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Photocatalytic oxidation of water to O_2 on AgCl-coated electrodes

Martin Lanz, David Schürch, Gion Calzaferri*

Department of Chemistry and Biochemistry, University of Bern, Freiestrasse 3, CH-3012, Bern, Switzerland

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Abstract

Sustained photocatalytic oxidation of water to O_2 on AgCl-coated electrodes is reported. Thin silver chloride layers on different electrode substrates evolve oxygen under near-UV–Vis illumination in aqueous solution at appropriate conditions. The AgCl layers work photocatalytically in the oxidation of water to O_2 in the presence of a small excess of Ag^+ ions, with a maximum O_2 evolution rate at pH 4–5. The light sensitivity in the visible is due to self-sensitization caused by reduced silver species. Many catalytic turnovers with respect to the total amount of AgCl were experimentally realized. Reduced silver species produced during the photocatalytic oxidation of water to O_2 on AgCl-coated electrodes can be electrochemically reoxidized by anodic polarization of the electrode. Electrochemical reoxidation can be performed simultaneously with the photochemical water oxidation reaction. The photocurrent is of reversed sign with respect to what has been known as the Becquerel-type photocurrent. Different electrode preparation techniques were investigated, and electrochemical reoxidation turned out to be more efficient on electrochemically prepared AgCl layers than on precipitated AgCl layers. Very stable photoelectrodes have been obtained on $SnO_2:F$-coated glass plates modified with a very thin gold layer. Such electrodes were employed as the anodic part in a photoelectrochemical cell for light-assisted water splitting.

Keywords: Photocatalytic oxygen evolution; Photocatalysis; Water oxidation; Silver chloride; Photoelectro chemistry; Silver clusters; Self-sensitization; Watersplitting

1. Introduction

The photocatalytic oxidation of water to oxygen is one of the most challenging problems in the solar splitting of water into H_2 and O_2 [1–3]. The systems for photocatalytic water oxidation investigated so far turned out to be photochemically unstable and inefficient in most cases [2]. In contrast, we have recently reported that silver chloride layers on $SnO_2:F$-coated glass plates produce O_2 from water with a high quantum yield when irradiated under appropriate conditions. The system shows self-sensitization of photochemical O_2 evolution, which means that new photoactive colour centres in the visible spectral range are formed on near UV illumination, composed of reduced or partially reduced silver species. The reaction is favored in the presence of a small excess of Ag^+ ions, with a maximum O_2 evolution rate at pH 4–5.5. The Ag^+ ions act as electron acceptors, according to Eq. (1)[4].

$$[n\mathrm{Ag}^+, m\mathrm{AgCl}] + \frac{r}{2}\mathrm{H_2O} \xrightarrow{h\nu} [(n-r)\mathrm{Ag}^+, m\mathrm{AgCl}, r\mathrm{Ag}^0] + r\mathrm{H}^+ + \frac{r}{4}\mathrm{O_2} \qquad (1)$$

Eq. (1) suggests that AgCl acts as a photocatalyst in the oxidation of water, since it is not consumed during the photochemical reaction. However, no experimental evidence was given that this formulation of the photoreaction is correct, at the time when Eq. (1) was postulated. Furthermore, the reduced silver species must be reoxidized if the photochemical water oxidation on silver chloride should become useful for a photocatalytic water splitting device

$$[(n-r)\mathrm{Ag}^+, m\mathrm{AgCl}, r\mathrm{Ag}^0] \rightarrow [n\mathrm{Ag}^+, m\mathrm{AgCl}] + re^- \qquad (2)$$

Realizing Eq. (2) by electrochemical means as illustrated in Fig. 1 is challenging, because this implies the spatial separation of the oxidative and reduction half-reactions of water photolysis [1]. We thus investigated the combined photochemical and electrochemical properties of AgCl-coated $SnO_2:F$ and other electrodes under chemical conditions where photochemical water oxidation takes place. We found that silver chloride layers on SnO_2: F-coated glass plates and on other substrates are photocatalysts for the oxidation of water to O_2, and we found a way how reduced silver produced during the photochemical oxidation of water to O_2 on AgCl can be electrochemically reoxidized. We now provide a full account of our preliminary note published recently [5]. First, we briefly review the present knowledge

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*Corresponding author.

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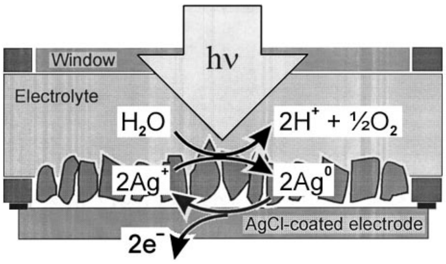

Fig. 1. Photocatalytic oxidation of water to O_2 on an AgCl-coated electrode and electrochemical reoxidation of the reduced silver.

about photochemical water oxidation with silver chloride and the photoelectrochemistry of silver chloride.

1.1. Photocatalytic O_2 evolution on AgCl

Since the invention of silver halide photography, the photochemistry of silver chloride has been investigated intensively [6–11]. However, only a few of these studies focused on the photochemical oxidation of water to oxygen with silver chloride. The first report on photochemical O_2 evolution in an aqueous AgCl suspension under near UV illumination was given by Baur and Rebmann [12], who were looking for a system for the photolysis of water. The understanding of water oxidation in natural photosynthesis or the creation of an artificial system for photochemical water splitting were the driving forces for later studies on photochemical oxidation of water to O_2 on AgCl colloids [13–16]. However, no way to the reoxidation of the reduced silver was given. We became interested in the water-oxidizing ability of Ag^+–A zeolite-containing systems when we observed that self-sensitization takes place: as the reaction proceeds, the sensitivity is extended from the near UV to the visible spectral range [17,18]. We further investigated the photochemical properties of systems containing AgCl and Ag^+–A zeolite in a series of studies [4,19–25], in the course of which we realized that the AgCl was responsible for the photochemical activity in each case [4,24]. Efficient photochemical oxidation of water to O_2 on AgCl takes place in the presence of a small excess of Ag^+ ions ($\sim 10^{-3}$ M), with a maximum evolution rate at pH 4–5.5. We suggested a mechanism for the photochemical water oxidation on AgCl which starts with light absorption of AgCl from its semiconductor valence band into the conduction band (Eq. (3)) [4]. The valence band of AgCl consists mainly of chlorine 3p orbitals, and the conduction band is largely derived from silver 5s orbitals [11]. Thus, the light absorption can be considered as a charge transfer absorption from Cl^- to Ag^+, if we change from an infinitely extended model to a more localized description, which seems to be more appropriate. The electron hole-pair may recombine (Eq. (4)), or electrons and holes may separate and finally be trapped as reduced silver atoms $Ag^0_{s,i}$ (Eq. (5)), or $Cl^\bullet_s$ radicals (Eq. (6)). The indices s and i refer to surface and interstitial species.

$$AgCl \xrightarrow{h\nu} AgCl + h^+ + e^- \tag{3}$$

$$h^+ + e^- \rightarrow kT \tag{4}$$

$$Ag^+_{s,i} + e^- \rightarrow Ag^0_{s,i} \tag{5}$$

$$Cl^-_s + h^+ \rightarrow Cl^\bullet_s \tag{6}$$

The $Cl^\bullet_s$ radicals may recombine to form Cl_2 (Eq. (7)). Under the applied conditions ($\sim 10^{-3}$ M Ag^+, pH 4–5), Cl_2 reacts with water to produce molecular oxygen, protons, and chloride ions, presumably according to Eqs. (8) and (9).

$$2Cl^\bullet_s \rightarrow Cl_2 \tag{7}$$

$$Cl_2 + H_2O \rightleftharpoons HOCl + H^+ + Cl^- \tag{8}$$

$$2HOCl \xrightarrow{Ag^+} O_2 + 2H^+ + 2Cl^- \tag{9}$$

Eq. (10), which is equivalent to Eq. (1), is the total reaction derived from Eqs. (3)–(9).

$$H_2O + 2Ag^+ \xrightarrow{h\nu,\, AgCl} 2H^+ + \frac{1}{2}O_2 + 2Ag^0 \tag{10}$$

In the presence of a small excess of Ag^+ ions, AgCl is not consumed during the reaction; it rather serves as a catalyst. The catalytic activity of AgCl in the suggested reaction sequence will be confirmed experimentally in the present study. The reduced silver atoms produced in Eq. (5) may react with other silver species (Ag^0 atoms, Ag^+ ions, or silver clusters), according to Eq. (11), forming positively charged or neutral silver clusters. In its first stages, this reaction is certainly related to the fundamental process of latent image formation in the silver halides. Continuous illumination leads to the formation of printout silver [9].

$$Ag^0 + Ag_r^{q+} \rightarrow Ag_{(r+1)}^{q+} \quad (r \geq 1; 0 \leq q \leq r) \tag{11}$$

We have good evidence that self-sensitization [4,18,19,23] of the photochemical activity of AgCl is due to silver clusters which are formed according to Eq. (11). Quantum chemical calculations on small silver clusters give estimates for the energetic position of their occupied and empty energy levels [26,27]. A comparison with the energetic position of the semiconductor band gap of AgCl [28] shows that the silver clusters have empty energy levels below the conduction band of AgCl. The silver clusters probably act in a similar way as the so-called impurities in silver halide crystals, which often have energy states in the forbidden gap of the silver halide [9]. The situation is depicted in Fig. 2. In the absence of silver clusters AgCl does not absorb light below the indirect band gap transition, which is in the near UV spectral range at 3.3 eV (380 nm) [11]. Their presence enables a new electronic transition from the AgCl valence band to the empty silver cluster energy levels. The energy for this transition is lower than the energy needed for an optical transition from the AgCl valence band into the AgCl conduction band. Nevertheless, this new optical transition in the visible spectral range may initiate

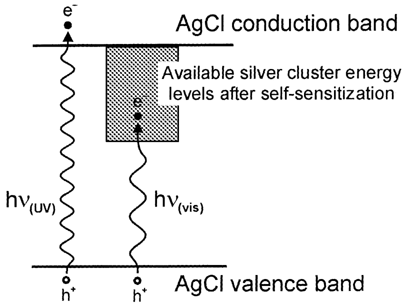

Fig. 2. Energy level diagram illustrating the self-sensitization of AgCl. The photochemical activity is extended from the near UV into the visible range of the spectrum upon near UV illumination due to the formation of silver clusters. They provide empty energy states below the AgCl conduction band for charge injection from the AgCl valence band.

the oxidation of water, according to Eqs. (6)–(9), because the conduction band is not directly involved in water oxidation. Thus, the photocatalytic oxidation of water on AgCl is extended from the near-UV into the visible range of the spectrum. Self-sensitization as observed by us should not be confused with spectral sensitization affected by silver clusters (also termed the 'photographic Becquerel effect'). The latter observation has been attributed to an electron injection from electron-donating silver clusters into the AgCl conduction band. However, both processes are related to the presence of silver clusters.

1.2. Photoelectrochemical properties of AgCl

The first investigation of the photoelectrochemical properties of AgCl-coated electrodes was made by E. Bequerel in 1839 [29], shortly after H.F. Talbot had realized the first photographic pictures on paper based on AgCl [6,7]. An AgCl-coated platinum working electrode and a blank platinum counter electrode were immersed in a aqueous nitric acid electrolyte solution. Illumination of the AgCl-coated electrode by sunlight generated a photovoltage that produced a reductive photocurrent at the AgCl-coated electrode. This result, termed the 'Becquerel effect', represented the first reported photovoltaic device. A photocurrent of reversed sign with respect to the Becquerel-type photocurrent is observed in the photogalvanic silver chloride cell [21,30]. In one variant of this cell, an AgCl-coated silver grid working electrode and a platinum counter electrode are immersed in an acid chloride electrolyte in close vicinity to each other, that is, just separated by a porous membrane. Under illumination of the cell, AgCl is decomposed, and the platinum counter electrode takes the Cl_2/Cl^- redox potential, whereas the AgCl-coated silver electrode takes the $AgCl/Ag_{bulk}{}^0$ redox potential. Thus, an oxidative photocurrent at the AgCl-coated silver electrode arises in the photogalvanic silver chloride cell. Anodic photocurrents at AgCl-coated silver electrodes in halide solutions were also observed by M.A. Butler in a three-electrode photoelectrochemical experiment [31]. They were interpreted in terms of a charged photoemission across the silver/silver chloride interface, an interpretation that does not apply in our case. Beyond this, we refer to a few more reports on photoelectrochemical experiments on silver chloride electrodes, mainly concerned with the effect of spectral dye sensitization [28,32–34].

2. Experimental

2.1. Flow photoreactor apparatus

The apparatus used to study the photochemical and electrochemical properties of thin substrate layers on illumination was based on a flow photoreactor system, as depicted in Fig. 3. A similar apparatus had been used in the experiments described in Refs. [4,5,23]. Its main part was a photoreactor made of poly(chlorotrifluoroethylene) (PCTFE), with an electrolyte volume of approximately 1 ml, connected to a N_2-purged electrolyte reservoir (volume, 130 ml). A peristaltic pump transported the electrolyte solution from the reservoir, via a capillary system, through the cell and back to the reservoir at a rate of about 1 ml min^{-1}. As an electrolyte, 0.1 M $NaNO_3$ (Merck, p.a.) aqueous solution with 1 mM $AgNO_3$ (Merck, p.a.) was used. The pH was measured with a combined glass electrode (Metrohm, double junction; outer filling, 1 M $NaNO_3$ aqueous solution) and maintained at a value of 4.8 ± 0.5 throughout the experiments described. If necessary, it was adjusted with 0.1 M $HClO_4$ (aq) or 0.1 M NaOH (aq). The experiments were carried out at room temperature

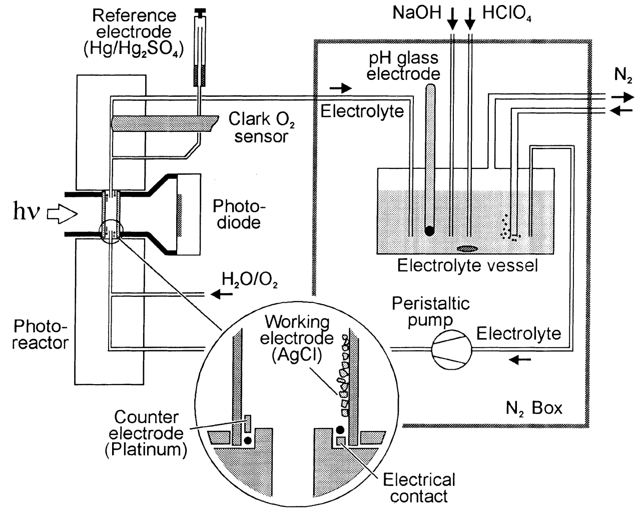

Fig. 3. Flow photoreactor apparatus for experiments on AgCl-coated electrodes. Left: photoreactor with an integrated three-electrode system, a Clark O_2 sensor, a photodiode behind the reaction window, and a capillary for injection of air-saturated water for calibration of the Clark sensor. Right: electrolyte reservoir with N_2 bubbler, pH glass electrode and acid/base injection in a N_2-purged box. A peristaltic pump transports the electrolyte solution from the reservoir via a capillary system through the cell and back to the reservoir.

(22 ± 1°C). The AgCl layer (area, 1 cm^2) was coated on an electrode disc which was placed in the photoreactor and illuminated through a quartz window. The coating procedure is described in the next sections. The AgCl-coated electrode was the working electrode of a three-electrode system for electrochemical experiments. A platinum sheet was used as counter-electrode and a mercury/mercurous sulfate electrode (Hg/Hg_2SO_4; electrolyte filling, 1 M Na_2SO_4 aqueous solution) as reference electrode. In the chronoamperometric experiments, the AgCl-coated electrode was polarized at 0.0 V versus Hg/Hg_2SO_4 (+0.64 V vs. NHE) with a potentiostat (Metrohm 641 VA-Detector). The photoreactor also contained a Clark O_2 sensor (WTW Instruments, Germany) which was calibrated by injecting air-saturated water (O_2 concentration, 0.28 mM at 22°C [35]) was injected at a rate of 0.003 ml min^{-1} into the N_2-purged electrolyte flowing through the photoreactor. Due to different geometrical locations of the photochemical O_2 evolution site and the injection capillary for calibrations in the photoreactor (see Fig. 3), an estimated relative error of about 10% had to be admitted in the O_2 measurement. The O_2 evolution and photocurrent were measured simultaneously. The AgCl-coated electrode was illuminated with white light from a 450 W xenon arc lamp. The light was passed through a water filter and a pyrex lens to remove the IR and far UV light, respectively. Additionally, in most experiments the light was passed through a cold light filter (Schott–Schleiffer, glass filter-type KG 3, transmission range ~330–750 nm), to prevent unwanted warming of the electrolyte in the photoreactor. The light intensity at the AgCl-coated electrode was approximately 60 mW cm^{-2} if illuminated through the cold light filter; without the cold light filter the light intensity was approximately 150 mW cm^{-2}. Only part of the incoming light was absorbed by the AgCl coating, consisting of about 0.5 µmol AgCl cm^{-2}. In the experiments described, the AgCl-coated electrode was exposed to successive illumination and dark periods of 100 and 25 min duration each, respectively.

2.2. Preparation of AgCl-coated electrodes by precipitation of AgCl

Silver chloride layers on electrodes were produced either by precipitation of AgCl or by electrochemical deposition. Electrically conducting $SnO_2:F$-coated glass (Glaverbel SA, Belgium) and platinum were used as electrode substrates. Before coating, the substrate discs were polished with an aqueous suspension of Al_2O_3 (0.3 µm Al_2O_3, Presi, ultrapure), cleaned ultrasonically in ethanol or 1,1,1-trichloroethane, and dried. To prepare a precipitation coating of AgCl, the electrode substrate disc was placed in a small beaker (bottom diameter, 23 mm) and covered with 2 ml of bidistilled water. First, 20 µl of 0.1 M $AgNO_3$ (aq) (Merck, p.a.) was added, followed by 20 µl of 0.1 M NaCl (aq) (Merck, p.a.); after stirring, sedimentation of the precipitated AgCl was allowed overnight in the dark. The colour of the produced AgCl layer was white. The AgCl-coated electrode was dried at 50°C for a few minutes, and the coating was fixed with 20 µl of polyvinylchloride (PVC) dissolved in tetrahydrofuran (THF) (0.5 mg ml^{-1}). The small amount of PVC was used to provide sufficient mechanical stability. However, it played no role in the photochemistry or electrochemistry taking place. AgCl was wiped away from the border of the substrate electrode where electrical contact was made with a copper ring in the photoreactor. The part where electrical contact was made was carefully protected from any contact with the electrolyte and light. The electrode area exposed to the light was about 1 cm^2 and the amount of AgCl in this area was 65 µg (0.46 µmol, corresponding to an equivalent charge of 44 mC).

2.3. Preparation of AgCl-coated electrodes by electrochemical deposition of AgCl

To prepare an AgCl coating electrochemically, an $SnO_2:F$-coated glass disc was first coated with a thin layer (~50 nm) of metallic silver by vapour deposition (Balzers high vacuum vapour deposition equipment BA 350 E). The border of the substrate electrode was shielded with adhesive tape during the silver deposition to keep it uncovered. The substrate electrode area covered with silver was about 1 cm^2. The silver coverage was then electrochemically reoxidized in 0.2 M KCl (Merck, p.a.) aqueous solution at pH 2 (acidified with HCl). The electrochemical reoxidation was performed by an anodic potential sweep (EG&G Model 273A potentiostat) in a three-electrode cell with a platinum sheet counter-electrode and an Ag/AgCl reference electrode. The silver-coated working electrode disc was dipped into the argon-purged electrolyte and contacted at the silver-free border with a gold clip, which was prevented from dipping into the electrolyte. The potential was swept from 0 V to +1.2 V versus Ag/AgCl, with a sweep rate of 100 mV s^{-1}. The sweep showed an oxidation peak with a maximum current density of ~15 mA cm^{-2} at about +0.5 V versus Ag/AgCl. After reaching the peak maximum, the current decreased sharply, indicating that all of the silver on the electrode was electrochemically oxidized. The colour of the produced AgCl layer was weak red–brown. The amount of AgCl produced, as calculated from the integrated sweep current, was 86 µg (0.61 µmol, corresponding to an equivalent charge of 58 mC) on an electrode area of 1 cm^2. Thus, the amount of AgCl was in the same range as with the coatings prepared by precipitation of AgCl. The AgCl-coated electrode disc was carefully rinsed with bidistilled water and dried at 50°C. The coating was fixed with 20 µl of PVC dissolved in THF (0.5 mg ml^{-1}) in the same way as the precipitated AgCl coating.

2.4. Scanning electron micrographs

The morphology of AgCl-coated $SnO_2:F$ electrodes before and after a photoelectrochemical experiment was analyzed by scanning electron microscopy (SEM). A JEOL JSM-840 scanning electron microscope was used, and the samples were sputtered with gold for the measurements.

2.5. Photoelectrochemical cell for light-assisted water splitting

The photoelectrochemical properties of AgCl-coated electrodes with respect to light-assisted water splitting were investigated in a two-compartment photoelectrochemical cell. The cell is schematically shown in Fig. 4. AgCl was coated electrochemically, as described in the previous section, on a $SnO_2:F$-coated glass disc, which was the working electrode in the anodic (oxidative) cell compartment. The illuminated, AgCl-coated area was about 5 cm^2 in this cell, and the amount of AgCl coated on the electrode was about 0.3 $\mu mol\ cm^{-2}$. The AgCl-coated electrode was illuminated through its transparent back side. A platinum wire served as counter-electrode in the cathodic (reductive) cell compartment. The reductive cell compartment also contained a mercury/mercurous sulfate reference electrode (Hg/Hg_2SO_4; electrolyte filling, saturated K_2SO_4 aqueous solution). The two cell compartments with a volume of ~15 ml each, were separated by a silver-resistant anion exchange membrane (Pall RAI, type R4030). The membrane was based on a polytetrafluoroethylene (PTFE) polymer and contained quaternized ammonium chloride ionic groups. The electrolyte was 0.1 M $NaNO_3$ aqueous solution with 1 mM $AgNO_3$ in the oxidative compartment and 0.1 M $NaNO_3$ aqueous solution in the reductive compartment. The electrolyte was deoxygenated with N_2 in both compartments before photoelectrochemical experiments. During the experiments no N_2 purge was applied. A small gas outlet was left open at the top of the two cell compartments. Due to equilibration of the electrolyte with the surrounding air, a slow increase in O_2 concentration was observed in the electrolyte after purging with N_2 even in the absence of a photochemical O_2 production, which however, did not disturb the experiments. Beside the AgCl-coated $SnO_2:F$ window, the oxidative cell compartment contained a Clark O_2 sensor, a pH glass electrode with chlorine-free reference system (Ross, model 81-03), and an inlet for pH adjustment with 0.1 M NaOH(aq). The pH adjustment was needed to keep the pH in the oxidative half-cell at a value of ~5 during the measurement. The AgCl-coated $SnO_2:F$ window was illuminated with a 200 W mercury arc lamp, through a cold light filter (Schott–Schleiffer, glass filter-type KG 3, transmission range ~330–750 nm) and a blue light filter (Schott–Schleiffer, glass filter type BG 23, transmission range 350–600 nm). The light intensity was about 25 $mW\ cm^{-2}$ in the range 350—600 nm. During the measurements, the AgCl-coated $SnO_2:F$ window was polarized at 0.0 V versus Hg/Hg_2SO_4 (+0.64 V vs. NHE) with a potentiostat (Metrohm 641 VA-Detector).

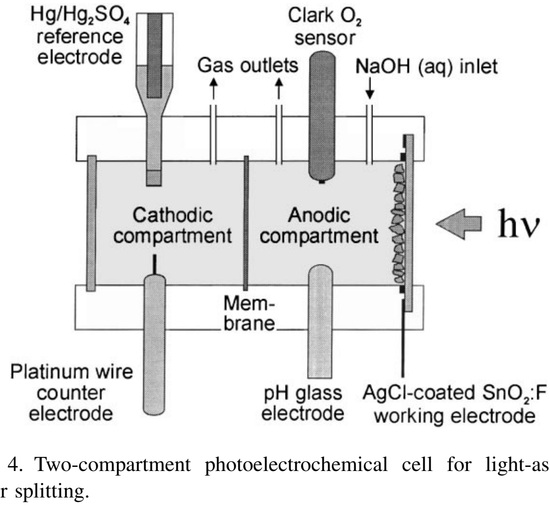

Fig. 4. Two-compartment photoelectrochemical cell for light-assisted water splitting.

3. Results and discussion

Chronoamperometric experiments with simultaneous measurement of photocurrent and O_2 evolution under illumination were performed to investigate the photoelectrochemical properties of AgCl-coated electrodes under O_2-evolving conditions. A 0.1 M $NaNO_3$ aqueous solution with 1 mM $AgNO_3$ at pH ~5 was used as electrolyte throughout the experiments described. The AgCl-coated electrode was polarized at 0.0 V versus Hg/Hg_2SO_4 (+0.64 V vs. NHE). The choice of the polarization potential was based on the following thermodynamic considerations. The equilibrium redox potential of a silver electrode in an aqueous electrolyte containing 10^{-3} M Ag^+ is $E = +0.62$ V versus NHE at 22°C ($E^\circ[Ag^+/Ag_{bulk}{}^0] = +0.80$ V), as calculated from the Nernst equation [36]. Anodic polarization of the silver electrode with respect to this redox potential causes an oxidation of the silver electrode. Cathodic polarization, on the other hand, causes a reduction of Ag^+ ions in the electrolyte solution. Thus, from the thermodynamic point of view, any bulk silver produced on the AgCl-coated electrode under illumination should be reoxidizable at a polarization potential of 0.0 V versus Hg/Hg_2SO_4 (+0.64 V vs. NHE). Sufficient electrical contact between the reduced silver and electrode substrate is a presupposition for such an electrochemical reoxidation. These considerations neglect the occurrence of photovoltage on the AgCl-coated electrode, which may change the current response of the electrode.

3.1. Precipitated AgCl layer on $SnO_2:F$ conducting glass

The first experiments discussed here were carried out with AgCl-coated electrodes produced by precipitation of AgCl, as described in Section 2. Fig. 5 shows the result of a chronoamperometric experiment with an AgCl-coated $SnO_2:F$ electrode. Illumination periods of 100 min duration alternate with dark periods of 25 min duration; the total time of this experiment is 10.5 h. It is remarkable that O_2 signal

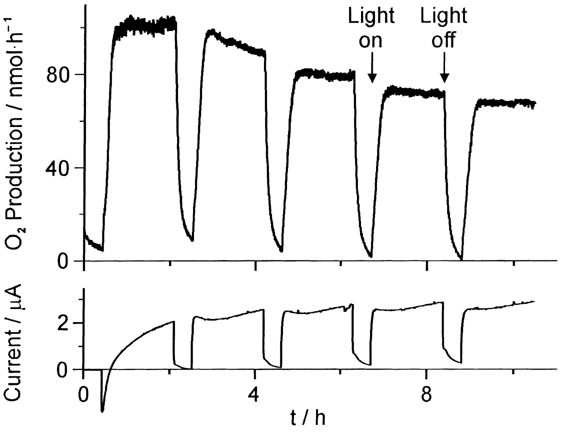

Fig. 5. Chronoamperometry of a precipitated, AgCl-coated $SnO_2:F$ electrode at 0.0 V vs. Hg/Hg_2SO_4, with illumination and dark periods. The O_2 production rate (nmol h^{-1}) and the photocurrent (μA; anodic current is drawn upwards) are plotted vs. time.

and the photocurrent coincide when the light is switched on and off, which is observed in all experiments. Interestingly, the photocurrent is cathodic (reductive) during the first 12 min of the first illumination period and turns anodic (oxidative) afterwards. It reaches a steady anodic value of about 2.5 μA after a few hours. The O_2 production rate reaches a maximum around 100 nmol h^{-1} in the first illumination period and then slowly decreases to an almost steady value of about 70 nmol h^{-1}. The experiment clearly shows a sustained photochemical O_2 evolution on the AgCl-coated electrode and a simultaneous electrochemical reoxidation of reduced silver. During dark periods, the O_2 production is interrupted and the reoxidation current decreases sharply. The O_2 signal does not immediately decline to zero at the beginning of the dark periods because of the experimental set-up, that is, because of a mixing of the O_2-enriched electrolyte in the photoreactor with freshly incoming N_2-purged electrolyte from the electrolyte reservoir.

During the whole experiment shown in Fig. 5, a total of 670 nmol of O_2 is produced. This means that 2680 nmol of reduced silver is produced in the photochemical reaction, since O_2 production is a four-electron process, according to Eq. (1). The amount of reduced silver corresponds to about six turnovers with respect to the total amount of AgCl coated on the electrode (0.46 μmol), as calculated from Eq. (12). $n(O_2)$ in Eq. (12) is the amount of O_2 produced during the experiment, $n(Ag^0)$ is the amount of reduced silver derived from $n(O_2)$ according to the stoichiometry of Eq. (1), and $n(\mathrm{AgCl})$ is the amount of AgCl coated on the electrode.

$$\text{turnover number} = \frac{4n(\mathrm{O_2})}{n(\mathrm{AgCl})} = \frac{n(\mathrm{Ag^0})}{n(\mathrm{AgCl})} \tag{12}$$

The integrated polarization current in the experiment in Fig. 5 is 69 mC. This charge corresponds to an equivalent amount of 715 nmol of reoxidized silver, $n(\mathrm{Ag_{reox}})$ according to Eq. (13). I_{pol} in Eq. (13) is the polarization current, and $F = 96\,485$ C mol^{-1} is the Faraday constant. Eq. (13) is based on the assumption that the polarization current is entirely due to reoxidation of reduced silver.

$$n(\mathrm{Ag_{reox}}) \approx \frac{1}{F}\cdot\int_{\mathrm{start}}^{\mathrm{end}} I_{\mathrm{pol}}\,\mathrm{d}t \tag{13}$$

From a comparison of $n(\mathrm{Ag_{reox}})$ with $n(O_2)$, we deduce that 27% of the reduced silver is electrochemically reoxidized in the experiment in Fig. 5, according to Eq. (14). The remaining 73% of the reduced silver is not accessible in this experiment.

$$\begin{aligned}\text{reoxidation percentage} &= \frac{n(\mathrm{Ag_{reox}})}{4n(\mathrm{O_2})} \times 100\% \\ &= \frac{n(\mathrm{Ag_{reox}})}{n(\mathrm{Ag^0})} \times 100\% \end{aligned} \tag{14}$$

This experiment gives clear evidence that the AgCl layer is photocatalytically active in the oxidation of water to O_2, under the simultaneous photoreduction of Ag^+ ions continuously provided by the electrolyte. Part of the reduced silver species are deposited on the AgCl-coated electrode and is available for electrochemical reoxidation, but the other part of the reduced silver is electrochemically not accessible in this experiment; it is probably carried away in the electrolyte flowing through the photoreactor and lost in the large electrolyte reservoir.

3.2. *Precipitated AgCl layer on platinum*

We observed similar behaviour in an analogous experiment on a precipitated AgCl layer, but this time with platinum as the electrode substrate (see Fig. 6). 360 nmol of O_2 is produced until the experiment is stopped after 10.5 h, corresponding to more than three turnovers of the AgCl layer coated on the electrode. The integrated photocurrent is 43 mC. This means that 31% of the reduced silver is reoxidized. It is remarkable that the photocurrent

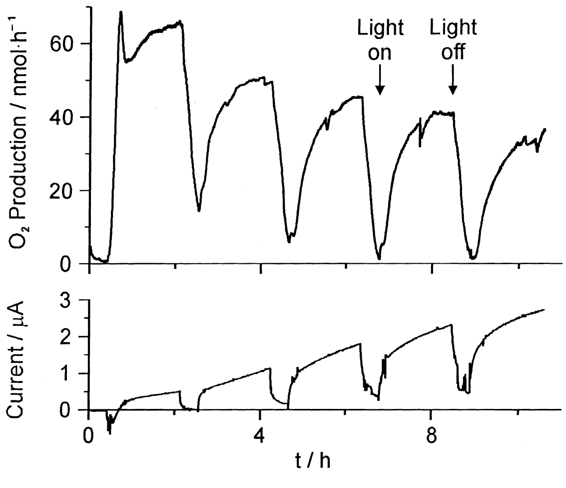

Fig. 6. Same chronoamperometric illumination experiment as in Fig. 5, but with a precipitated, AgCl-coated platinum electrode.

increases from one illumination period to the next. If only the last two illumination periods in Fig. 6 are considered, 67% of the silver produced during these two periods is simultaneously reoxidized. if the AgCl-coated platinum electrode was illuminated for a longer time (with longer illumination periods), the current and the O_2 production reached almost a steady value. After 60 h illumination, the current was still 3 μA, and the O_2 production rate amounted to ~40 nmol h^{-1}. The photochemical O_2 production rate is smaller in the experiment on an AgCl-coated platinum electrode (Fig. 6), than on an AgCl-coated $SnO_2:F$ electrode (Fig. 5). This might be due to a partial electrochemical reduction of the reaction product O_2 at the electrocatalytically active platinum electrode [37], diminishing the amount of produced O_2.

3.3. Reoxidation after illumination

We observed in the experiments shown in Figs. 5 and 6 that the anodic current does not usually drop completely to zero during the dark periods applied. Therefore it seems possible to oxidize at least part of the reduced silver deposited on the photoelectrode during reaction 1 after illumination. To verify this hypothesis, an AgCl-coated $SnO_2:F$ electrode (AgCl coating produced by precipitation) was illuminated in the same way and for the same time as in the experiments shown in Figs. 5 and 6, but at zero current, that is, without an applied potential. The result of this experiment is shown in the upper part of the Fig. 7. The amount of O_2 evolved was 730 nmol, close to the value in the experiment of Fig. 5. At the end of illumination, a potential of 0.0 V versus Hg/Hg_2SO_4 was applied to the electrode. This is shown in the lower part of Fig. 7. The polarization led to an anodic dark current which was 30 μA at the beginning and decreased to zero within 150 min. Integrating the current yielded a charge of 61 mC, which means that 22% of the reduced silver was reoxidized. The amount is somewhat smaller than that in the experiments of Figs. 5 and 6, but readily shows that part of the silver is deposited on the electrode during illumination and can be reoxidized electrochemically.

3.4. Electrochemically prepared AgCl layer

AgCl layers on electrode substrates can be produced conveniently by electrochemical oxidation of a silver coating in a chloride solution [38]. We have thus prepared AgCl coatings on $SnO_2:F$-glass discs by an electrochemical method, as described in Section 2. The growth speed of the AgCl coating during the electrochemical oxidation determines the morphology of the AgCl layer, which in turn affects the photochemical activity of the AgCl layer. It is important to work at sufficiently high current densities during the electrochemical oxidation of the silver, in order to get the desired photoactive AgCl morphology [21,38]. A current density of approximately 15 mW cm^{-2} (at the peak maximum of the reoxidation sweep) turned out to be appropriate. A chronoamperometric experiment on an electrochemically prepared, AgCl-coated $SnO_2:F$ electrode is shown in Fig. 8. The experiment is similar as in Figs. 5 and 6, but this time more illumination and dark periods were recorded. The general behaviour of the electrochemically prepared AgCl layer is similar as in the case of the precipitated AgCl layers, and the photochemical activity, that is, the O_2 production rate, lies in the same range. The polarization current, however, is larger than in the experi-

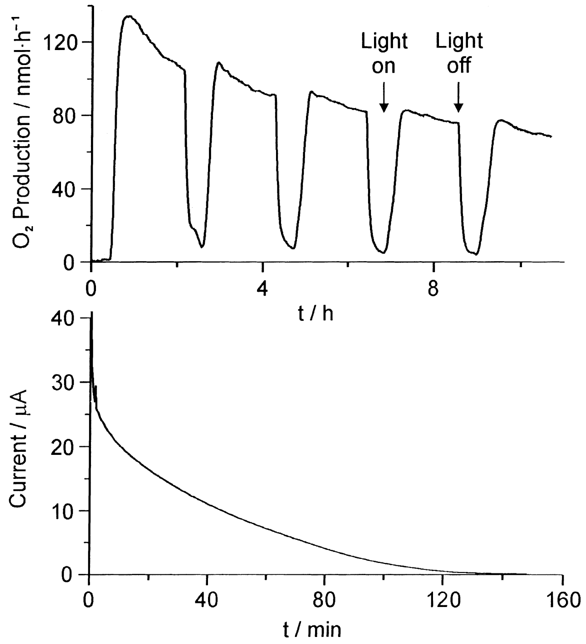

Fig. 7. Oxidation of water to O_2 on a precipitated, AgCl-coated $SnO_2:F$ electrode under illumination, followed by electrochemical reoxidation of the reduced silver by chronoamperometry at 0.0 V vs. Hg/Hg_2SO_4.

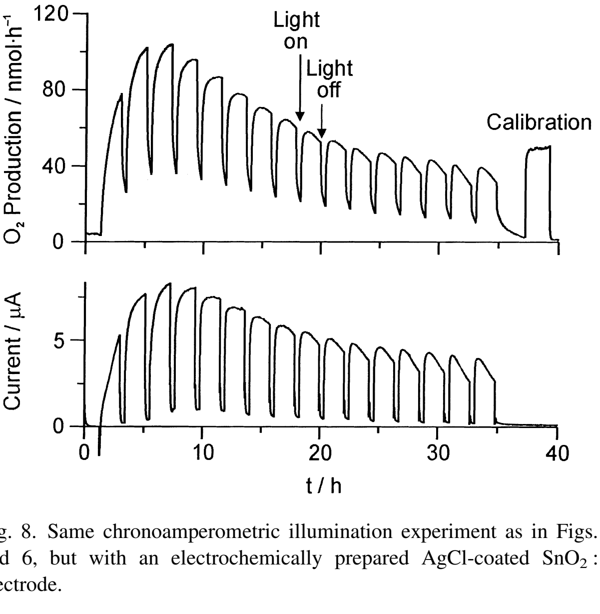

Fig. 8. Same chronoamperometric illumination experiment as in Figs. 5 and 6, but with an electrochemically prepared AgCl-coated $SnO_2:F$ electrode.

ments on precipitated AgCl layers, indicating that reoxidation efficiency is higher in the case of the electrochemically prepared AgCl layer. During the whole experiment shown in Fig. 8, 1840 nmol of O_2 is produced. This corresponds to 12 turnovers with respect to the amount of AgCl covered on the electrode. The total reoxidation current integrates to 530 mC, corresponding to an equivalent amount of 5490 nmol. Therefore, 75% of the produced silver is electrochemically reoxidized. The reoxidation percentage for the electrochemically prepared AgCl layer is much higher than for the precipitated AgCl layers. We conclude that the electrical contact of the AgCl coverage with the electrode substrate is better in the case of the electrochemically prepared AgCl layer. This can largely be explained by a more suitable morphology of the electrochemically prepared AgCl coverage, that is, a more even distribution of the AgCl on the electrode substrate, as was revealed by scanning electron micrographs (see Section 3.5). During the first few illumination periods of the experiment in Fig. 8, the photochemical O_2 production and the photocurrent pass through a maximum. The variation in photochemical activity may be due to change in the morphology of the AgCl layer during the experiment. During the last illumination periods the signals are quite steady. However, a continuous, small decrease in the photochemical activity can still be observed, which may be due to a slow degradation of the AgCl layer or the Ag^+-containing electrolyte under illumination. It is interesting to compare the first five illumination periods of the experiment in Fig. 8 with its last five illumination periods. During the first five illumination periods, 800 nmol of O_2 are produced, corresponding to 5.3 turnovers of AgCl, and the reoxidation amounts to 66%. During the last five illumination periods, 370 nmol of O_2 are produced, corresponding to 2.4 turnovers of AgCl, and the reoxidation amounts to 83%. Thus, the electrochemical reoxidation becomes more efficient with respect to the amount of photochemically produced O_2 in the course of the photoelectrochemical experiment. The experiments in Figs. 5 and 6 show a similar effect. Part of the reduced silver which is produced during the first illumination periods is probably accumulated on the AgCl-coated electrode without being reoxidized. In later stages of the experiments, a steady state is reached, where accumulation of reduced silver is balanced by electrochemical reoxidation. An additional account for the observed behaviour may enhance losses of reduced silver into the electrolyte during the first illumination periods.

3.5. Morphology of the AgCl layers

The morphology of the AgCl-coated $SnO_2:F$-electrodes was analyzed by SEM. Fig. 9 shows scanning electron micrographs of precipitated and electrochemically prepared AgCl layers on $SnO_2:F$ electrodes before and after a photoelectrochemical experiment as described above. The duration of the photoelectrochemical experiments was about 10 h. The amount of AgCl covered on the electrode substrate is $\sim 0.5\ \mu mol\ cm^{-2}$ in each case. The morphologies of the precipitated and electrochemically prepared AgCl layers are quite different from each other. In the case of the precipitated AgCl layers, the AgCl forms aggregates with an average size of the order of 1 μm covering about half of the electrode surface. The other half of the electrode surface remains uncovered. The electrochemically prepared AgCl aggregates are smaller, and they cover the electrode surface completely. Thus, the electrochemically prepared AgCl layers have a larger contact area with the electrode substrate than the precipitated AgCl layers. This is probably the main reason why electrochemically prepared AgCl layers show a larger reoxidation percentage during photoelectrochemical experiments than precipitated AgCl layers. The larger contact area provides a better electrical contact, and reduced silver is reoxidized more efficiently. Therefore, less reduced silver is lost into the electrolyte. The texture of the silver chloride aggregates of a fresh AgCl layer is rather soft. It becomes sharper after a photoelectrochemical experiment. In the case of an electrochemically prepared AgCl layer, the change in texture is more pronounced than in the case of a precipitated AgCl layer, where just a minor change is observed. No significant deposits of reduced silver are identified after a photoelectrochemical experiment. From the experiment shown in Fig. 5, a rough estimate can be made of the amount of reduced silver staying on the AgCl-coated electrode during the steady state of a photoelectro-

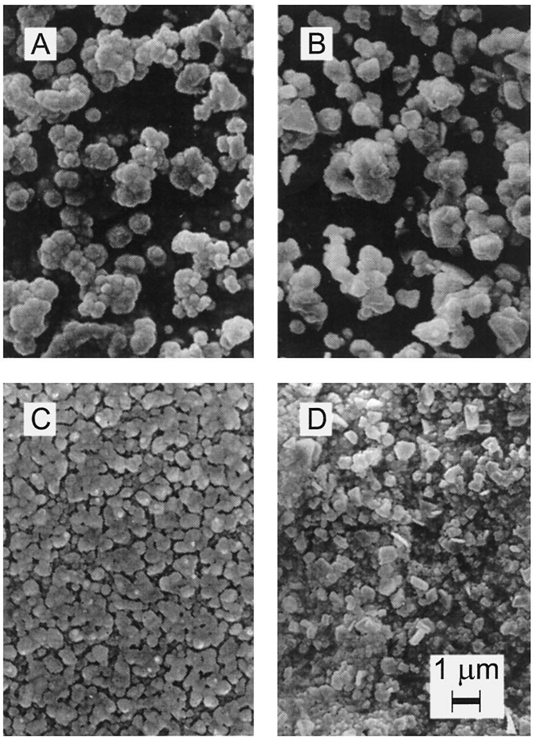

Fig. 9. Scanning electron micrographs of AgCl layers on $SnO_2:F$ electrodes; (A) fresh, precipitated AgCl layer; (B) precipitated AgCl layer after a photoelectrochemical experiment; (C) fresh, electrochemically prepared AgCl layer; (D) electrochemically prepared AgCl layer after a photoelectrochemical experiment.

chemical experiment. The integrated reoxidation current is distinctively smaller in the first illumination period than in the following illumination periods, though the O_2 production rate is roughly the same. The difference in the integrated reoxidation current corresponds to an amount of about 90 nmol of reduced silver, which is not reoxidized during the first illumination period. Assuming that none of this reduced silver was lost into the electrolyte, the percentage of reduced silver on the electrode would be about 15%. This amount is probably an overestimate, since some reduced silver is expected to be lost into the electrolyte. Further, no significant deposits of reduced silver were identified after a photoelectrochemical experiment, as stated before.

3.6. Photoelectrochemical cell for light-assisted water splitting

The photoelectrochemical experiments on AgCl-coated electrodes described so far encouraged use of the AgCl-coated electrode as the anodic part of a photoelectrochemical cell for light-assisted water splitting. We thus devised a two-compartment photoelectrochemical cell with an AgCl-coated $SnO_2:F$-working electrode in the anodic compartment and a platinum wire counter electrode as well as an Hg/Hg_2SO_4 reference electrode in the cathodic compartment, as shown in Fig. 4. To provide the necessary polarization potential for silver reoxidation at the working electrode, according to Eq. (2), and for water reduction at the counter electrode, the cell was connected with a potentiostat, and the working electrode was polarized at 0.0 V versus Hg/Hg_2SO_4 (+0.64 V vs. NHE) during the illumination experiment. The two overall half-cell reactions expected to occur in this photoelectrochemical cell are given as Eq. (15) for the anodic process and as Eq. (16) for the cathodic process. The H^+ ions produced according to Eq. (15) and the OH^- ions produced according to Eq. (16) are expected to react with each other across the cell membrane to form H_2O. Thus, the overall process is water splitting according to Eq. (17).

$$H_2O \overset{h\nu,\mathrm{AgCl}}{\rightarrow} 2H^+ + \frac{1}{2}O_2 + 2e^- \quad (15)$$

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \quad (16)$$

$$H_2O \rightarrow H_2 + \frac{1}{2}O_2 \quad (17)$$

Fig. 10 shows the result of a photoelectrochemical experiment on an electrochemically prepared, AgCl-coated $SnO_2:F$ electrode (electrode area, 5 cm^2). Illumination periods of 2 h alternate with dark periods of 0.5 h during the first 10 h; for the rest of the experiment the AgCl-coated electrode was illuminated continuously. Before the start of the experiment shown in Fig. 10, the AgCl layer had already been illuminated under O_2-evolving conditions, but without an applied potential (i.e. at zero current), for about 20 min. The upper half of Fig. 10 shows the increase of the O_2 concentration in the electrolyte of the anodic compartment, as measured with the Clark O_2 sensor. The photochemically produced O_2 accumulated in the initially deoxygenated electrolyte until saturation was reached after several hours. Under the assumption of an equilibrium between the electrolyte and the air surrounding the cell, the O_2 saturation concentration in the electrolyte was 280 μM [35]. The actual O_2 saturation concentration in the electrolyte was probably higher than this value, because equilibration with the air was sluggish. After saturation of the electrolyte, the Clark O_2 sensor signal remained constant. This does not mean that the photochemical O_2 production had stopped. However, sustained O_2 production led to the evolution of oxygen gas, so that small bubbles sticking on the walls of the plexiglas cell were observed during the illumination experiment. During the dark periods of the experiment, the O_2 concentration signal decreased slightly (see Fig. 10). This might be due to slow diffusion of O_2 through the membrane into the reductive compartment of the cell. The lower half of Fig. 10 shows the polarization current. It is anodic throughout the experiment and passes a maximum of almost 45 μA (current density, 9 μA cm^{-2}) after a few hours of illumination; afterwards it decreases slowly but steadily. The polarization current goes on after O_2 saturation of the electrolyte in the anodic compartment. This is clear evidence that the photochemical activity of the AgCl layer is maintained in the presence of the reaction product O_2 in the electrolyte. The steady decrease of the current might be due to an unfavorable change in the morphology of the AgCl layer

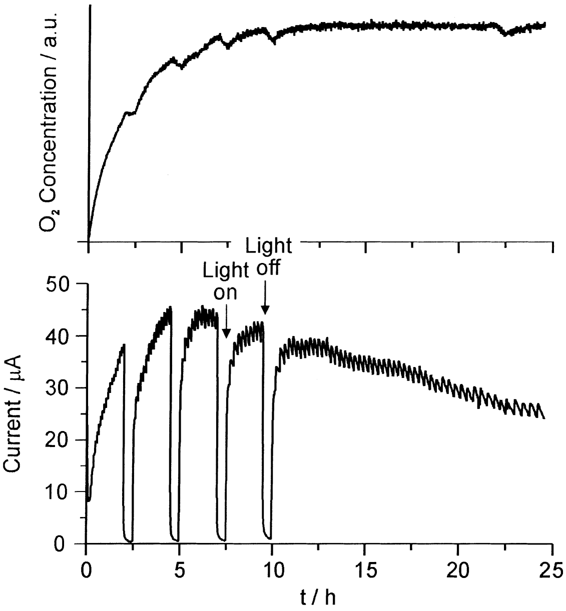

Fig. 10. Chronoamperometry of an electrochemically prepared, AgCl-coated $SnO_2:F$ electrode (area, 5 cm^2) at 0.0 V vs. Hg/Hg_2SO_4, with illumination and dark periods, in a two-compartment photoelectrochemical cell for light-assisted water splitting. Upper curve: concentration of dissolved O_2 in the anodic cell compartment (arbitrary units); O_2 saturation is reached after a few hours. Lower curve: polarization current (μA; anodic current is drawn upwards).

or to the degradation of the Ag^+-containing electrolyte solution under illumination [39]. Calculating the reoxidation percentage in this experiment is not useful, because the precise amount of produced O_2 is not known. However, almost all quantitative reoxidation can be assumed, since the reoxidation current density is in the same range as in Fig. 8 (we estimate that O_2 production rate per cm^2 is about the same in the experiments shown in Figs. 8 and 10, although the illumination as well as the amount of AgCl coated on the electrode are different in the two experiments). Further, the electrolyte is stationary in this experiment, and thus reduced silver which is produced at the AgCl-coated electrode cannot be carried away. The small oscillations superimposed on the current signal in Fig. 10 are due to pH variations in the order of 0.3 pH units. Whenever the pH value of the electrolyte in the oxidative compartment fell below 5, it was adjusted with a few µl of 0.1 M NaOH(aq). Each addition of NaOH(aq) caused a small temporary increase in the photocurrent. The need to adjust the pH value shows that the H^+ ions produced in the anodic cell compartment (Eq. (15)) and the OH^- ions produced in the cathodic cell compartment (Eq. (16)), did not quantitatively react with each other across the cell membrane to form H_2O. In fact, the pH became basic in the cathodic cell compartment, and a pH gradient of a few pH units was built up across the cell membrane. In some experiments, minor deposits of reduced silver were found on the platinum wire counter electrode indicating that water reduction according to Eq. (16) was not the only reaction at the platinum wire counter electrode. Instead, some Ag^+ ions contaminating the reductive cell compartment were reduced at the platinum wire in these instances. If a perfluorinated cation exchange membrane (Aldrich, Nafion 117) was used instead of the anion exchange membrane to separate the anodic and the cathodic half-cell, large deposits of reduced silver were found on the counter electrode. Thus, diffusion of Ag^+ ions through the Nafion membrane and subsequent reduction at the platinum wire counter-electrode occurred. The main conclusion of the experiment shown in Fig. 10 with respect to the water-oxidizing ability of AgCl-coated electrodes is that the photocatalytic O_2 production is still preserved in an electrolyte containing dissolved O_2 up to its saturation concentration.

3.7. *Reductive and oxidative photocurrents*

The photocurrent was reductive during the first minutes of illumination of an AgCl-coated electrode in the photoelectrochemical experiments shown in Figs. 5, 6 and 8. Afterwards the photocurrent was oxidative throughout these experiments. The initial reductive current lasted for 12 or 16 min in the experiments in Figs. 5 and 6, respectively, where a precipitated AgCl layer was investigated; in the case of the electrochemically prepared AgCl layer (Fig. 8) the reductive current lasted just for 6 min. In additional experiments, we found that the initial reductive photocurrent persisted longer if the AgCl layer was illuminated at lower light intensity. In the experiment shown in Fig. 10, the current was oxidative from the beginning, but this AgCl layer had been illuminated without applying a potential (i.e. at zero current) for about 20 min before the experiment. It seems that a certain amount of reduced silver is needed before an appropriate contact to the electrode is achieved for silver reoxidation. Cathodic photocurrents on AgCl-coated electrodes were reported for the first time by E. Becquerel [29], as stated previously in Section 1. We assume that the cathodic (reductive) current in the present experiments is due to the reduction of reaction intermediates arising during the photo-oxidation of water. According to Eqs. (6)–(9), $Cl^{\cdot}$ radicals, Cl_2 and HOCl are formed as reaction intermediates of photochemical water oxidation on AgCl. The redox potentials for electrochemical reduction of these reaction intermediates are higher (more oxidative) than the polarization potential which is applied to the electrode, that is, higher than +0.64 V versus NHE [40]. Thus, electrochemical reduction of these reactive intermediates is possible at the electrode surface. In the case of a platinum substrate electrode, even the reaction product O_2 itself may be electrocatalytically reduced at the electrode surface [37], diminishing the amount of produced O_2. This might be the reason why the photochemical O_2 production rate is smaller in the experiment on an AgCl-coated platinum electrode (Fig. 6) than on an AgCl-coated $SnO_2 : F$ electrode (Fig. 5). A short comment on carbon electrode substrates: we did not use glassy carbon or graphite as electrode substrates, in spite of their widespread usage, because chlorine is intercalated into the graphite layers, precluding efficient water oxidation according to Eqs. (3)–(9)[22,41]. As the photoexperiment is continued, an increasing amount of reduced silver species is produced at the photoelectrode, according to Eq. (11). The electrode is set at a potential where silver oxidation takes place under applied electrochemical conditions. This leads to the observed anodic (oxidative) current. Thus, the observed polarization current is in fact a superposition of a reductive photocurrent and a reoxidation current for silver reoxidation. However, the reductive part of the polarization current should be small compared to the oxidative part as soon as a certain amount of reduced silver is deposited on the AgCl-coated electrode, since the electrochemical reduction of chlorine compounds is kinetically unfavorable on a silver electrode, a fact which forms the basis of the photogalvanic silver chloride cell [21,30]. For this reason, calculating the amount of reoxidized silver $n(Ag_{reox})$ from the integrated polarization current, according to Eq. (13), remains a satisfactory approximation. The reoxidation percentage, calculated according to Eq. (14), should not be affected by the approximation at all, because the reductive part of the photocurrent is counter-parted by an oxidative current for reoxidation of that part of reduced silver which is not related to O_2 production, but to the production of those reaction intermediates that are electrochemically reduced. In the case of an electrochemically prepared AgCl layer, the contact area of silver chloride with the electrode surface is larger than in the case of a precipitated AgCl layer. Obviously, less reduced silver has to be produced in this case to reach the condition for silver reoxidation. Thus, the photocurrent turns oxidative earlier for electrochemically prepared AgCl layers than for precipitated AgCl layers. If a sufficient amount of reduced silver is photochemically produced on the AgCl-coated electrode before applying a polarization potential, then the polarization current is anodic right from the beginning. This was observed in the experiment shown in Fig. 10. If the polarization current contains a cathodic part which is due to the reduction of reaction intermediates arising during the photo-oxidation of water, then this should diminish the O_2 production rate. We checked this hypothesis in a photoelectrochemical experiment on an AgCl-coated $SnO_2 : F$ electrode by switching on and off the electrochemical polarization of the AgCl-coated electrode at intervals of several hours. The electrode was illuminated continuously at an intensity of 15 mW cm^{-2} in the range 350–600 nm, under otherwise same experimental conditions as in the other experiments (Figs. 5, 6 and 8). In fact, the O_2 production rate was found to be decreased by about 2 nmol h^{-1} each time the electrode was electrochemically polarized.

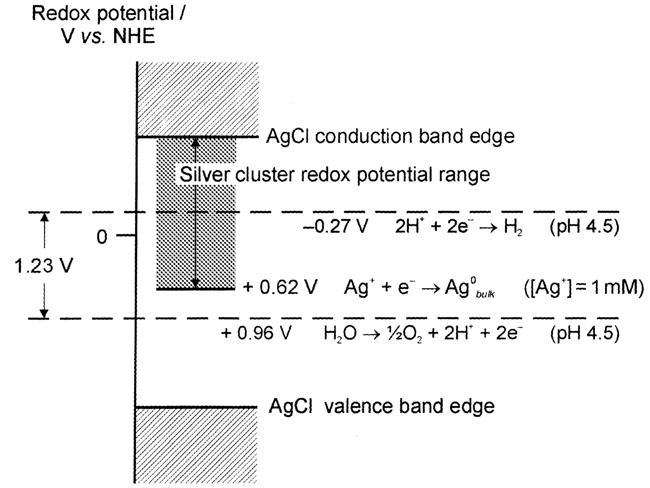

Fig. 11. Redox potentials for $Ag^+/Ag_{bulk}{}^0$ at $[Ag^+] = 10^{-3}$ M, for the oxidation (O_2/H_2O) and reduction (H_2O/H_2) of water at pH 4.5, and position of the semiconductor band edges of AgCl. The band edges are approximately at +2.1 V (valence band) and at −1.2 V vs. NHE (conduction band [28]). The electrochemical potential range of small silver cluster is indicated (shaded region).

3.8. Thermodynamic considerations

The electrochemical reoxidation of photochemically reduced silver was performed at 0.0 V versus Hg/Hg_2SO_4 (+0.64 V vs. NHE) in the chronoamperometric experiments. This polarization potential was just about 20 millivolts anodic with respect to the equilibrium redox potential of a silver electrode, which is $E[Ag^+/Ag_{bulk}{}^0] = +0.62$ V versus NHE at 22°C ($E^\circ[Ag^+/Ag_{bulk}{}^0] = +0.80$ V) in an aqueous electrolyte containing 10^{-3} M Ag^+, according to the Nernst equation [36]. As long as reduced silver species on the AgCl-coated electrode will take the equilibrium redox potential of a silver electrode under the applied conditions, reduced silver species tend to form bulk silver because of their large binding energy [42]. If it was possible to prevent the reduced silver clusters from forming electrochemical bulk silver, then the thermodynamic situation would be different. It is well known that the redox potential of silver, $E^\circ[Ag^+/Ag_n^0]$, becomes more negative with decreasing n, that is, with a decreasing size of the reduced silver species. In the limiting case of a single Ag^0 atom ($n = 1$), the redox potential is $E^\circ[Ag^+/Ag_1{}^0] = -1.80$ V versus NHE. A photoelectrochemical system based on AgCl, but with no formation of bulk silver, would allow to reoxidize the reduced silver at a more negative redox potential, which would mean a higher gain in energy from the absorbed photons. Fig. 11 shows the redox potential range of reduced silver species with respect to thermodynamically required redox potentials for water oxidation and reduction at a pH value of 4.5, as well as the approximate position of the AgCl valence and conduction band edges [28]. The redox potentials for electrochemical water oxidation (Eq. (15)) and for water reduction (Eq. (16)), are $E[O_2/H_2O] = +0.96$ V and $E[H_2O/H_2] = -0.27$ V versus NHE at pH 4.5, as calculated with the Nernst equation from standard data [36], and the thermodynamically required potential difference for water splitting is $\Delta E[H_2O \rightarrow H_2 + (1/2)O_2] = -1.23$ V, which is independent of pH. The AgCl valence band edge is positioned at about +2.1 V and the AgCl conduction band edge is at about −1.2 V versus NHE. The lower edge of the silver cluster redox potential range lies at $E[Ag^+/Ag_{bulk}{}^0] = +0.62$ V versus NHE. It can be associated with the position of the Fermi level of bulk silver, if the redox potential diagram (Fig. 11) is associated with a quantum chemical orbital energy diagram. However, orbital energy diagrams are just related to ionization potentials and do not take into account binding energy, solvatation, and entropic effects arising during the associated electrochemical half-cell reactions. Thus, care should be taken when such comparisons are made. In fact, the ionization potential of silver clusters decreases with increasing cluster size, whereas the redox potential shows the opposite effect, that is, it becomes more anodic (positive) with increasing cluster size [42]. The redox potential of the holes created in the AgCl valence band under illumination is amply sufficient to oxidize water, for example, via some chemical intermediates as described in Eqs. (6)–(9). On the other hand, the polarization potential applied to the electrode to reoxidize the photochemically reduced silver, $E_{pol} = +0.64$ V versus NHE, is cathodic with respect to the thermodynamic redox potential for water oxidation, $E[O_2/H_2O] = +0.96$ V versus NHE. The potential difference, $E_{pol} - E[O_2/H_2O] = -0.32$ V, is gained from the energy of the absorbed photons. In other words, the photochemical water oxidation with a simultaneous electrochemical reoxidation of Ag^0 on AgCl-coated electrodes is not just a photocatalytic process, but it is endergonic thus a photosynthetic process. To achieve complete water splitting, water oxidation has to be combined with water reduction. If the AgCl system for water oxidation is combined with a system for photocatalytic water reduction in a photoelectrochemical cell, then an additional potential difference of $E[H_2O/H_2] - E_{\mathrm{pol}} = -0.91$ V has to be generated in the reductive half-cell to accomplish photoelectrochemical water splitting (overpotentials are neglected in this thermodynamic consideration). In the photoelectrochemical cell for light-assisted water splitting described in this report, this potential difference was provided by a potentiostat. In a purely light-driven water splitting device, the potentiostat has to be replaced by a photochemical water reduction system which generates the necessary voltage. Semiconductor-based systems, for example, should be suitable for this purpose [43].

4. Conclusions

The experiments presented in this report clearly show that AgCl is a photocatalyst in the oxidation of water to O_2 and H^+, under the simultaneous reduction of Ag^+ ions. Many catalytic turnovers with respect to the total amount of AgCl were experimentally realized. To have electrochemical access to the reduced silver species, AgCl was coated as a thin layer ($\lesssim 1\ \mu$m) on an electrode substrate. $SnO_2:F$-coated glass plates and platinum were used as electrode substrates. Reduced silver species produced during the photocatalytic oxidation of water to O_2 on AgCl-coated electrodes were electrochemically reoxidized by anodic polarization of the electrode. Electrochemical reoxidation could be performed simultaneously with the photochemical water oxidation reaction or, less completely, afterwards. The polarization potential applied for silver reoxidation was about 20 millivolts anodic with respect to the $Ag^+/Ag_{\mathrm{bulk}}{}^0$ equilibrium redox potential. Different electrode preparation techniques were investigated, and electrochemical reoxidation turned out to be more efficient on electrochemically prepared AgCl layers than on precipitated AgCl layers, which could be explained by a larger contact area with the electrode substrate in the case of the electrochemically prepared AgCl layers. In the reported chronoamperomeric experiments, a sustained O_2 evolution with a simultaneous electrochemical reoxidation of reduced silver species was measured over many hours. The initial period of these experiments, before reaching steady state, was characterized by the accumulation of a certain amount of reduced silver on the AgCl-coated electrode, which was necessary to maintain a reoxidation current. From the point of view of silver halide photography, this initial period resembles the formation of printout silver brought on by light exposure of the silver halide. In fact, the photogenic drawings reported by H.F. Talbot in 1839, which were the first photographic pictures on paper based on AgCl, were produced in a printout process [6,7]. On the other hand, the self-sensitization of the photochemical activity of AgCl observed by us [4,18,19,23] takes place at the very beginning of exposure to near UV light, and it is presumably related to the formation of the latent image in silver halide photography.

The AgCl system was employed as the anodic part in a photoelectrochemical cell for light-assisted water splitting. Photocatalytic O_2 evolution was still maintained in the presence of O_2 dissolved in the electrolyte up to its saturation concentration. A current density of about $10\ \mu A\ cm^{-2}$ was reached at a light intensity of about $25\ mW\ cm^{-2}$ in the range 350–600 nm. The oxidation of water to O_2 with a coupled reduction of Ag^+ ions according to Eq. (1) is an endergonic reaction under the applied conditions, and thus the photochemical water oxidation on AgCl is a photosynthetic process. The free enthalpy change of reaction 1, expressed as a voltage is $E[Ag^+/Ag_{\mathrm{bulk}}{}^0] - E[O_2/H_2O] = -0.34$ V under the applied conditions. Since the reduced silver species can be reoxidized without a remarkable electrode over potential, this free enthalpy change is a fully available gain in energy from the absorbed photons in a photoelectrochemical cell. Thus, the investigated system is a useful candidate for the oxidative part of a light-driven water-splitting device. The stability of the electrodes discussed so far has not been satisfactory. We have found, however, that it can be improved, for example by depositing

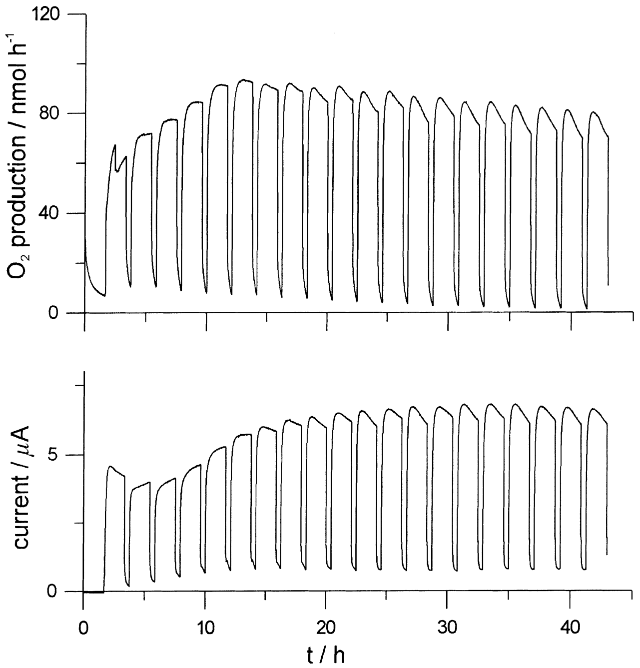

Fig. 12. Chronoamperometry of an electrochemically prepared AgCl-coated $SnO_2:F$ electrode (1 cm^2), modified with a thin gold layer (100 Å), at 0.0 V vs. Hg/Hg_2SO_4, with illumination and dark periods, similar as in Figs. 5–8. The O_2 production rate ($nmol\ h^{-1}$) and the photocurrent (μA; anodic current is drawn upwards) are plotted vs. time. The light intensity at the AgCl-coated electrode was approximately $50\ mW\ cm^{-2}$ (illuminated through the cold light filter). During the period shown, the reoxidation was 64% and the number of turnovers of AgCl was 11.

a thin gold layer (about 100 Å) on the SnO_2 : F-coated glass before preparing the AgCl layer as described in Section 2.3. The outcome of an experiment carried out on such a photoelectrode is illustrated in Fig. 12. From this we conclude that very stable materials can be prepared for photocatalytic water oxidation based on the silver chloride as photocatalyst.

Acknowledgements

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