

# Water Splitting with Silver Chloride Photoanodes and Amorphous Silicon Solar Cells

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## Abstract

A thin silver chloride layer deposited on a conducting support photocatalyzes the oxidation of water to  $O_2$  in the presence of a small excess of silver ions in solution. The light sensitivity in the visible part of the spectrum is due to self-sensitization caused by reduced silver species. Anodic polarization reoxidizes the reduced silver species. To test its water splitting capability, AgCl photoanodes as well as gold colloid modified AgCl photoanodes were combined with an amorphous silicon solar cell. The AgCl layer was employed in the anodic part of a setup for photoelectrochemical water splitting consisting of two separate compartments connected through a salt bridge. A platinum electrode and an amorphous silicon solar cell were used in the cathodic part. Illumination of the AgCl photoanode and the amorphous Si solar cell lead to photoelectrochemical water splitting to  $O_2$  and  $H_2$ . For AgCl photoanodes modified with gold colloids an increased photocurrent, and consequently a higher  $O_2$  and  $H_2$  production were observed.

## Introduction

The aim of artificial photosynthesis is the solar splitting of water in  $O_2$  and  $H_2$ , driven by a non-biological system. For that purpose, materials are necessary which upon light absorption can drive the water splitting reaction. Different ways have been chosen to convert solar energy into a chemically stored form as  $H_2$ .<sup>1-3</sup> Photoelectrolysis is the general term used to describe light-driven water splitting based on semiconductors. There are a number of approaches possible.<sup>4</sup> Basically, arrangements using either photovoltaic cells<sup>5-7</sup> or semiconductor-liquid junctions,<sup>8-11</sup> or combinations of the two were realized.<sup>12-15</sup>

Herein we present an approach towards water photoelectrolysis where a semiconductor photoanode is used together with a photovoltaic cell. An AgCl photoanode was combined with a single junction amorphous silicon solar cell connected to a platinum cathode. The AgCl layer was employed in the anodic part and the platinum electrode

in the cathodic part of a setup for water photoelectrolysis consisting of two separate compartments connected through a salt bridge. Illumination of both, the AgCl photoanode and the amorphous Si solar cell, lead to photoelectrochemical water splitting to  $O_2$  and  $H_2$ .<sup>16</sup> A schematic representation of the principle is shown in Figure 1. On one side, the photoanode oxidizes water to  $O_2$ , and on the other side the photocathode reduces water to  $H_2$ . The electron transfer from system 1 (photoanode) to system 2 (photocathode) is achieved by illumination. We also present the effect of gold colloids on the photocatalytic properties of AgCl photoanodes in photoelectrochemical water splitting experiments. An increased photocurrent, and consequently a higher  $O_2$  and  $H_2$  production were observed.

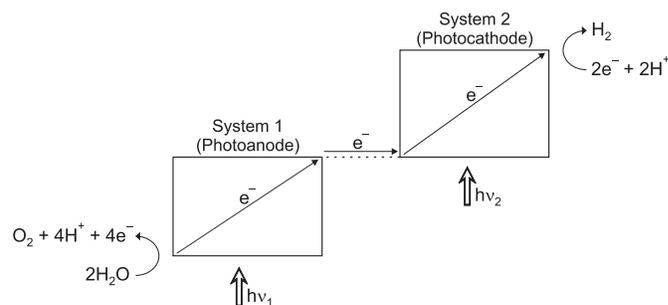
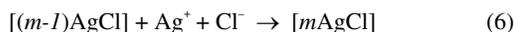
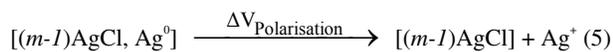
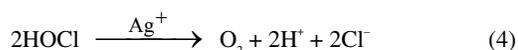
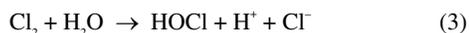
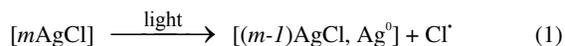


Figure 1. Schematic representation of the photoelectrochemical water splitting experiment. For the oxidation of water to  $O_2$  an AgCl photoanode was used (System 1). As photocathode, a single junction amorphous silicon solar cell connected to a platinum cathode was employed for the  $H_2$  production (System 2).

## Results and Discussion

We have reported that appropriately prepared silver chloride electrodes photocatalytically oxidize water to  $O_2$  under suitable conditions.<sup>17-20</sup> The nanostructured silver chloride layer acts as photocatalyst in the presence of a small excess of silver ions in solution, with a maximum evolution rate between pH 4 and 6. AgCl is a semiconducting material

with an indirect band gap of 3.3 eV (~380 nm).<sup>21</sup> The sensitivity of the AgCl water oxidation system extends from the near UV into the visible light region due to the formation of silver species during the course of the photoreaction, in a process we call self-sensitization. Concisely, the overall reaction can be seen as the oxidation of water to O<sub>2</sub> plus protons and the reduction of silver cations to silver upon illumination. The light absorption can be considered to drive the charge transfer from Cl<sup>-</sup> to Ag<sup>+</sup> (Eq. 1). The chloride radicals recombine very fast to form Cl<sub>2</sub> (Eq. 2). Under suitable conditions ([Ag<sup>+</sup>] ~10<sup>-3</sup> M, pH ~4.5) Cl<sub>2</sub> reacts very fast with water to produce hypochlorous acid, HOCl (Eq. 3), which further decomposes in an Ag<sup>+</sup> catalyzed reaction to form molecular O<sub>2</sub>, H<sup>+</sup>, and Cl<sup>-</sup> (Eq. 4). The reduced silver atoms may react with other silver species to form charged silver clusters. Anodic polarization reoxidizes the produced silver species (Eq. 5). The AgCl photoanode is polarized at 0.65 V vs. a normal hydrogen electrode (NHE). The chloride ions are bound by Ag<sup>+</sup> ions to form AgCl (Eq. 6). These reactions are very fast and it is reasonable to assume that they take place at or very near the surface of the electrode. The water oxidation reaction and the reoxidation of the reduced silver species take place simultaneously, making the system catalytic. Our understanding of the reaction mechanism and dynamics,<sup>18-20</sup> as well as the system's energetics<sup>19,22</sup> have been reported.



An AgCl photoanode was combined with an amorphous silicon solar cell and platinum as cathode. The AgCl layer was employed in the anodic part of a setup for photoelectrochemical water splitting consisting of two separate compartments connected through a salt bridge. A platinum electrode and an amorphous silicon solar cell were used in the cathodic part.<sup>16</sup>

Hot-wire chemical vapor deposition (HWCVD) was used for the deposition of hydrogenated amorphous silicon films (a-Si:H) as the absorbing intrinsic layer in single junction n-i-p structured solar cells (n-i-p a-Si:H). The n- and p-doped layers were deposited by plasma enhanced chemical vapor deposition (PECVD).<sup>23</sup> The a-Si:H solar cells used were characterized by current-voltage measurements.<sup>16</sup> They had an open-circuit voltage around 0.84 V, a short-circuit current density around 9.2 mA·cm<sup>-2</sup>, and a fill factor of 0.5, resulting in an efficiency of the cell

of 3.9 %. The band gap of the amorphous silicon was approximately 1.8 eV. For details on the preparation and the properties of the amorphous silicon solar cells used, as well as on n-i-p a-Si:H solar cells with higher efficiency up to 7 % see reference 23.

In Figure 2 the O<sub>2</sub> and H<sub>2</sub> production and the anodic photocurrent vs time are shown for several light and dark cycles. Illumination of the AgCl photoanode and the a-Si:H solar cell lead to photoelectrochemical water splitting to O<sub>2</sub> and H<sub>2</sub>. Sustained and stable O<sub>2</sub> and H<sub>2</sub> production can be observed. The system was exposed to successive illumination and dark periods of 120 and 45 min duration each. The AgCl photoanode showed an O<sub>2</sub> production between 90–100 nmol·h<sup>-1</sup> and the platinum cathode an average H<sub>2</sub> production around 180 nmol·h<sup>-1</sup>. The anodic photocurrent was between 10–11 μA. During the dark periods of an experiment, the O<sub>2</sub> and H<sub>2</sub> sensor signals decreased because of constant inert gas purging.

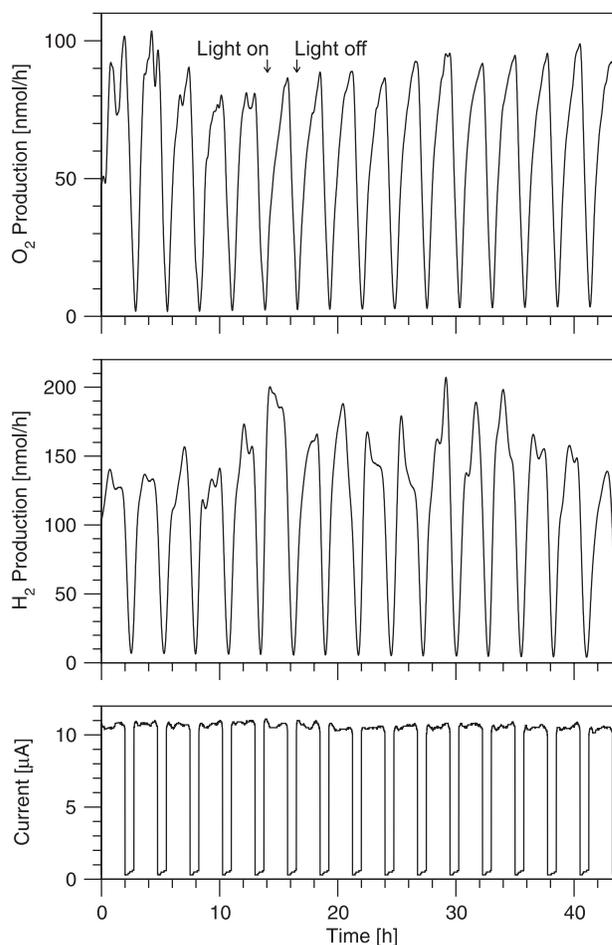


Figure 2. O<sub>2</sub> and H<sub>2</sub> production and anodic photocurrent vs time for an AgCl layer combined with a Pt cathode and an a-Si:H solar cell for several light and dark cycles.

We have also carried out water oxidation experiments with AgCl layers in a flow photoreactor system, where anodic polarization of the AgCl electrode by means of a

potentiostat was used for reoxidizing the produced silver species. They showed that AgCl layers modified with Au colloids have a higher photoactivity compared to AgCl layers without Au colloids. The  $O_2$  production and the photocurrent were increased by a factor of about 3. Details on the effect of gold colloids on the photocatalytic oxidation of water to  $O_2$  with silver chloride as photocatalyst were reported elsewhere.<sup>17</sup> Therefore, a number of photoelectrochemical water splitting experiments were also carried out with gold colloid modified AgCl layers. Gold colloids were produced by reduction of gold chloride with sodium citrate. This method was found to be particularly easy and suitable for our studies in aqueous solution. The colloids produced are spherical in shape with a diameter of 15–20 nm.<sup>24</sup> The gold particles were sedimented on the AgCl layer by immersing it overnight into a colloidal solution. In Figure 3 the  $O_2$  and  $H_2$  production and the anodic photocurrent vs time for an AgCl layer modified with Au colloids are shown for several light and dark cycles. The AgCl photoanode showed an  $O_2$  production around  $190 \text{ nmol}\cdot\text{h}^{-1}$  and the platinum cathode an average  $H_2$  production around  $380 \text{ nmol}\cdot\text{h}^{-1}$ . The anodic photocurrent was around  $22 \mu\text{A}$ . Averaging over several experiments, we observed that small traces of Au colloids greatly influenced the photoelectrochemical activity of the AgCl system. The  $O_2$  and  $H_2$  production, as well as the photocurrent were usually increased by a factor of about 2, depending on the layer's performance. Taking into account the differences in the experimental setups and conditions, this improvement can be considered satisfactory compared to the increase in  $O_2$  production and photocurrent for experiments carried out in a flow photoreactor mentioned above.

In-situ characterization of AgCl electrodes were carried out with UV/vis diffuse reflectance spectroscopy. Silver chloride layers modified with gold colloids show throughout the experiment a higher absorbance of about 20 % compared to layers without colloids.<sup>17</sup> The higher absorbance cannot account for the increased activity of gold modified AgCl layers. It has been reported that gold deposited on  $\text{TiO}_2$  nanoparticles promotes the charge transfer process at the semiconductor/electrolyte interface, improving the photocatalytic oxidation capability of the semiconductor.<sup>25</sup> Deposition of Au particles on  $\text{Fe}_2\text{O}_3$  film also increased the anodic photocurrent by promoting the transfer of holes in the conduction band of the semiconductor to the electrolyte.<sup>26</sup> The hole transfer in the oxidation process is improved because the metal nanoparticles on the semiconductor accept greater amounts of electrons.<sup>27</sup> A similar effect has also to be considered in the present case. Therefore, the higher photoactivity of gold modified AgCl layers can be explained by an increased absorption of the layer due to Au colloids (spectral sensitization), as well as the effect of gold particles in promoting the charge transfer process at the semiconductor/electrolyte interface, improving the photocatalytic oxidation capability of the AgCl system.

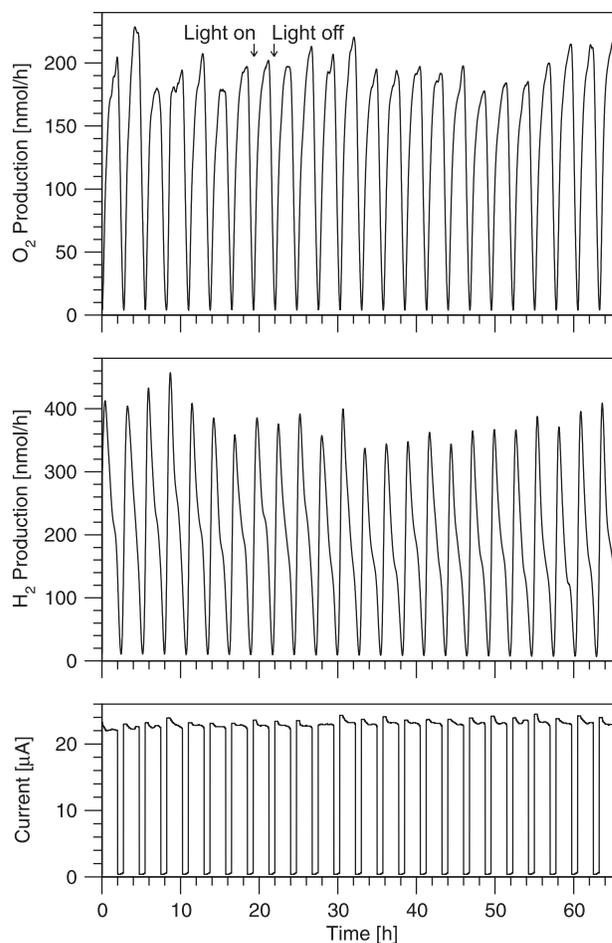


Figure 3.  $O_2$  and  $H_2$  production and anodic photocurrent vs time for an AgCl layer modified with Au colloids combined with a Pt cathode and an a-Si:H solar cell for several light and dark cycles.

## Conclusion

For the first time, AgCl photoanodes were used for the photoelectrolysis of water without applying a polarization potential by means of a potentiostat. An AgCl photoanode was combined with a platinum cathode and an amorphous silicon solar cell. The  $O_2$  producing AgCl system was coupled to a platinum cathode and a photovoltaic device, leading to an overall water splitting system.

An increased photocurrent, and consequently a higher  $O_2$  and  $H_2$  production were observed with AgCl electrodes modified with Au colloids. Small traces of Au colloids greatly influenced the photoelectrochemical activity of the AgCl system. The  $O_2$  and  $H_2$  production, as well as the photocurrent were increased by a factor of about 2, depending on the layer's performance. The higher photoactivity of gold modified AgCl layers can be explained by an increased absorption of the layer due to Au colloids (spectral sensitization), as well as the effect of gold particles in promoting the charge transfer process at the

semiconductor/electrolyte interface, improving the photocatalytic oxidation capability of the AgCl system.

The overall efficiency of the system is still low. Much improvement is required especially in the photocatalytic activity of the AgCl photoanode, which we intend to achieve by further modifying the preparation and sensitization process of the layer.

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## Biography

Antonio Currao graduated in Chemistry from the Swiss Federal Institute of Technology (ETH) in Zürich, Switzerland, in 1992, where he also received his Ph.D. in Solid State Chemistry in 1996. Afterwards, he spent two years of a postdoctoral stay at the Kyushu National Industrial Research Institute in Tosu, Japan. Since 1998 he is working as a researcher at the University of Bern on the photoelectrochemical splitting of water to H<sub>2</sub> and O<sub>2</sub> using solar energy. His research interests are in the area of solid state photoelectrochemistry related to water splitting, as well as the synthesis and characterization of solid state materials in general.