141. Photoelectrochemistry with Colloidal Semiconductors: Laser Studies of Halide Oxidation in Colloidal Dispersions of TiO₂ and α-Fe₂O₃

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Summary

Aqueous sols of TiO₂ (anatase, particle radius 25 Å) were excited with (347.1 nm)-laser light and the reaction of valence-band holes with halide ions (X⁻ = I⁻, Br⁻, Cl⁻) was investigated. Hole transfer takes place within the duration of the (10 ns)-laser pulse and results in the formation of anion radicals according to the sequence:

\[ \text{X}^- + h^+ \rightarrow \text{X}^· \rightarrow \text{X}_2^\cdot \]

The quantum yield of X₂ increases in the order Cl⁻ < Br⁻ < I⁻, attaining 0.8 for I⁻ at pH 1. It is affected by pH, halide concentration and the presence of a protective agent for the sol.

RuO₂ deposited onto TiO₂ enhances markedly Cl⁻- and Br⁻-formation, but has no effect on the yield of I⁻.

Laser-photolysis investigation of halide oxidation were also carried out with colloidal Fe₂O₃ (particle radius 600 Å). For I⁻-formation, the quantum yield exceeds 0.9 indicating almost quantitative hole scavenging by iodide.

Introduction. - In a series of recent investigations [1] we have demonstrated that colloidal semiconductors exhibit exceptionally high activity in artificial photosynthetic devices, producing fuels from visible light. Thus, ultrafine (50–100 Å)-sized particles of CdS or TiO₂, when loaded with appropriate catalysts, intervene as efficient mediators in the visible-light-induced cleavage of water [2] and hydrogen sulfide [3].

In order to elucidate the detailed mechanism of the photochemical events occurring in such systems, we have initiated laser-photolysis studies of interfacial electron-transfer process in colloidal semiconductor dispersions [4]. Moreover, the luminescence properties of CdS-particles have been exploited to study the nature of surface states and their annihilation by adsorbed species [4]. A kinetic model has also been conceived to analyze the dynamics of electron transfer and fluorescence events [5].

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In this communication, we pursue our studies on photoelectrochemical processes in colloidal semiconductor dispersions. The focus of our investigations is the reaction of valence-band holes of colloidal TiO₂ and Fe₂O₃ with adsorbed halide ions.

Experimental Part. - Colloidal solutions of TiO₂ were prepared by slowly adding 5 g of TiCl₄ (Fluka puriss.) to 200 ml water at 0°C. The solution was dialyzed until the pH reached a value around 3. A precise determination of the TiO₂-concentration was made by dissolving an aliquot of (10 ml)-solution (TiO₂-concentration = 5 g/l) in 20 ml conc. HCl-solution and refluxing for approx. 30 min. Subsequently, a Ti(IV)peroxo complex was formed by addition of 3 droplets of 30% H₂O₂-solution, which was spectrophotometrically analyzed [6] (λ(max) = 415 nm, ε(max) = 6400 M⁻¹ cm⁻¹ in 6% HCl). The reference lightbeam was passed through a Ti(IV)-solution which had not been treated with H₂O₂. At pH > 3 polyvinylalcohol (PVA) was used to stabilize the sol. Commercial PVA (Mowiol 98110, Hoechst, W. Germany) was pretreated in 5% aqueous solution by UV light (450 W Xe-lamp, 4 h of irradiation to remove impurities that absorb 347.1 nm laser-light).

The size of the TiO₂-particles was determined by quasi-elastic light-scattering technique. The particle diameter derived from correlation functions was 50 Å. These particles consist mainly of anatase with a small proportion of amorphous material as shown by X-ray analysis.

Laser-photoysis experiments were performed with a frequency-doubled JK-2000 ruby laser. The (347.1 nm)-pulse had a duration of 10 ns and delivered 6.2 × 10¹⁶ photons. From the absorbance of the TiO₂-solutions (A = 1.3 at 347.1 nm and 0.5 g TiO₂/l) and the irradiated volume of the sample cell (0.03 cm²) one derives 4 × 10⁻⁵ Einstein/l for the absorbed photon concentration. Chemical actinometry with deoxygenated (methylviologen/TiO₂)-solutions at pH 8.5) yielded for the absorbed photon concentration a value which was within 10% of this calculated value.

All materials employed were at least reagent grade. Dionized water was refluxed over alkaline permanganate and subsequently distilled twice from a quartz still.

Results and discussion. - 1. Reaction of halide ions with TiO₂ valence-band holes. The transient spectrum obtained immediately after the 347.1 nm laser excitation of colloidal TiO₂ (500 mg/l) in 0.5N HCl can be assigned to Cl₂-radical ions [7] (λ(max) = 340 nm, ε(max) = 8800 M⁻¹ cm⁻¹). The formation of Cl₂ can be rationalized in terms of band-gap excitation of the TiO₂-particle.

\[
\text{TiO}_2 \rightarrow \text{TiO}_2 (\varepsilon_{CB}^e, h^+) \tag{1}
\]

generating conduction-band electrons (ε_{CB}^e) and valence-band holes (h⁺). The latter react with Cl⁻-ions to give (Cl⁻-)-radicals:

\[
h^+ + \text{Cl}^- \rightarrow \text{Cl}^{-} \tag{2}
\]

which subsequently undergo rapid complexation [7] by excess Cl⁻-ions

\[
\text{Cl}^{-} + \text{Cl}^- \rightarrow \text{Cl}_2^- \tag{3}
\]

\[a\] A detailed description of methylviologen reduction by conduction band electrons of TiO₂ is given in [4]. The quantum yield of this process at pH 8 is practically unity.

\[b\] This value of the extinction coefficient is based on a recent NBS-publication [7c]. For calculation of quantum yields we have employed ε_(340) = 7000 M⁻¹ cm⁻¹ [7c].
The prompt nature of Cl₂-formation which occurs concomitantly and within the (10 ns)-laser pulse must be attributed to the fact that hole scavenging occurs predominantly by Cl⁻-ions that are adsorbed at the surface of TiO₂. If the hole-transfer reaction 2 involved bulk diffusion of Cl⁻ towards the TiO₂-particle, then significantly longer reaction times would be required depending on Cl⁻-concentration. Surface-adsorbed species, on the other hand, can react extremely rapidly with photogenerated charge-carriers in colloidal semiconductors. In the case of a TiO₂-particle with a radius of 25 Å, the average transit time of a hole from the interior to the surface is calculated as only 1.2 ps [5] if the hole mobility is assumed to be equal to that of the electron. Thus, if interfacial charge transfer occurs promptly upon arrival of the charge carrier at the phase boundary, then oxidation of Cl⁻ is expected to occur in the picosecond-time domain.

Earlier photoelectrochemical studies with TiO₂-electrodes have shown [8] that holes readily react with water to produce oxygen:

\[ 4h^+ + 2H_2O \rightarrow 4H^+ + O_2 \]  

(4)

This process competes with chloride oxidation. In Figure 1 is depicted the influence of pH on the Cl₂-concentration determined at the end of the laser pulse. The Cl₂-

![Diagram](image_url)

*Fig. 1. Laser photolysis of TiO₂-sol in the presence of chloride. a) Effect of pH on the yield of Cl₂ measured immediately after the laser pulse. □ represents the quantum yield for Cl₂-formation, TiO₂]- = 500 mg/l, [Cl⁻] = 0.1 n, pH adjusted with HNO₃/NaOH, aerated solution.

- Unprotected TiO₂-sol
- PVA (1 g/l) protected TiO₂-sol

b) Effect of Cl⁻-concentration on the yield of Cl₂-formation pH = 1, concentration of Cl⁻ adjusted with NaCl (includes 0.1 n HCl) unprotected sol, aerated solution.

- The TiO₂-particles were loaded with 0.8% RuO₂ according to a previously published procedure [1c]*
yield decreases sharply with increasing pH and is below detection limit at pH > 2.5. Apparently, at higher pH water oxidation is favored over that of Cl\textsuperscript{-}. This can be explained by thermodynamic arguments: for the (Cl\textsuperscript{-}/Cl\textsubscript{2})-couple, the standard potential ($E^\circ$) is 2.3 V [9] and independent of pH. The first oxidation step of water

$$H_2O \rightarrow OH^- + H^+ + e^-$$  \hspace{1cm} (5)

requires 2.2 V at pH 0 but the potential decreases by 59 mV/pH. As the valence-band potential of our colloidal TiO\textsubscript{2} shows the same pH-dependency [1c]

$$E_{VB}(TiO_2) = 3.07 - (0.059 \cdot pH)$$ \hspace{1cm} (6)

the driving force of water oxidation is not affected, while that for Cl\textsuperscript{-}-oxidation decreases with increasing pH.

Figure 1 shows also that at a given pH, the Cl\textsubscript{2}-yield is reduced by a factor of approximately two when PVA is introduced as a protective agent for the TiO\textsubscript{2}-colloid. This polymer can apparently compete with H\textsubscript{2}O and Cl\textsuperscript{-} for valence-band holes. Nevertheless, it is surprising in view of the ease of oxidation of PVA, that Cl\textsubscript{2}-formation is not completely suppressed in its presence. Figure 1b shows that the quantum yield of Cl\textsubscript{2}-formation is also affected by Cl\textsuperscript{-}-concentration. At pH 1 an upper limit of $\Phi$ (Cl\textsubscript{2}) = 0.08 is obtained when [Cl\textsuperscript{-}] 0.4 M.

Investigations analogous to those with Cl\textsuperscript{-} were also carried out with Br\textsuperscript{-} and I\textsuperscript{-}. The intermediates produced from the laser photolysis of colloidal TiO\textsubscript{2} in the presence of these halide ions are readily identified with Br\textsubscript{2}- and I\textsubscript{2}-radicals formed via the valence-band process (Eqn. 7).

$$h^+ + X^- \rightarrow X \cdot \rightarrow X_2^-(X^- = Br^-, I^-)$$ \hspace{1cm} (7)

Figures 2 and 3 illustrate that the X\textsubscript{2}-yield decreases sharply with increasing pH. At a given pH the quantum yield increases in the order Cl\textsubscript{2} > Br\textsubscript{2} > I\textsubscript{2}. (The highest quantum yield measured for I\textsubscript{2} at pH 1 is 0.8, indicating that 80% of the holes produced by the laser flash in the colloidal semiconductor are scavenged by iodide).

It should be noted that this sequence is related to the redox potential\textsuperscript{4} in that $E'(Cl^-/Cl_2) = 2.3$ V > $E'(Br^-/Br_2) = 1.7$ V > $E'(I^-/I_2) = 1.0$ V [9]. Apart from the driving force, the effect of pH reflects also coulombic interactions since the particle charge changes from positive to negative at pH > 3.3 [1c] (point of zero zeta-potential of TiO\textsubscript{2}-particles of similar size). Note that for all halide ions the yield of oxidation is comparatively small at pH > 3.5 indicating repulsion of X\textsuperscript{2-} from the TiO\textsubscript{2}-surface.

Figure 4 shows that the quantum yield of X\textsubscript{2}-formation increases with concentration of halide ions. The experimental curves display a Langmuir-absorption isotherm type behavior as was found for Cl\textsuperscript{-}-ions. This finding amplifies our earlier

\textsuperscript{4} Herrmann & Pichat [10] have investigated the oxidation of halide ions by oxygen in irradiated TiO\textsubscript{2} dispersions. No oxidation of Cl\textsuperscript{-} was observed. The quantum yield for I\textsuperscript{-}-oxidation (2%) was 80 times that for Br\textsuperscript{-}-oxidation.
conclusion that only halide ions adsorbed to the surface of TiO$_2$ can intervene as hole scavengers.

The effect of protective agent concentration on the yield of Br$_2$ is illustrated in Figure 5. Surprisingly, after an initial decrease by a factor of two the quantum yield of Br$_2$-formation increases slightly with PVA-concentration until a plateau is attained. This shows that the intervention of PVA as a hole scavenger is rather inefficient even at high surface coverage of the TiO$_2$-particle.

2. Effect of RuO$_2$ on the quantum efficiency of halide oxidation. RuO$_2$ is known to be an electrocatalyst for both, the oxidation of water and halide ions [11]. Dimen-

![Graph showing the effect of pH on the quantum yield of Br$_2$-formation with and without PVA.]

Fig. 2. Laser photolysis of colloidal TiO$_2$ in the presence of bromide: effect of pH on the quantum yield of Br$_2$-formation. [Br$^-$]=0.2M. pH adjusted with NaOH/HNO$_3$, aerated solution.

☐ Unprotected sol.
☒ Unprotected sol loaded with 0.8% RuO$_2$.
● PVA (1 g/l)-protected sol.
★ PVA (1 g/l)-protected sol loaded with 0.8% RuO$_2$. 
sionally stable RuO$_2$-anodes have been employed in industrial chloride-electrolysis. Our previous studies have shown that RuO$_2$-deposits on CdS- [2], TiO$_2$-[1] or WO$_3$-[12] powders enhance hole transfer from the valence band of the particle to water resulting in oxygen generation.

Figures 1, 2 and 3 show the influence of RuO$_2$-deposits on TiO$_2$-particles on the reaction of halide ions with h$^+$ (TiO$_2$). A pronounced increase in the quantum

Fig. 3. Laser photolysis of colloidal TiO$_2$ in the presence of iodide, effect of pH on the quantum yield of I$_2$ formation, aerated solution, $[\text{I}^-]=0.2 \text{N}, [\text{TiO}_2]=500 \text{ mg/I}, \text{pH adjusted with HClO}_4/\text{NaOH}; \text{concentrations of I}_2$ were calculated using an extinction coefficient of $k_{390}=1.4 \times 10^4 \text{M}^{-1} \text{cm}^{-1}$ [18]. Higher and smaller $\epsilon$ values have also been reported [7c].

- PVA (1 g/l) protected sol, no RuO$_2$
- PVA (1 g/l) protected sol, loaded with RuO$_2$ (0.8%)
- Unprotected sol without RuO$_2$
- Unprotected sol with RuO$_2$
efficiency of Cl\textsuperscript{2}- and Br\textsuperscript{2}-generation is observed while the I\textsubscript{2}-formation is not affected. For Cl\textsuperscript{2}, the enhancement is 2.25 fold and for Br\textsuperscript{2} it is 2.7 or 1.8 fold in solutions with and without PVA, respectively.

These results illustrate a pronounced catalytic effect of RuO\textsubscript{2} on the oxidation of chloride and bromide ions by TiO\textsubscript{2}-valence band holes. In contrast, for iodide no catalysis is observed. Apparently, in the latter case the driving force for the reaction is high enough to insure very efficient hole transfer even in the absence of RuO\textsubscript{2} deposits.

3. Light-induced halide oxidation by colloidal Fe\textsubscript{2}O\textsubscript{3}. We wish to report some preliminary experiments with a-Fe\textsubscript{2}O\textsubscript{3}-sols\textsuperscript{5}). These colloidal dispersions exhibit an absorption band rising steeply towards the UV, below 600 nm, which coincides with the 2.2 eV band-gap of crystalline a-Fe\textsubscript{2}O\textsubscript{3}. Laser experiments were performed with solutions containing 20 mg Fe\textsubscript{2}O\textsubscript{3}/l. (At this concentration, the absorbance at 347.1 nm is identical with that of 500 mg/l TiO\textsubscript{2}-sol). Iodide (0.2 M, pH 1) was employed as a hole scavenger. Laser excitation of Fe\textsubscript{2}O\textsubscript{3}-particles under these conditions leads to extremely rapid (~10 ns) formation of I\textsubscript{2}. The quantum yield of I\textsubscript{2}-formation is surprisingly high and amounts to more than 80%. In a subsequent reaction I\textsubscript{2} disappears according to a second-order rate law with a specific rate of

![Figure 4](imageURL)

**Fig. 4.** Effect of halide concentration on the yield of Br\textsuperscript{2} and I\textsubsuperscript{2} measured immediately after laser excitation of colloidal TiO\textsubscript{2} (500 mg/l)

\(\Box\) Br\textsuperscript{-}, concentration adjusted with NaBr, pH 0.5 (adjusted with HNO\textsubscript{3}); PVA (1 g/l)-protected sols.
\(\bullet\) I\textsuperscript{-}, concentration adjusted with NaI, pH = 2 (adjusted with HClO\textsubscript{4}); PVA (1 g/l)-protected sols.

\textsuperscript{5)} These a-Fe\textsubscript{2}O\textsubscript{3} sols were kindly supplied by Dr. Eisenlauer, BASF, Ludwigshafen, West Germany. Their hydrodynamic radius is 600 Å.
Fig. 5. Effect of protective agent concentration on the yield of Br\textsuperscript{2}, measured immediately after laser exposure of colloidal TiO\textsubscript{2} (500 mg/l) ([Br\textsuperscript{-}] = 0.28, pH 0.5 (adjusted with HNO\textsubscript{3}) aerated solutions)

\[ k = 7 \times 10^9 \text{M}^{-1}\text{s}^{-1} \]. A similar decay was observed for the halide radical ions in the TiO\textsubscript{2}-dispersions. It is attributed to the diffusion-controlled dismutation reaction

\[ 2X_2 \rightarrow X_2^+ + 2X^- \]  \hspace{1cm} (8)

The fact that photogenerated holes in Fe\textsubscript{3}O\textsubscript{4}-particles can be scavenged with high efficiency by electron-donors such as iodide is important with regard to the use of such particles in solar-energy-conversion devices. Single crystal [13] and polycrystalline [14] a-Fe\textsubscript{3}O\textsubscript{4}-electrodes show disappointingly small efficiencies as photo anodes for the oxidation of water and other substrates. This arises from the low mobility of charges carriers [15] (\( \sim 0.1 \text{ cm}^2 \text{ V}^{-1}\text{s}^{-1} \)), a short hole-diffusion length (20-40 \AA) [16]) and fast surface recombination [17]. The advantage of employing Fe\textsubscript{3}O\textsubscript{4}-sols is that the particle dimension can be reduced to a size where practically all the photo-induced charge carriers attain the particle surface before recombination can occur. In this context, our recent finding of efficient oxygen generation by visible light in colloidal Fe\textsubscript{3}O\textsubscript{4}-dispersions is particularly encouraging. Such systems are suitable to become the oxygen-producing part in a complete water cleavage system.

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