nanoporous scaffold that accomplishes CO_2 or H^+ reduction. We report here an oxygen-evolving photocatalytic unit inside silica mesopores that consists of a single framework Cr^{VI} center as a visible light-absorbing electron pump coupled to an Ir oxide nanocluster.

The choice of Ir oxide clusters as multielectron-transfer catalyst for water oxidation was based on the high rates and robustness.[3b−d] The catalyst has been used as bulk material,[3c,5] in colloidal form in suspension or supported by Nafion,[6,7] or on inorganic oxide supports such as silica or zeolites.[3b,7] In all reports, strong oxidants such as Ce^{4+} [8] or $Ru(bpy)_3^{3+}$ (as complex[3b,c] or in the form of poly(pyridyl) polymer[7]) were used for driving the water oxidation. In most recent studies, Mallouk achieved turnover rates of 160 s^{-1},[9] which is sufficient to keep up with the solar irradiance.[2b]

Chromium framework substituted MCM-41 ($Cr/Si = 0.01-0.05$, $Al/Si = 0.02$) was synthesized by a co-assembly hydrothermal method[10] followed by calcination in air at 630 °C for 10 h.[11] Figure 1A, trace 1, shows the characteristic FT-Raman band of isolated $(SiO)_2Cr^{VI}(=O)_2$ centers on the silica pore surface assigned to $\nu_s(O=Cr^{VI}=O)$.[12] For samples with $Cr/Si \leq 0.02$, no Raman bands originating from di-, tri-, or polychromate[12b−d] were observed in the 950−800 cm^{-1} region (Supporting Information, Figure S1).[13] This was further confirmed by FT-IR spectra of CrMCM-41 ($Cr/Si = 0.02$) shown in Figure 1B, trace 1. The broad absorption at 889 cm^{-1} is characteristic for $\nu_{as}(O=Cr^{VI}=O)$ of isolated $(SiO)_2Cr^{VI}(=O)_2$ centers,[14] while bands due to di- or polychromate are absent in the 950−900 cm^{-1} region for $Cr/Si \leq 0.02$ samples (Figure S2).[13]

For the preparation of Ir oxide nanoclusters inside the pores, 500 mg calcined CrMCM-41 particles were added to 50 mL of 0.09 mM $Ir(acac)_3$ solution in toluene and stirred in the dark inside a N_2 glovebox (acac: $CH_3COCH=C(O^-)CH_3$). The pale green powder was filtrated, washed in the glovebox, and dried in a vacuum for 8 h ($Ir/Si = 0.007$). FT-Raman and IR spectroscopy revealed that the Ir^{III} complex underwent anchoring by reaction with $Cr^{VI}=O$ surface sites.[15]

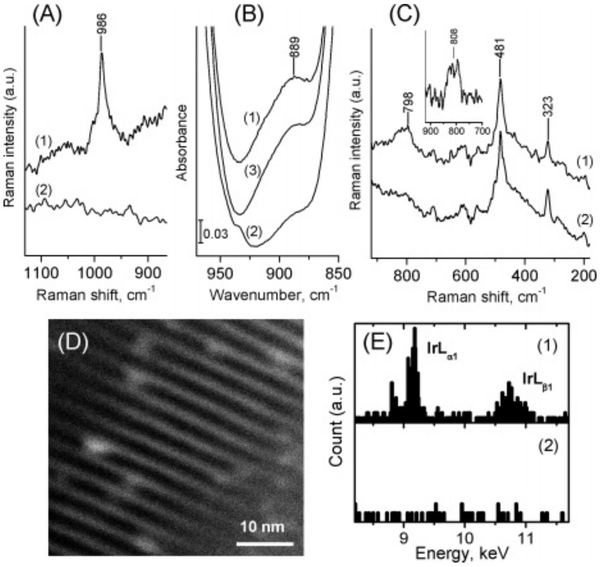

Figure 1. (A) FT-Raman spectra of dehydrated CrMCM-41 ($Cr/Si = 0.02$) (1) before and (2) after grafting of $Ir(acac)_3$; (B) FT-IR spectra of dehydrated CrMCM-41 ($Cr/Si = 0.02$) (1) before and (2) after grafting of $Ir(acac)_3$ and (3) after calcination at 300 °C; (C) FT-Raman spectra of (1) CrMCM-41 ($Cr/Si = 0.02$) after grafting of $Ir(acac)_3$ and (2) MCM-41 after grafting of $Ir(acac)_3$. Insert shows difference of trace 1 and 2 around 800 cm^{-1}. Bands at 481 and 323 cm^{-1} are due to acac ligands. Panel D shows *Z*-contrast high-resolution electron micrograph of Ir_xO_y-MCM-41; mesoporous channels are clearly visible. Shown also are (E) EDX spectra of (1) bright spot and (2) dark mesopore section of image D.

$$Cr^{VI}=O + Ir^{III}(acac)_3 \rightarrow Cr^{V}-O-Ir^{IV}(acac)_2 + acac$$

The reaction is readily detected by loss of the $O=Cr^{VI}=O$ modes upon reaction with $Ir^{III}(acac)_3$ at 986 cm^{-1} (Raman, Figure 1A, trace 2) and 889 cm^{-1} (IR, Figure 1B, trace2), consistent with reduction to Cr^V. At the same time, a new Raman band appears at 808 cm^{-1}, which is attributed to the asymmetric stretching mode of the newly formed $Cr-O-Ir$ bridge (Figure 1C, trace 1, and inset).[15,16] This band is not formed when the precursor is loaded into MCM-41 free of Cr (Figure 1C, trace 2). Following grafting of the Ir complex, the material was calcined at 300 °C for 10 h under O_2 flow, resulting in the formation of Ir oxide nanoclusters. Comparison of HRTEM images of Ir_xO_y-CrMCM-41 and CrMCM-41shows that the mesoporous order of the silica is not perturbed by Ir oxide formation (Figure S4).[13] High-resolution *Z*-contrast imaging combined with EDX spot analysis confirms the formation of Ir_xO_y nanoclusters inside the pores (Figure 1D and E). The reoxidation of Cr^V to Cr^{VI} upon calcination is indicated by the growth of the 889 cm^{-1} infrared absorption, and no concurrent growth of di- or polychromate species

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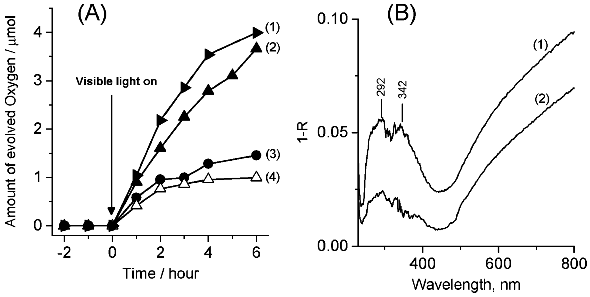

Figure 2. (A) Photochemical O_2 evolution from aqueous suspension of Ir_xO_y−CrMCM-41 with Cr/Si (1) 0.01, (2) 0.02, and (3) 0.05 in the presence of 0.01 M $S_2O_8^{2-}$; (4) same experiment (Cr/Si = 0.02) in the absence of $S_2O_8^{2-}$; (B) DRS of dehydrated Ir_xO_y−CrMCM-41(Cr/Si = 0.02) pellet after 6 h oxygen evolution (1) with (2) without $S_2O_8^{2-}$ added.

was detected (Figure 1B, trace 3). We conclude that the Ir_xO_y−CrMCM-41 material so obtained consists of single Cr^{VI} centers and Ir oxide nanoclusters inside the mesopores.

Photochemical water oxidation experiments were conducted in a 250 mL Pyrex reaction vessel connected to a vacuum system that allowed capturing of 2.5 cm^3 aliquotes of evolving O_2 gas, which was injected periodically into a quadrupole mass spectrometer (Pfeiffer model Omnistar 422). The $Cr^{VI}-O^{II} \rightarrow Cr^{V}-O^{I}$ LMCT transition of the Ir_xO_y−CrMCM-41 particles (150 mg) suspended in 150 mL of H_2O was irradiated with the 458 nm emission (156 mW) of an Ar ion laser with the beam expanded to 1 in. diameter, or with visible light of a Xe-arc lamp (Corning filter # 3-74). Figure 2A shows the amount of oxygen gas evolved when the aqueous solution contained 0.01 M $Na_2S_2O_8$ electron acceptor and the pH was kept at 5.4 (buffer: KH_2PO_4 (1.1×10^{-2} M) and $Na_2B_4O_7$ (4.4×10^{-4} M)).[7] No O_2 was formed in the dark, under illumination for CrMCM-41 free of Ir_xO_y or for Ir_xO_y−MCM-41 free of Cr. This demonstrated that water oxidation is driven by charge-transfer-excited $Cr^{VI}O$ coupled to Ir oxide clusters. Furthermore, Figure 2A shows that of the three Cr samples, Cr/Si = 0.01, 0.02, and 0.05, the low concentration materials Cr/Si ≤ 0.02 have much higher O_2 yields than Cr/Si = 0.05. Since the Cr/Si = 0.05 material has significant concentrations of di- and polychromate (Figure S1),[13] the result implies that single Cr^{VI} centers, not Cr oxide clusters, are the photoactive centers that pull electrons from the Ir oxide clusters. Water oxidation at a multielectron transfer catalyst driven by a directly coupled molecular charge-transfer moiety has not been reported before to our knowledge.

As expected, the visible light-induced water oxidation also proceeds in the absence of the electron acceptor, as shown by trace 4 of Figure 2A. However, O_2 formation levels off rapidly compared to experiments in the presence of the electron acceptor (trace 2) because of the stoichiometric reduction of Cr^{VI} to Cr^{V}. This is confirmed by the corresponding optical and EPR spectra.[13,17] As can be seen from the DRS in Figure 2B, trace 1, the $Cr^{VI}O$ LMCT absorption of Ir_xO_y−CrMCM-41 particles (peaks at 292 and 342 nm, tail extending to 500 nm, Figure S5)[13] remains unchanged upon 6 h of oxygen evolution if $S_2O_8^{2-}$ is present. This indicates that the acceptor continuously reoxidizes Cr^{V}, while the hole on the O hops into the Ir oxide cluster (the continuous absorption at $\lambda > 500$ nm is due to Ir_xO_y). By contrast, more than 90% of the intensity of the $Cr^{VI}O$ charge-transfer absorption is lost in the same experiment if the acceptor is absent (Figure 2B, trace 2). Comparison of the amount of oxygen produced in the presence (Figure 2A, trace 2) and absence of $S_2O_8^{2-}$ (trace 4) indicates a turnover number of 4 for the active Cr centers.[18]

In conclusion, visible light-induced water oxidation has been demonstrated at a polynuclear catalyst coupled directly to a molecular charge-transfer moiety in a nanoporous solid. Covalently anchored metal centers as charge-transfer chromophores open up opportunities for coupling the oxygen-evolving site to a reducing metal-to-metal charge-transfer unit in the nanoporous solid for accomplishing CO_2 reduction under H_2O oxidation in a sequential two-step process.[19]

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Supporting Information Available: FT-Raman, FT-IR, UV−vis spectra, HRTEM images, XRD data. This material is available free of charge via the Internet at http://pubs.acs.org.

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