# 177. Photoreduction of Thiosulfate in Semiconductor Dispersions

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*Summary*

Conduction band electrons produced by band gap excitation of $TiO_2$-particles reduce efficiently thiosulfate to sulfide and sulfite.

$$2\,e^-_{cb}(TiO_2) + S_2O_3^{2-} \longrightarrow S^{2-} + SO_3^{2-}$$

This reaction is confirmed by electrochemical investigations with polycrystalline $TiO_2$-electrodes. The valence band process in alkaline $TiO_2$-dispersions involves oxidation of $S_2O_3^{2-}$ to tetrathionate which quantitatively dismutates into sulfite and thiosulfate, the net reaction being:

$$2h^+(TiO_2) + 0.5\,S_2O_3^{2-} + 1.5\,H_2O \longrightarrow SO_3^{2-} + 3\,H^+$$

This photodriven disproportionation of thiosulfate into sulfide and sulfite:

$$1.5\,H_2O + 1.5\,S_2O_3^{2-} \xrightarrow{h\nu} 2\,SO_3^{2-} + S^{2-} + 3\,H^+$$

should be of great interest for systems that photochemically split hydrogen sulfide into hydrogen and sulfur.

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**Introduction.** – We have shown in a previous investigation [1] that illuminations of aqueous $CdS/RuO_2$-suspensions by visible light leads to efficient cleavage of hydrogen sulfide into $H_2$ and S. The mechanism involves band gap excitation of the CdS particle followed by reaction of conduction band electrons with water produce to $H_2$.

$$2\,e^-_{cb} + 2\,H_2O \longrightarrow H_2 + 2\,OH^- \qquad (1)$$

Valence band holes oxidize sulfide to sulfur.

$$2\,h^+ + S^{2-} \longrightarrow S \tag{2}$$

Subsequently, we found [3], and this has been confirmed [3], that in the presence of sulfite *Reaction 2* is followed by *Reaction 3.*

$$S + SO_3^{2-} \longrightarrow S_2O_3^{2-} \tag{3}$$

The net valence-band process is therefore *Reaction 4*

$$2\,h^+ + S^{2-} + SO_3^{2-} \longrightarrow S_2O_3^{2-},\ (E^\circ = -0.72\,V.NHE) \tag{4}$$

and the overall reaction corresponds to the photogeneration of $H_2$ and $S_2O_3^{2-}$ *via Reaction 5.*

$$S^{2-} + SO_3^{2-} + 2\,H_2O \xrightarrow{2h\nu} S_2O_3^{2-} + 2\,OH^- + H_2 \tag{5}$$

While *Reaction 5* under standard condition (pH 14, 298 °K) stores only 0.11 eV of free energy per absorbed photon, as compared to 0.36 eV for the cleavage of $H_2S$, it has the advantage over the latter process of giving high yields of $H_2$ [2] [3] without formation of insoluble products. We were intrigued, therefore, by the idea of using it as the $H_2$-generating part in a hydrogen sulfide cleavage cycle and attempted to identify a photosystem capable of reducing $S_2O_3^{2-}$ back to $S^{2-}$ and $SO_3^{2-}$.

**Experimental.** – $TiO_2$-P25 (*Anatase*, 55 $m^2/g$) was a kind gift of Dr. *Peter Kleinschmidt, Degussa* GmbH, Hanau, West Germany. Deionized water was doubly distilled from a quartz apparatus. All other chemicals were at least reagent grade and used as supplied.

Irradiations were carried out with a *Hanau* suntest lamp equipped with a glass filter to remove wavelengths below 340 nm. The global irradiance in the wavelength domain between 300 and 830 nm is 100 $mW/cm^2$, the spectral distribution of the intensity reflecting AM1 solar radiation. Solution volume was invariably 40 ml, placed in cylindrical glass vials (irradiated surface approx. 15 $cm^2$) equipped with a septum for GC analysis of the gas. Prior to irradiation samples were deoxygenated by bubbling with $N_2$ or Ar. All photolysis experiment are carried out in 1N NaOH, $10^{-2}$M $S_2O_3^{2-}$ and 2 g/l $TiO_2$.

Electrochemical experiments employed polycrystalline $TiO_2$-electrodes prepared from Ti-sheets (*Siber-Hegner Raw Materials*, 99.99%) spot-welded to a Ti-wire. For the fabrication of $TiO_2$-cathodes a Ti-sheet ($15 \times 1 \times 0.02$ $cm^3$) was spiralled to form a cylinder. The photo-anode had a size of $1 \times 1 \times 0.05$ $cm^3$. Ti was washed subsequently with $CH_2Cl_2$, EtOH and $H_2O$ and then etched for 30 s in an aq. solution of HF (4%, w/w) and $HNO_3$ (30%, w/w). After rinsing with $H_2O$ and drying in air, the electrodes were heated at 780° for 5 h in a stream of $O_2$ (flow rate 10–15 ml/min.). The thickness of the grey $TiO_2$-layer was estimated from the weight difference before and after heating to be approx. 4 µm. One side of the photo-anode was spray-insulated.

Conventional two- and three-electrode cells *(Pyrex)* were used for galvanostatic and potentiostatic experiments. The solution (*ca.* 20 ml volume) was agitated by a magnetic stirrer. A Ti-wire coated with $RuO_2$ according to *Galizzioli et al.* [4] and a commercial calomel reference electrode (S.C.E.) were separated from the working electrode compartment by sintered glass frits.

The potentiostats *Wenking POS 76* and *Pine RDE 6* were used in connection with a *Watanabe* xy-recorder or a *Metrohm* single-channel recorder. Irradiations were carried out with a 250-W tungsten-halogen lamp *(Oriel)* equipped with a 12-cm water filter and a *Corning CS 7-59* filter (390-nm band-filter). The light beam was focused onto the $TiO_2$-electrode and the intensity measured with a *Yellow Springs Instrument Kettering Model 65A* radiometer.

$O_2$ was measured in solution by a *Clark* electrode from *Instrumentation Laboratory* ($O_2$-meter *376*). $H_2$ was detected similarly by a membrane covered gas detector *YSI 4004* from *Yellow Springs Instruments.* The Pt-disc was cleaned and platinized according to [5]. The $H_2$-oxidation was performed in 1.5M KCl at 0.5 V *vs.* Ag/AgCl. The *Clark* electrodes were calibrated for every solution by injecting appropriate amounts of air- or $H_2$-saturated water into the liquid phase. The temperature was kept constant during $O_2$- and $H_2$-analysis by immersing the electrochemical cell into a thermostated water-bath.

$S_2O_3^{2-}$ and $SO_4^{2-}$ were analyzed quantitatively by ion-exchange chromatography on a *Wescan 261* ion analyzer equipped with a *Wescan 213 A* detector and a *Wescan Standard* column *269-001.* Phtalate buffer (4 mM, pH 4.8) was used as an eluant at a flow rate of 4.5 ml/min. $BaCl_2$ was used in addition to test for $SO_4^{2-}$- and $S_2O_6^{2-}$-ions. (The latter dismutates in hot HCl to $SO_4^{2-}$ and $SO_2$.)

$S^{2-}$-concentrations were determined by potentiometric titration with $Ag^+$ on a *Metrohm Titroprocessor 636* and *Dosimat E635* using a $Ag_2S$-indicator electrode *(Oriel 94-16).* $SO_3^{2-}$ was analyzed by differential pulse polarography *(Metrohm Polarorecord 626)* in 1N HCl under an atmosphere of $N_2$. The reduction peak occurred at −0.32 V *vs.* Ag/AgCl (3M KCl). The peak at −0.17 V was due to $H_2S$ and the height of the peak always agreed with the $S^{2-}$-concentration found by titration.

**Results.** – 1. *Irradiation of $TiO_2$-dispersions.* Illumination of alkaline $TiO_2$-suspensions in presence of $S_2O_3^{2-}$ leads to consumption of thiosulfate and appearance of $S^{2-}$ and $SO_3^{2-}$. A quantitative illustration of this effect is given in *Fig. 1.* After 20 h of illumination, $4.8 \times 10^{-3}$M $SO_3^{2-}$ and $2.4 \times 10^{-3}$M $S^{2-}$-ions are produced while $3.6 \times 10^{-3}$M $S_2O_3^{2-}$ have been consumed. Note that the 2:1 stoichiometric ratio of $SO_3^{2-}$ to $S^{2-}$ is maintained during the whole irradiation time. Tests for the presence of $SO_4^{2-}$- and $S_2O_6^{2-}$-ions in irradiated samples gave negative results. The only products obtained from the photoreaction are $S^{2-}$- and $SO_3^{2-}$-ions apart from trace amounts of $H_2$ which was found sometimes after extensive illumination. Blank experiments established that both $TiO_2$ and light are required

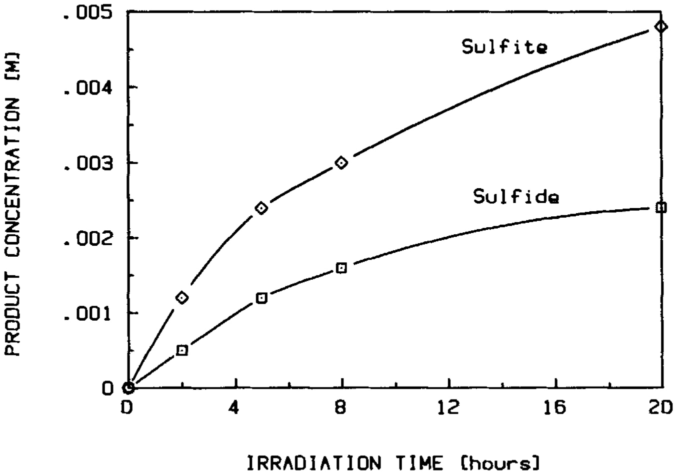

Fig. 1. *Photoreduction of $S_2O_3^{2-}$ in $TiO_2$-dispersions* (pH 14, 30°)*, temporal evolution of $S^{2-}$- and $SO_3^{2-}$-concentrations*

to afford $S_2O_3^{2-}$-reduction. Thus, sunlamp irradiation of alkaline thiosulfate solution produced no detectable sulfide after 20 h exposure time. Similarly, no reaction occurs in $TiO_2/S_2O_3^{2-}$-dispersions (pH 14) in the dark.

2. *Electrochemical Experiments with Polycrystalline $TiO_2$-electrodes. Fig. 2* shows current-potential curves obtained with $TiO_2$-electrodes in the dark and under light in 1 M NaOH and 1 M NaOH in the presence of $10^{-1}$ M $Na_2S_2O_3$. If no thiosulfate is present, one observes $H_2$-generation at $E < -1.3$ V (S.C.E). The overvoltage for $H_2$-production at $-0.1$ mA/cm² is *ca.* 200 mV larger than that observed with $TiO_2$-electrodes prepared according to [6] (600°, 30 min). This is ascribed to an increase in the thickness of the $TiO_2$-layer (4 instead of *ca.* 0.5 µm) when our procedure of electrode preparation is applied. A photocurrent is observed at potentials positive of the flat-band potential of $TiO_2$. In the presence of $S_2O_3^{2-}$ the cathodic current is shifted to more positive potentials (curve *B*) but the anodic photocurrent is not affected. *In situ* analysis of $H_2$ during galvanostatic electrolysis

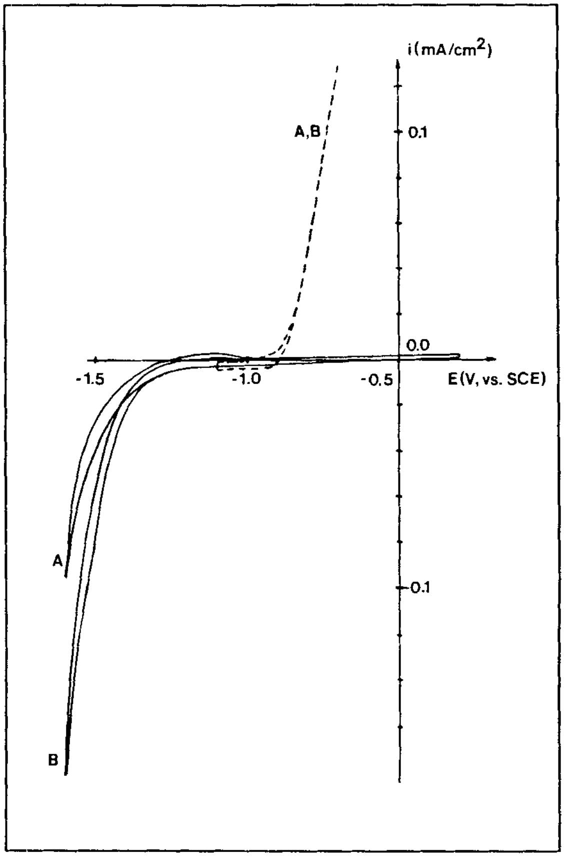

Fig. 2. *Photocurrent (----) and dark current (——) for polycrystalline $TiO_2$-electrodes* (Scan rate 2 mV $s^{-1}$, light intensity 170 mW $cm^{-2}$; A: 1 M NaOH, B: 1 M NaOH, 0.1 M $Na_2S_2O_3$)

revealed that 41±6% of the current corresponds to $H_2O$-reduction. The major fraction of the current (48±2%) is due to thiosulfate reduction, and we find the stoichiometry:

$$S_2O_3^{2-} + 2\,e_{cb}^- \longrightarrow S^{2-} + SO_3^{2-} \qquad (6)$$

for this conduction band reaction[1]). *Fig. 3* shows that the current efficiency for $S_2O_3^{2-}$-reduction is decreased by lowering the $S_2O_3^{2-}$-concentration and increasing the current density.

The anodic reaction in 1 M NaOH at illuminated $TiO_2$-electrodes (conditions 0.0 V *vs.* S.C.E., 0.4 mA $cm^{-2}$, 20 ml of electrolyte) was quantitatively oxidation of $H_2O$. In the presence of 0.01 M or 0.05 $S_2O_3^{2-}$ the current efficiency for $O_2$-formation was decreased to 61 and 38%, respectively, indicating significant hole transfer to $S_2O_3^{2-}$. $O_2$-generation is completely prevented when $TiO_2$-electrodes were illuminated in the presence of $S^{2-}$ or $SO_3^{2-}$ (both 0.01 M). However, the photocurrent-potential curve is not affected by these ions. We found that $O_2$ oxidizes both $S^{2-}$ or $SO_3^{2-}$ but not $S_2O_3^{2-}$ within seconds or minutes under our conditions. This reaction could lead to a rapid consumption of $O_2$ formed during photoelectrolysis. One concludes from these observations that $S^{2-}$ and $SO_3^{2-}$, though acting as efficient hole scavengers at n-CdS [7] and n-$WO_3$ (pH 1 [8]) electrodes are surprisingly inactive towards $TiO_2$-valence band holes in alkaline solution. ***Frank & Bard*** [9] inferred from the absence of current doubling at illuminated $TiO_2$-electrodes (0.1 M NaOH, 1 M$S^{2-}$) that no holes are transferred from $TiO_2$ to $S^{2-}$. This agrees with our finding that no $H_2$ is produced under UV illumination of $TiO_2$-dispersions in 0.1 M $Na_2S$ (pH 14).

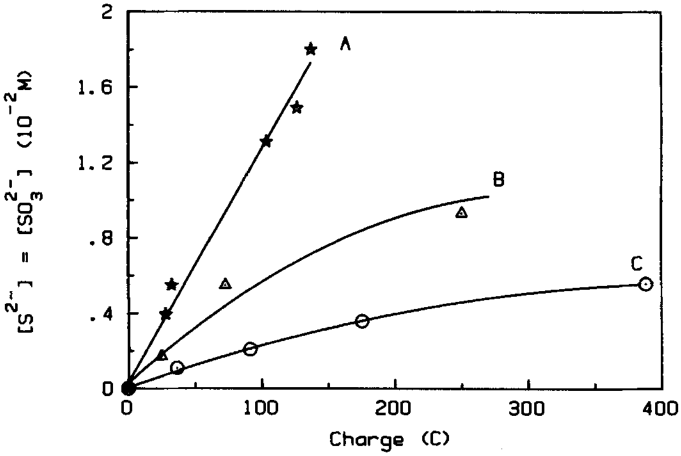

Fig. 3. *Galvanostatic reduction of $S_2O_3^{2-}$ in 20 ml 1 M NaOH. $S^{2-}$ and $SO_3^{2-}$ as a function of the electric charge passed through the cell* (A: 0.1 M $Na_2S_2O_3$, i = −0.017 mA $cm^{-2}$; B: 0.01 M $Na_2S_2O_3$, i = −0.017 mA $cm^{-2}$; C: 0.01 M $Na_2S_2O_3$, i = −0.65 mA $cm^{-2}$)

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[1]) The remaining 11% of the current might be due to systematic analytical errors or to small amounts of $O_2$ which leaked into the cell during electrolysis.

**Discussion.** – The photogeneration of $S^{2-}$ and $SO_3^{2-}$ in alkaline $TiO_2$/thiosulfate dispersions can be accounted for by reaction of $e_{cb}^-$ with $S_2O_3^{2-}$ according to *Reaction 6*, accompanied by hole transfer to thiosulfate

$$2\,S_2O_3^{2-} + 2\,h^+ \longrightarrow S_4O_6^{2-} \tag{7}$$

Tetrathionate is known to undergo disproportionation in alkaline solution:

$$1.5\,H_2O + S_4O_6^{2-} \longrightarrow SO_3^{2-} + 1.5\,S_2O_3^{2-} + 6\,H^+ \tag{8}$$

which gives for the net valence band process:

$$1.5\,H_2O + 2\,h^+ + 0.5\,S_2O_3^{2-} \longrightarrow SO_3^{2-} + 3\,H^+ \tag{9}$$

and for the overall photoreaction

$$1.5\,H_2O + 1.5\,S_2O_3^{2-} \xrightarrow{h\nu} 2\,SO_3^{2-} + S^{2-} + 3\,H^+ \tag{10}$$

*Reaction 10* is energy-storing the standard free enthalpy (pH 14, 298°K) being +0.38 eV. The experimental finding that for 1.5 moles of $S_2O_3^{2-}$ consumed, there are 2 moles of $SO_3^{2-}$ and 1 mole of $S^{2-}$ formed agrees well with the stoichiometry of this equation.

The electrochemical reduction of $S_2O_3^{2-}$ to $S^{2-}$ and $SO_3^{2-}$ has been previously studied by *Konopik & Holzinger* [10] on Hg, Sn and Pt. Hg-electrodes require the highest overpotential and the reduction seems to involve Na-atoms. On Pt, the main reaction is $H_2O$-reduction. The overvoltage for $H_2$-generation is sufficiently high on $TiO_2$ and Sn[2]) to observe increased cathodic currents due to $S_2O_3^{2-}$-reduction and establish their catalytic intervention in the latter process.

The fact that $H_2$ is generated on $TiO_2$-electrodes in parallel with $S_2O_3^{2-}$-reduction indicates that H-atoms are the primary intermediates formed from the reaction of $e_{cb}^-$ with $H_2O$ which recombine to give $H_2$ or reduce $S_2O_3^{2-}$ to $S^{2-}$ and $SO_3^{2-}$. Such a competitive process is in agreement with the observed decline of the current conversion efficiency with decreasing $S_2O_3^{2-}$-concentration and increasing current density. That no $H_2$ is produced on $TiO_2$-powders is a very interesting observation which confirms further such a mechanism. The reaction due to the large surface area proceeds here at a very low current density and therefore small H surface concentration, rendering recombination to $H_2$ improbable. We encounter here an instructive example of how the efficiency of a catalytic process can increase when electrodes are substituted by particle suspensions.

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[2]) We confirmed the finding of *Konopik & Holzinger* [10] that Sn has good electrocatalytic properties for $S_2O_3^{2-}$-reduction with Sn disk-electrodes prepared from Sn-rods (*Fluka*, 99.999%).

The photoinduced dismutation of $S_2O_3^{2-}$ into $SO_3^{2-}$ and $S^{2-}$, discovered here, could be very useful for systems that attempt to photogenerate $H_2$ from $H_2S$-solutions. *Fig. 4* describes the features of a two-compartment system where $H_2$ is generated in the $CdS/RuO_2$-containing halfcell and $S^{2-}$ concomitantly oxidized to $S_2O_3^{2-}$. The latter is transferred in a second halfcell containing $TiO_2$-particles where the dismutation of $S_2O_3^{2-}$ is driven by light. The overall process

$$3\,H_2O + S^{2-} \xrightarrow{h\nu} SO_3^{2-} + 3\,H_2 \tag{11}$$

$$\Delta_r G^\circ_{298} = +1.4\ \text{eV} = +32\ \text{kcal/mol}$$

produces 3 moles of $H_2$ instead of 1 mole obtained from the simple cleavage of $H_2S$ and stores a significant amount of light energy. One additional mole of $H_2$ could be obtained from the photooxidation of $SO_3^{2-}$ to $SO_4^{2-}$. Further advantages of this system are that there is no sulfur or $S_2O_3^{2-}$-accumulation, rendering the photoreaction very efficient.

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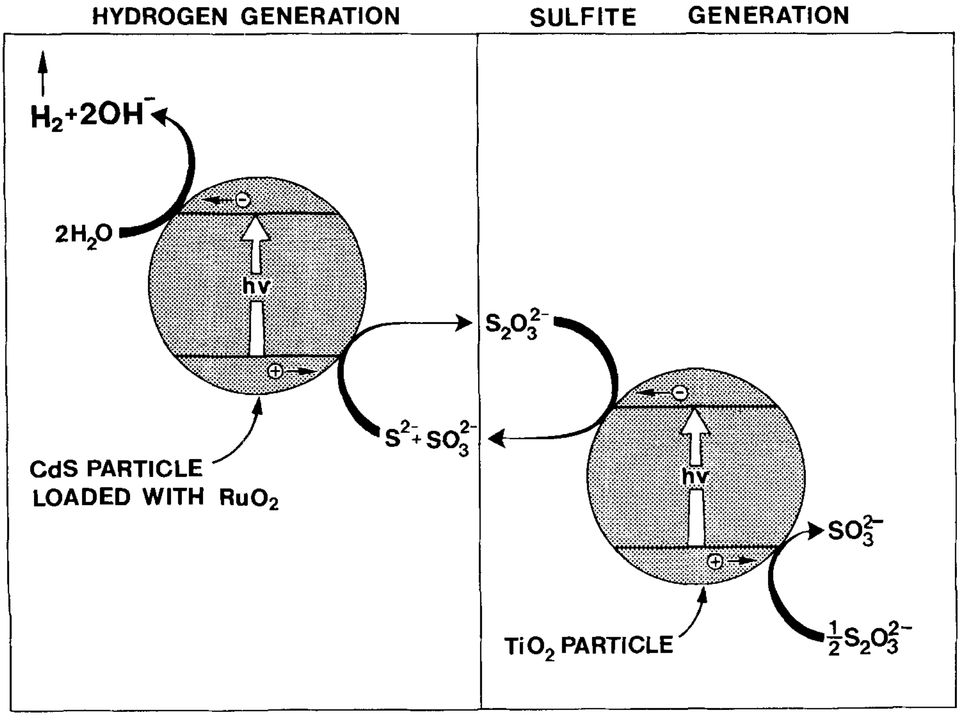

Fig. 4. *Schematic illustration of $H_2S$-decomposition by two photosystems, linked through the $S^2O_3^{2-}$/$S_2^{2-}$/$SO_3^{2-}$ redox system*

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