Ferrocenium Titration of 1 in Acetonitrile Containing Pyrrolidine. A solution of $Cp_2Fe^+PF_6^-$ (165.5 mg, 0.50 mmol) in acetonitrile (2.50 mL) was added slowly with a syringe to a vigorously stirred solution of **1** (54.2 mg, 0.20 mmol) and pyrrolidine (16.7 μL, 0.20 mmol) in acetonitrile (3 mL). The persistent greenish tint indicating the presence of unreacted ferrocenium was seen after the addition of ca. 2.1 mL of the ferrocenium solution, whereupon the addition was stopped. The amount of solution added corresponds to the consumption of 2.1 equiv of the oxidizing agent. The solvent was removed by vacuum transfer, and the residue was washed with ether (3 × 2 mL) to remove the ferrocene. The remaining solid was dissolved in dichloromethane (4 mL), and the solution was washed with aqueous ammonium chloride (3 × 2 mL), dried ($MgSO_4$), and filtered through Celite. Recrystallization twice from dichloromethane/ether yielded a pale yellowish brown powder (65.1 mg). ^1H NMR analysis showed **2** to be the only product (71% yield).

Constant-Current Coulometry and Preparative Electrolysis Experiments. Constant-current electrolyses with DCV monitoring of the disappearance of substrate were performed in a H-shaped cell, the compartments of which were separated by a fritted-glass junction. A Pt-gauze working electrode was used. Solutions that contained 2.0 mM of **1** in 20 mL of acetonitrile/0.1 M $Bu_4N^+PF_6^-$ were electrolyzed with a constant current of 10 mA. The procedure was identical for coulometry experiments performed in the presence of 2,6-lutidine (20 mM).

The preparative electolyses were carried out in acetonitrile/0.05 M $Me_4N^+BF_4^-$. A solution of **1** (30 mg, 0.111 mmol) in the electrolyte solution (20 mL) was electrolyzed for the time that was required for the passage of 1.0 faraday/mol of charge. The IR spectrum of an aliquot revealed two equally intense CO absorptions at 1950 and 1980 cm^{-1}. The solution was concentrated by rotary evaporation, and the residue was extracted with dichloromethane (5 mL). The filtered extract was concentrated, and the product (21.5 mg, 49%) was precipitated by the addition of ether. ^1H NMR spectroscopy showed the product to be **2** contaminated with a trace of the two isomers of **5**.

Preparative electrolysis in the presence of 2 equiv of pyrrolidine was carried out similarly, except that a 2-electron oxidation was performed. IR analysis showed only one CO absorption at 1980 cm^{-1}. During workup, the dichloromethane extract was washed with a 5% aqueous ammonium chloride solution (2 × 3 mL) in order to remove the conjugate acid of the base. The solution was dried ($MgSO_4$), filtered, and concentrated, and the residue was crystallized from dichloromethane/ether to provide **2** in a yield of 54%.

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Registry No. **1**, 87985-84-0; **2**, 136947-47-2; **2**-d_3, 136947-51-8; **3**, 110142-04-6; **4**, 136947-48-3; **4**-d_9, 136947-52-9; **5a**·BF_4, 136947-50-7; **5b**·BF_4, 137036-32-9; $Cp_2Fe^+PF_6^-$, 11077-24-0; (p-$MeOC_6H_4$)Ph_2C^+-BF_4^-, 1881-93-2.

Visible Light Photolysis of Hydrogen Iodide Using Sensitized Layered Semiconductor Particles

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Abstract: Surface sensitization of internally platinized layered oxide semiconductors $K_{4-x}H_xNb_6O_{17}\cdot nH_2O$ ($x \approx 2.5$), $H_2Ti_3O_7$, and $HTiNbO_5$ by RuL_3^{2+} (L = 4,4′-dicarboxy-2,2′-bipyridine) yields photocatalysts for the production of H_2 and I_3^- in aqueous iodide solutions. Flash photolysis experiments show that, at pH 3.0, excited-state RuL_3^{2+} injects an electron into $K_{4-x}H_xNb_6O_{17}\cdot nH_2O$ and is rapidly re-reduced by I^-. Steady-state photolysis at 450 nm in 50 mM aqueous KI (pH 3.0) yields H_2 and I_3^- in stoichiometric amounts, with an initial quantum yield of 0.3%. While H_2 and I_3^-, once formed, do not recombine at an observable rate, the rate of hydrogen evolution decreases as the concentration of I_3^- increases in the solution.

Despite the successes realized with solid-state and liquid-junction photoelectrochemical devices, there are very few chemical systems (apart from natural photosynthesis) which make energy-rich oxidized and reduced products from abundant feedstocks photochemically (i.e., without wires attached[1,2]) using light of visible wavelengths. Homogeneous or particle-based photochemical systems for hydrogen or oxygen generation typically employ "sacrificial" reducing or oxidizing agents which are irreversibly decomposed in the reaction; these systems are not of interest in practical energy conversion schemes, because in one of the half-reactions an expensive chemical (e.g., EDTA or persulfate) is consumed.

For nonsacrificial systems, i.e., those which employ chemically reversible electron donors *and* acceptors, the problem is one of spatial compartmentalization. Following photochemical charge separation, energetic oxidized and reduced products are produced at catalytic surfaces. These products must be prevented from recombining (the recombination reaction is necessarily favorable, if free energy is being stored) at the same catalyst. In photoelectrochemical cells this problem is conveniently overcome by carrying out the oxidation and reduction half-reactions at spatially well separated electrodes. However, in photochemical systems, products are made at the same particle, or in the same homogeneous solution, and keeping them separate requires sieving at the molecular level.

Recently, Domen, Onishi, and co-workers have reported that the layered semiconductor $K_4Nb_6O_{17}\cdot 3H_2O$, when internally loaded with elemental nickel or platinum as a hydrogen evolution

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(1) We are counting multipanel photoelectrode systems, which can decompose hydrohalic acids or water into their elements without input of electrical power, as internally wired photoelectrochemical devices. Examples are the Texas Instruments silicon microsphere system for HBr photolysis (Kilby, J. S.; Lathrop, J. W.; Porter, W. A. U.S. Patents 4,021,323 (1977), 4,100,051 (1978), 4,136,436 (1979); Johnson, E. L. In *Electrochemistry in Industry*; Landau, U., Yeager, E., Eds.; Plenum Press: New York, 1982; pp 299–306) and CdSe/CoS multipanel devices for water photolysis (Smotkin, E. S.; Cervera-March, S.; Bard, A. J.; Campion, A.; Fox, M. A.; Mallouk, T. E.; Webber, S. E.; White, J. M. *J. Phys. Chem.* **1987**, *91*, 6).

(2) To our knowledge there are three examples of "non-sacrificial" molecular systems which produce hydrogen or oxygen photochemically: sensitized oxygen evolution from water using Fe(III) or Hg(II) as an electron acceptor (Christensen, P. A.; Erbs, W.; Harriman, A. *J. Chem. Soc., Faraday Trans. 2* **1985**, *81*, 575), sensitized hydrogen evolution in which the surface of a TiO_2 colloid is oxidized to form peroxo groups (Frank, A. J.; Willner, I.; Goren, Z.; Degani, Y. *J. Am. Chem. Soc.* **1987**, *109*, 3568), and sensitized hydrogen evolution using $Ru(bpy)_3^{2+}$ or dimethoxybenzene as an electron donor with ultraviolet excitation (Slama-Schwok, A.; Avnir, D.; Ottolenghi, M. *J. Phys. Chem.* **1989**, *93*, 7544; *J. Am. Chem. Soc.* **1991**, *113*, 3984).

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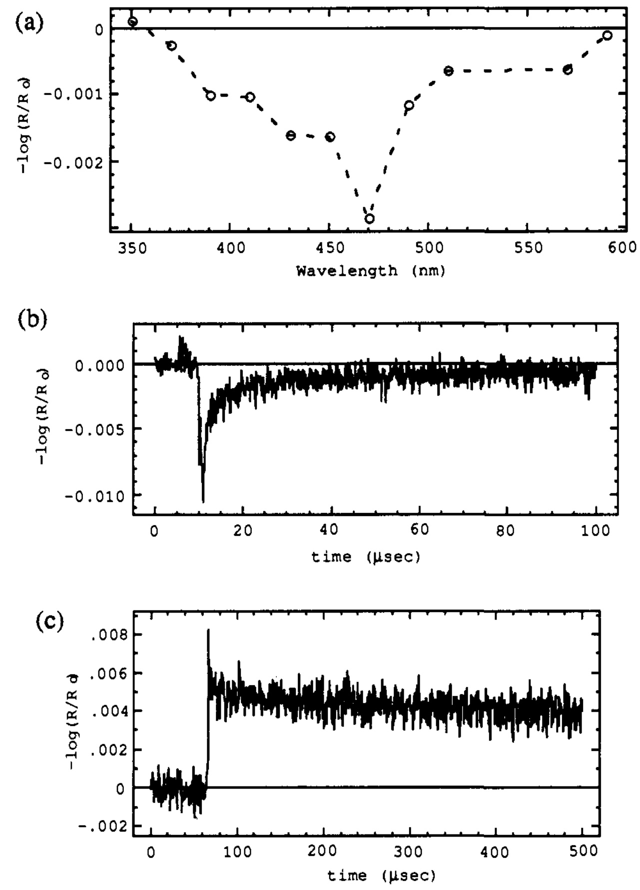
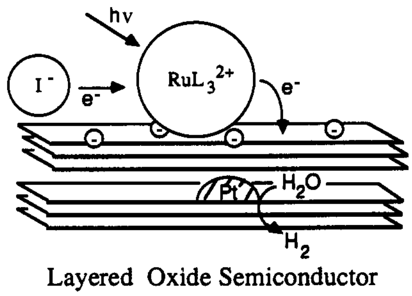


Figure 1. Laser flash photolysis/transient diffuse reflectance of $K_{4-x}H_xNb_6O_{17}{\cdot}nH_2O$ sensitized with 5×10^{-7} mol RuL_3^{2+}/g, suspended in water, pH 3.0: (a) transient spectrum recorded 5.9 μs after 532-nm excitation; (b) decay of RuL_3^{2+} bleaching monitored at 455 nm; (c) same sample with 100 mM KI added, monitored at 380 nm.

catalyst, photodecomposes water to hydrogen and oxygen with bandgap ($\lambda \leq 330$ nm) excitation.[3] Remarkably, the products do not recombine at an observable rate, indicating that the metal catalyst is confined to sites which are inaccessible to oxygen. We report here that the same material, ion-exchanged with acid and containing the surface-adsorbed photosensitizer[4] RuL_3^{2+} (L = 4,4′-dicarboxy-2,2′-bipyridine), photodecomposes acidic KI solutions to hydrogen and triiodide using visible light.

Figure 1 shows the results of laser flash photolysis/transient diffuse reflectance experiments for aqueous suspensions of $K_{4-x}H_xNb_6O_{17}{\cdot}nH_2O$ ($x \approx 2.5$) sensitized with RuL_3^{2+}. Visible laser excitation of the photosensitizer causes immediate bleaching of the MLCT absorption centered at 460–470 nm (Figure 1a). This transient, which undergoes a biphasic decay as shown in Figure 1b, is attributed to the formation of a $Ru^{3+} - e^-_{\text{semiconductor}}$ charge-separated state. When KI is added to the suspension, the bleaching at 460–470 nm cannot be observed on the shortest instrumental time scale (ca. 100 ns), and a positive transient at 380 nm, attributed to $I_2^{\bullet-}$, is instead seen. This reaction sequence shown in eqs 1–3 gives rise to an $I_2^{\bullet-} - e^-_{\text{semiconductor}}$ charge-separated state which decays very slowly on the 500 μs time scale of the flash photolysis experiment. $I_2^{\bullet-}$ is known to form rapidly from $I^\bullet$ and I^- (reaction 3) under the conditions of this experiment.[5] The decay pathway for $I_2^{\bullet-}$ is complex, involving formation of I_3^- and back-electron transfer between $I_2^{\bullet-}$ and the semiconductor. The quantum yield for formation of $I_2^{\bullet-}$ under these conditions is approximately 10–15%.[6]



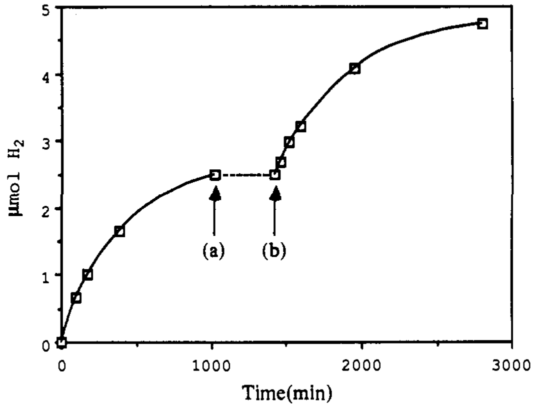


Figure 2. Photochemical hydrogen evolution from 100 mg of $K_{4-x}H_xNb_6O_{17}{\cdot}nH_2O/RuL_3^{2+}$ (5×10^{-7} mol/g)/Pt (0.05%) in 8.0 mL of 50 mM aqueous KI, pH 3.0. Irradiation was interrupted at point a, and a gas sample was taken at point b to check for recombination of H_2 and I_3^-; the sample was filtered and irradiation was continued in a fresh 50 mM KI solution. Light source: filtered Hg–Xe lamp, intensity 24 mW, λ = 450 ± 50 nm.

$$^*RuL_3^{2+} \rightarrow RuL_3^{3+} + e^-_{\text{conduction band}} \qquad (1)$$

$$RuL_3^{3+} + I^- \rightarrow RuL_3^{2+} + I^\bullet \qquad (2)$$

$$I^\bullet + I^- \rightarrow I_2^{\bullet-} \qquad (3)$$

$K_4Nb_6O_{17}$ may be internally platinized according to the method of Domen and co-workers by ion exchange with $Pt(NH_3)_4^{2+}$ and subsequent reduction with hydrogen.[3e] The semiconductor contains at this point both internally and externally sited platinum clusters, and the latter are removed by treatment with aqua regia at 95 °C. Since platinum is an excellent catalyst for the reduction of one-electron, outer-sphere oxidants by molecular hydrogen, its absence on the external surface of the semiconductor loaded with 0.01–0.05% Pt can be checked by the reaction of 0.1 mM $Fe(CN)_6^{3-}$ with hydrogen at pH 4.0. Ferrocyanide cannot ion exchange into the solid, which is a cation exchanger. This reaction is a sensitive test for exposed, catalytically active platinum,[7] and

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[3] (a) Domen, K.; Kudo, A.; Shinozaki, A.; Tanaka, A.; Maruya, K.; Onishi, T. *J. Chem. Soc., Chem. Commun.* **1986**, 356. (b) Domen, K.; Kudo, A.; Shibata, M.; Tanaka, A.; Maruya, K.; Onishi, T. *J. Chem. Soc., Chem. Commun.* **1986**, 1706. (c) Kudo, A.; Tanaka, A.; Domen, K.; Maruya, K.; Aika, K.; Onishi, T. *J. Catal.* **1988**, *111*, 67. (d) Kudo, A.; Sayama, K.; Tanaka, A.; Asakura, K.; Domen, K.; Maruya, K.; Onishi, T. *J. Chem. Soc., Chem. Commun.* **1989**, *120*, 337. (e) Sayama, K.; Tanaka, A.; Domen, K.; Maruya, K.; Onishi, T. *J. Phys. Chem.* **1991**, *95*, 1345.

[4] RuL_3^{2+} and related molecules have been extensively studied as photosensitizers for oxide semiconductor electrodes and colloids: (a) Duonghong, D.; Serpone, N.; Grätzel, M. *Helv. Chem. Acta* **1984**, *67*, 1012. (b) Desilvestro, J.; Grätzel, M.; Kavan, L.; Moser, J. *J. Am. Chem. Soc.* **1985**, *107*, 2988. (c) Furlong, D. N.; Wells, D.; Sasse, W. H. F. *J. Phys. Chem.* **1986**, *90*, 1107. (d) Vlachapoulos, N.; Liska, P.; Augustynski, J.; Grätzel, M. *J. Am. Chem. Soc.* **1988**, *110*, 1216. (e) Liska, P.; Vlachopoulos, N.; Nazeeruddin, M. K.; Comte, P.; Grätzel, M. *J. Am. Chem. Soc.* **1988**, *110*, 3686. (f) Amadelli, R.; Argazzi, R.; Bignozzi, C. A.; Scandola, F. *J. Am. Chem. Soc.* **1990**, *112*, 7099. (g) O'Reagan, B. F.; Grätzel, M. *Nature*, in press.

[5] Ellison, D. H.; Salmon, G. A.; Wilkinson, F. *Proc. R. Soc. London* **1972**, *328*, 23.

[6] The molar extinction coefficient of $I_2^{\bullet-}$ at 380 nm is approximately 1.4 × 10^4 M^{-1} cm^{-1} (Thomas, J. K. *Trans. Faraday Soc.* **1965**, *61*, 702). The quantum yield for its formation was estimated by comparison with the MLCT transient at 360 nm of $Ru(bpy)_3^{2+}$, assumed to be formed with unit quantum yield in a similar suspension containing no KI. This procedure is only semiquantitative because the extinction coefficient of the sensitizer, adsorbed on the semiconductor, may differ from that of $Ru(bpy)_3^{2+}$ in solution.

its non-occurrence on a time scale of several hours with platinized $K_4Nb_6O_{17}$ indicates that anionic redox couples such as ferro/ferricyanide or iodide/triiodide are not able to undergo the energy-wasting recombination reaction 4.

$$\text{oxidized donor} + \tfrac{1}{2}H_2 \rightarrow \text{reduced donor} + H^+ \qquad (4)$$

When RuL_3^{2+} is adsorbed onto platinum-loaded $K_{4-x}H_xNb_6O_{17}{\cdot}nH_2O$ ($x \approx 2.5$, prepared by acid exchange of platinized $K_4Nb_6O_{17}$), hydrogen and triiodide are evolved in stoichiometric amounts from acidic KI solutions under visible illumination. This optimum amount of sensitizer (ca. 7×10^{-6} mol/g) corresponds to roughly monolayer coverage of the external surface, and X-ray diffraction patterns do not show any evidence for intercalation of RuL_3^{2+} into the bulk of the solid. Precipitation of more than monolayer amounts of the sensitizer reduces the yield of photoproducts. Similar results are obtained with internally platinized, acid-exchanged $Na_2Ti_3O_7$ and $KTiNbO_5$. Control experiments show that only traces of hydrogen are formed in the absence of iodide, and that none is produced with visible light excitation in the absence of photosensitizer. Likewise, only traces of hydrogen are detected when internally platinized $K_4Nb_6O_{17}$ is replaced by TiO_2 (anatase) at the same platinum loading.

Figure 2 shows the time course of the HI photolysis reaction. Initially, the quantum yield for product formation is ca. 0.3%. That the initial rate is low, compared with the quantum yield for $I_2^{\bullet-}$ formation in the flash photolysis experiment, indicates that geminate charge recombination between the oxidized donor and electrons transferred to the semiconductor is a dominant pathway. The rate of hydrogen evolution decreases, approaching zero as the concentration of I_3^- in solution increases. Together with the low initial quantum yield, this leveling off indicates that *both* $I_2^{\bullet-}$ and I_3^- recombine efficiently with conduction band electrons. We note, however, that the decrease in rate *cannot* correspond to a photostationary state in which hydrogen forms and recombines thermally with I_3^-, since no back reaction between H_2 and I_3^- occurs in the dark between points a and b. Furthermore, the photocatalyst is still active, as demonstrated by renewed hydrogen evolution when a fresh KI solution is supplied at point b. The key point is that the structured photocatalyst, which keeps the oxidized donor physically separated from the platinum catalyst particles where hydrogen is produced, causes recombination reaction 4 to be imperceptibly slow. From these observations we conclude that the relevant back reactions are interception of electrons, before they reach the Pt catalyst, by oxidized donor species (reactions 6 and 7). Several strategies exist for modifying the photocatalyst in order to favor reaction 5 over reactions 6 and 7, including doping to promote band bending at the semiconductor/solution interface, and employing other sensitizers which might be more effective in blocking $I_2^{\bullet-}$ and I_3^- from contact with the semiconductor surface. We are currently exploring these possibilities.

$$2e^-_{\text{conduction band}} + 2H^+ \rightarrow H_2 \qquad (5)$$

$$e^-_{\text{conduction band}} + I_2^{\bullet-} \rightarrow 2I^- \qquad (6)$$

$$2e^-_{\text{conduction band}} + I_3^- \rightarrow 3I^- \qquad (7)$$

Experimental Section

General Procedures. Steady-state photolyses were carried out using a 200-W mercury-xenon lamp. Ultraviolet light was filtered out using a combination of Pyrex glass and 450-nm interference filters (Oriel), and the transmittance at wavelengths shorter than 390 nm was less than 10^{-4}. Infrared light was filtered with a 5-cm water cell. The sample, a magnetically stirred suspension consisting of an 8.0-mL solution of aqueous KI with a few drops of aqueous $HClO_4$ added to adjust the pH and 0.10-g of photocatalyst powder, was irradiated through a 1-cm² quartz window. The headspace in which gases were collected was typically 4–5 mL. The cell was sealed with a rubber septum and deaerated with argon prior to photolysis. Gas samples were periodically withdrawn via a syringe, and hydrogen was analyzed by gas chromatography. Following the photolysis the suspension was filtered and the concentration of I_3^- was determined spectrophotometrically. Light intensity was measured by ferrioxalate actinometry[8] using the same sample cell; calculated quantum yields are therefore corrected for reflection by the cell window but not for scattering by the photocatalyst. Nanosecond flash photolysis/transient diffuse reflectance experiments were carried out at the Center for Fast Kinetics Research (CFKR), University of Texas at Austin. The excitation source was a frequency-doubled Q-switched Nd:YAG laser (11 ns, 532 nm), and the monitoring light was a pulsed high-pressure xenon lamp. The transient diffuse reflectance optics were similar to those described by Willsher.[9] Flash photolysis experiments were typically carried out with 30 mg of the sensitized semiconductor suspended in 2.0 mL of aqueous solution, adjusted to pH 3.0 with dilute $HClO_4$. The suspension was deoxygenated by purging with nitrogen for 5–10 min.

Materials. Reagent grade K_2CO_3, Na_2CO_3, TiO_2, and Nb_2O_5 were obtained from commercial sources. $K_4Nb_6O_{17}$, $Na_2Ti_3O_7$, and $KTiNbO_5$ were prepared by heating stoichiometric amounts of the appropriate oxides and carbonates at 1050 °C for 2 days in an alumina crucible. X-ray powder diffraction patterns were consistent with literature reports[10] and showed single-phase materials. Platinization of all three layered semiconductors was carried out according to the method of Domen et al.;[3e] alkali cations were exchanged for $Pt(NH_3)_4^{2+}$ in stirred $1-3 \times 10^{-4}$ M solutions of the latter for 2–3 days. Reduction to elemental Pt was carried out in a hydrogen stream at 350 °C, and the solids were subsequently treated with 2:1 (volume) concentrated HCl/HNO_3 at 95 °C for 1–3 h in order to remove externally sited platinum particles. Subsequent acid exchange was carried out in 0.5 M HCl solutions. The solutions were filtered and replaced daily in order to ensure full ion exchange, which required 1–2 days for platinized $K_4Nb_6O_{17}$ and $KTiNbO_5$, and 4–5 days for $Na_2Ti_3O_7$. The alkali metal/transition-metal ratio in the acid-exchanged materials was determined by electron microprobe analysis. $RuL_3(PF_6)_2$ was prepared as previously described[11] and was adsorbed onto the acid-exchanged semiconductor powders from 1 to 5×10^{-4} M aqueous solutions at pH 4.

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Registry No. H_2, 1333-74-0; I_3, 14900-04-0; $H_2Ti_3O_7$, 99601-82-8; $HNbTiO_5$, 118955-75-2; Pt, 7440-06-4; HI, 10034-85-2; RuL_3^{2+} (L = 4,4′-dicarboxy-2,2′-bipyridine), 99837-92-0.

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