114. Integrated Systems for Water Cleavage by Visible Light; Sensitization of TiO_2 Particles by Surface Derivatization with Ruthenium Complexes

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Summary

Irradiation of acidic (pH 2) solutions of $RuL_3^{2+}\ 2Cl^-$ (L = diisopropyl 2,2'-bipyridine-4,4'-dicarboxylate) in the presence of TiO_2 at 100°C leads to the loss of one bipyridyl ligand and the chemical fixation of RuL_2 at the surface of the TiO_2 particles through formation of Ru-O-Ti bonds. These surface complexes are very stable and shift the absorption onset of TiO_2 beyond 600 nm. Efficient sensitization of H_2-generation is achieved with this system beginning in the wavelength domain between 590 and 665 nm. Preliminary water cleavage experiments with the bifunctional $TiO_2/Pt/RuO_2$ redox catalyst are reported.

Introduction. – Spectral sensitization of large band-gap semiconductors is widely applied in silver halide [1] and electrophotography [2]. Optimum results are achieved with systems where intimate contact between dye and semiconductor is established. Thus, in the case of ZnO, a successful strategy for sensitization, applied in patents by *Agfa-Gevaert* [3] and *Lee* [4] and established through the pioneering work of *Zollinger et al.* [5] and *Hauffe* [6], consists of the chelation of Zn^{2+} ions at the particle surface by suitable chromophores. Surface modification of semiconductors such as TiO_2 and SnO_2 by adsorbed or covalently linked photoactive dyes is also a subject of increasing investigation [7–9] in view of the potential applications to solar energy conversion. In both photoelectrochemical cells [7] and H_2-generating photochemical systems [8] [9], the phenomenon of photosensitized electron injection is used to effect charge separation with light of less than band-gap energy. Very interesting in this regard is our recent observation [9] that complexation of Ti^{4+} by 8-hydroxyquinoline on the surface of TiO_2 leads to *in situ* formation of an efficient sensitizer for H_2 generation by visible light. A drawback of the latter system, making necessary the use of sacrificial electron donors, is the inability of the oxidized sensitizer to produce oxygen from water. Here, we report on a new method for surface derivatization of TiO_2 by a more suitable chromophore which, we believe, should be of great importance for the design of reliable catalytic systems affording water cleavage by visible light with no assistance from sacrificial donors or acceptors.

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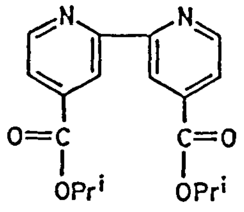
Experimental. – The ruthenium complex $[RuL_3]Cl_2$ (L = diisopropyl 2,2′-bipyridine-4,4′-dicarboxylate) was synthesized according to the procedures in [10]. TiO_2 (anatase, Nb content ≈ 600 ppm, primary crystallite size 100 Å, BET 145 m^2/g) was obtained from Dr. *P. Panek, Bayer AG,* Krefeld-Uerdingen, West Germany. To prepare bifunctional $TiO_2/Pt/RuO_2$ redox catalyst, we employed $TiCl_4$ *(Fluka, purissimum)* which was further purified by vacuum distillation [11]. This was hydrolyzed in cold water (0°), together with the required amount of $NbCl_5$ to obtain 0.1% Nb doping. The final pH of the solution was *ca.* 0.5. Through subsequent dialysis the pH was raised to 2. At this time, the required amount of H_2PtCl_6 *(Engelhard)* and RuO_4 *(Alfa Inorganics)* was added to obtain the (calculated) loading of 0.5% Pt and RuO_2 each, on the TiO_2 particles. The solution was placed in a glass bowl, evaporated to dryness at 60° and kept for 1 day at this temp. Spontaneous decomposition of RuO_4 [12] occurred under these conditions producing dark deposits of RuO_2. To reduce $PtCl_6^{2-}$ to Pt, 50 mg of this catalyst were suspended in 25 ml water and, after deaeration with Ar, irradiated in a *Pyrex* flask (50 ml volume) with a *XBO* 450-W Xe lamp. Reduction was carried out by conduction band electrons produced in the TiO_2 particles *via* band-gap excitation [13]. Photoplatinization was stopped after *ca.* 30 min of irradiation when significant amounts of H_2 appeared in the gas phase. For water cleavage experiments, the RuL_3^{2+} sensitizer was directly added to this $TiO_2/RuO_2/Pt$ dispersion. The total volume of the solution was increased to 40 ml, the final RuL_3^{2+} concentration adjusted to 1.5×10^{-4}M and the pH to 2 with HCl.



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Surface derivatization and water cleavage experiments were performed with the apparatus shown in *Fig. 1.* The 50 ml flask containing the TiO_2 dispersion is placed on a hot plate combined with a magnetic stirrer. It is connected through a ground glass joint to a cooler equipped with the two stopcocks B and C. Through a capillary glass tube, the latter is attached to a second flask containing 30 ml distilled water. Prior to irradiation, air is removed from the whole system by flushing with Ar. Ar is introduced through a needle inserted in the solution *via* septum A. Subsequent to deaeration, the temp. is increased to the boiling point and after closing stopcocks A, B and C, the solution is irradiated by a *XBO* 450-W Xe lamp equipped with a 420-nm cut-off filter and a water jacket to remove UV and IR radiation, respectively. Gas samples were taken at regular intervals through septum B with a microsyringe and injected in a gas chromatograph (*Gow Mac* detector, Ar carrier gas) for analysis. Except for these very brief moments, stopcock B remains closed during the photolysis avoiding contamination of the gas phase above the solution by air that could leak through the septum²).

Results and Discussion. – Visible light photolysis under reflux of a 40-ml aqueous (pH 2, HCl) dispersion containing 2×10^{-4}M RuL_3^{2+} and 50 mg TiO_2 leads to gradual loss of sensitizer from the solution and to an intense coloration of the TiO_2 particles. After one day of irradiation, followed by removal of the TiO_2 particles by centrifugation, one obtains a supernatant whose absorption spectrum is given in *Fig. 2.* The features of the spectrum of RuL_3^{2+} (ε_{max} (466 nm) 1.96×10^4M^{-1} cm^{-1} [13]) have almost

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²) Rubber septa are sometimes made out of materials through which O_2 diffuses more rapidly than N_2. While these diffusion processes are very slow, they can give problems with the O_2 analysis by GC technique if the amount of O_2 to be detected is smaller than or comparable to that which leaked across the membrane. In this case, the N_2/O_2 peak ratio obtained from injection of air cannot be safely used to correct for the leakage since the gas mixture after penetrating through the septum has a higher O_2 content than air. The present set-up avoids this ambiguity.

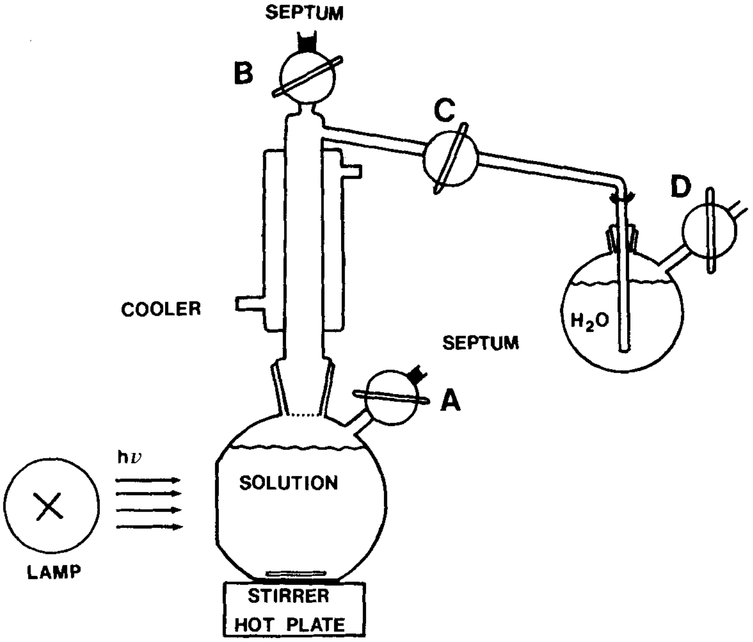

Fig. 1. *Experimental set-up used for photolysis of aqueous TiO_2 dispersions at 100°*

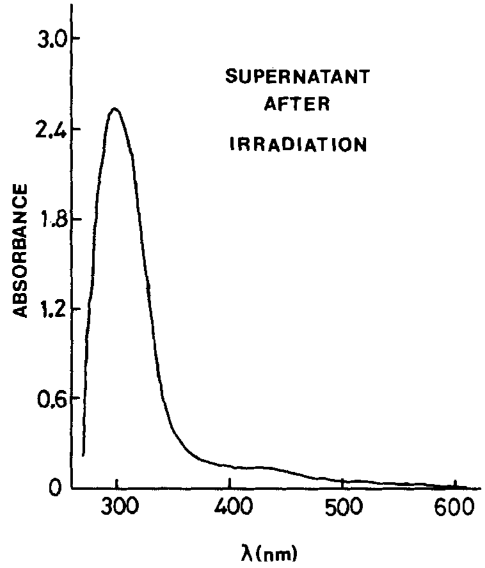

Fig. 2. *Absorption spectrum of a 2 × 10^{-4} M RuL_3^{2+} solution after photolysis in the presence of 2 g/l TiO_2* (anatase, *Bayer*) *for 3 days at 100° under Ar* (pH 2, HCl). Spectrum refers to supernatant of the dispersion after centrifugation of the derivatized TiO_2 particles. Background absorbance and scattering due to residual TiO_2 is estimated as 0.4–0.5 at 300 nm.

totally disappeared, the concentration in solution being less than 5% of what was initially present. On the other hand, the spectrum in *Fig. 2* shows a strong absorption in the UV with a maximum at 305 nm. We assign this spectrum to the free ligand (or its hydrolyzed form[3]) by comparing it to the spectrum of a solution of L in a mixture of 90% water and 10% methanol (pH 2); an absorption spectrum of very similar shape is obtained with a band maximum at ≈ 310 nm, $\varepsilon_{max} \approx 10^4 \text{M}^{-1}\,\text{cm}^{-1}$. Therefore, from *Fig. 2* the concentration of L in the supernatant is estimated as 2×10^{-4}M, which is close to the initial concentration of sensitizer. One infers from these observations that photolysis of RuL_3^{2+} at 100°C leads to the loss of a bipyridyl ligand *(Reaction 1)*.

$$RuL_3^{2+} \xrightarrow[\Delta]{h\nu} RuL_2^{2+} + L \qquad (1)$$

A similar reaction has been observed by *Durham et al.* [14] in CH_2Cl_2-solutions of $Ru(bipy)_3^{2+}$ and involves the lowest ligand field (d–d) excited state of the complex. The quantum yield reported for ligand loss in the case of $[Ru(bipy)_3](SCN)_2$ is 6.8% at 25°C. Earlier work by *Van Houten & Watts* [15] has suggested that in aqueous solution $Ru(bipy)_3^{2+}$ undergoes photochemical ligand labilization to form a six-coordinate complex possessing a unidentate bipy ligand, *i.e.* $Ru(bipy)_2(L)(py\text{-}py)^{2+}$ where L is Cl^- or H_2O. The quantum yield for this reaction was 4×10^{-5} in 0.01M HCl at 347 K. We observed ligand labilization also when aqueous $Ru(bipy)_3^{2+}$ solutions were photolyzed for 2 days under reflux in acidic (pH 1, HCl) dispersions of TiO_2. In this case, the product chromophore whose spectrum was identical with that of $Ru(bipy)_2Cl(py\text{-}py)^+$ remained in solution and did not associate to any significant extent with the TiO_2 particles. The RuL_3^{2+} sensitizer behaves differently from $Ru(bypy)_3^{2+}$ in that photolysis under reflux in aqueous acidic TiO_2 dispersions leads to ligand loss and *quantitative fixation* of the RuL_2^{2+} fragment at the particle surface. Binding does not consist in simple adsorption. Thus, repeated washings of the TiO_2 precipitate with water or stirring it for several hours in methanol did not remove the chromophore from the particles. An ion-exchange mechanism for RuL_2^{2+} binding can also be excluded since both sensitizer and TiO_2 substrate are positively charged at pH 2.

Further information on the nature of the surface bound RuL_2^{2+} chromophore was obtained from reflectance spectroscopy. *Fig. 3* refers to TiO_2 particles loaded with 0.5% RuO_2 and Pt. Derivatization with the RuL_2^{2+} chromophore was carried out by dissolving 25 mg of catalyst in 40 ml H_2O (pH 2, HCl) containing 1.5×10^{-4}M RuL_3^{2+} and subsequent photolysis under Ar at 100°C for *ca.* 36 hours. The carmin red particles were filtered (0.2 μ hydrophilic membrane filter) and after washing with H_2O and drying in air, the filter was placed in the integrating sphere attachment of a *Perkin-Elmer/Hitachi 340* spectrophotometer. The reflectance spectrum exhibits, apart from the band-gap transition of TiO_2 below 400 nm, a pronounced absorption in the visible with a maximum at 480 nm and a tail extending beyond 600 nm. The features in the visible are practically identical with those observed for *cis*-$Ru(bipy)_2(H_2O)_2^{2+}$ adsorbed

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[3]) Under the reaction conditions of *Fig. 2*, hydrolysis of the isopropyl ester might occur forming 2,2'-bipyridine-4,4'-dicarboxylic acid. We are presently determining the nature of this free ligand.

onto hectorite [16] and are therefore attributed to *cis*-RuL_2^{2+} chemically linked to the TiO_2 particles *via* two (or one) oxygen bridges4).

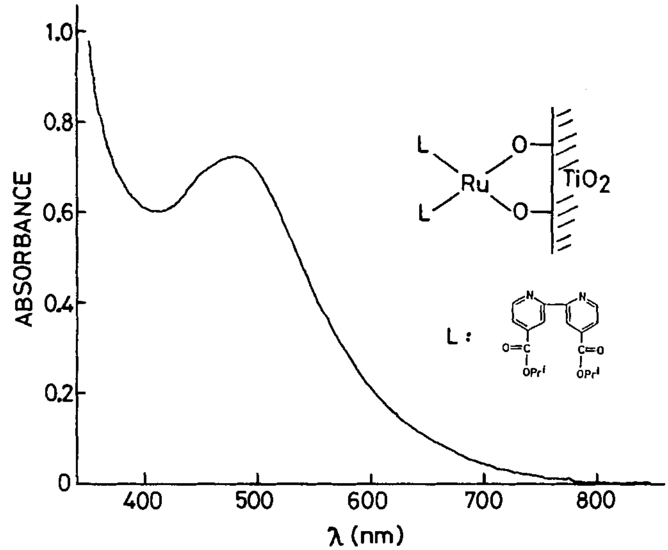

Fig. 3. *Reflectance spectrum of RuL_2^{2+}-derivatized TiO_2 particles loaded simultaneously with 0.5% Pt and RuO_2.* Absorption maximum in the visible is at 480 nm.

While *cis*-$Ru(bipy)_2(H_2O)_2^{2+}$ adsorbed on hectorite is inactive as a sensitizer [16], RuL_2^{2+}-derivatized TiO_2 particles proved to be excellent catalysts for hydrogen generation from water by visible light, both in the presence and the absence of a sacrificial electron donor. Thus, irradiation of a 5-ml solution containing 10^{-2}M triethanolamine (pH 10) and 10 mg $TiO_2/RuO_2/Pt$, derivatized with RuL_2^{2+} as in *Fig. 3,* with the visible ($\lambda > 405$ nm) output of a 450-W Xe lamp (total intensity 200 mW/cm^2) produced H_2 at a rate of 0.93 ml/h. The rate was only decreased by 20% when a 465-nm cut-off filter was placed in the light beam. Even with $\lambda > 590$ nm light, one still observes hydrogen generation, the rate being 50 μl/h. However, no H_2 was formed when a 660-nm cut-off filter was used.

Preliminary experiments showed that RuL_2^{2+}-derivatized TiO_2 particles loaded with RuO_2 and Pt are also active in producing hydrogen from water by visible light *in the absence of sacrificial organic donors.* Illumination at 100°C of 50 mg catalyst dissolved in 40 ml H_2O (pH 2, HCl) with light of $\lambda > 420$ nm in the apparatus shown in *Fig. 1* resulted in the formation of H_2 with an initial rate of 30 μl/h. Typically, 400 μl of H_2 were produced during 20 hours of irradiation. The catalyst maintained its activity over at least 2 weeks of photolysis at 100°C during which it was exposed to various pH

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4) When TiO_2 particles that do not contain noble metal deposit are derivatized with RuL_2^{2+}, their reflectance spectrum shows, apart from the peak at 480 nm, a weaker maximum around 670 nm, and a broad shoulder at ≈ 600 nm. We attribute the 670 nm absorption to the dimer [16] [20] [21] $L_2Ru(III)\text{-}O\text{-}Ru(III)L_2^{4+}$ formed through photooxidation of RuL_2^{2+} and subsequent dimerization at the TiO_2 surface.

conditions and repeatedly washed with water and centrifuged. The total amount of H_2 produced corresponded to a turnover number of 80 with respect to RuL_2^{2+}. We have also observed O_2 generation during photolysis at 100°C. A chromatogram from an injection of 400 μl gas, sampled through septum B after 12 hours of photolysis, and after correcting for a trace of air in the syringe showed that both H_2 and O_2 are produced during illumination in stochiometric amounts of 240 ($\pm$ 20) and 120 ($\pm$ 10) μl, respectively. Oxygen appearance in the gas phase was not consistently observed, however, especially at lower than boiling temperature where only H_2 was found. We attribute this effect to photo-uptake of O_2 by the TiO_2 particles and have presented convincing evidence for the occurrence of such a process in titania-based water cleavage systems elsewhere [17]. Boiling conditions where water steam bubbles purge the solution efficiently may favor the escape of O_2 to the gas phase.

In conclusion, we have discovered a new technique of chemical derivatization of TiO_2 with ruthenium-bipyridyl derivatives to redshift its wavelength response in the visible. Sensitization is made particularly effective by introducing the semiconductor surface directly onto the coordination sphere of the transition-metal complex allowing the charge transfer to occur *via* an inner sphere mechanism. Similar derivatization may have inadvertently played a role in our earlier water photolysis studies with RuL_3^{2+} using the bifunctional $TiO_2/RuO_2/Pt$ as the redox catalyst [18]. Apart from efficient electron injection, RuL_2^{2+} belongs to a class of complexes comprising molecules such as $Ru(bipy)_2(H_2O)_2^{2+}$ or its dimer which are known to be catalysts for a series of important reactions, such as oxygen transfer [19], water oxidation [16][20] and chlorine generation fom chloride [21]. Attachment of this class of chromophores onto semiconductor surfaces, as illustrated in this paper, opens up intriguing possibilities of combining their catalytic and sensitizing properties. These are presently being investigated in detail.

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