

# GOLD COLLOID MODIFIED SILVER CHLORIDE PHOTOCATALYST FOR WATER OXIDATION TO O<sub>2</sub>

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We have reported that appropriately prepared silver chloride electrodes photocatalytically oxidize water to O<sub>2</sub> under suitable conditions.<sup>[1, 2]</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>[3]</sup> The photoactivity of AgCl extends from the UV into the visible light region due to self-sensitization, caused by the formation of silver species during the photoreaction. Concisely, the overall reaction can be seen as the oxidation of water to dioxygen plus protons and the reduction of silver cations to silver upon illumination. The light absorption can be considered as a charge transfer from Cl<sup>-</sup> to Ag<sup>+</sup>. The chloride radicals recombine very fast to form Cl<sub>2</sub>. Under suitable conditions ([Ag<sup>+</sup>] ~ 10<sup>-3</sup> M and pH ~ 4.5) Cl<sub>2</sub> reacts very fast with water to produce hypochlorous acid HOCl, which further decomposes in an Ag<sup>+</sup> catalyzed reaction to form molecular oxygen. The reduced silver atoms may react with other silver species to form charged ions or silver clusters. Anodic polarization reoxidizes the produced silver species. The water oxidation reaction and the reoxidation of the reduced silver species take place simultaneously, making the system catalytic. The reaction mechanism has been analyzed experimentally<sup>[2, 4]</sup> and theoretically.<sup>[1b, 5]</sup> Experiments were carried out with gold colloids sedimented on AgCl layers. We observed that small traces of Au colloids greatly influenced the photoelectrochemical activity.<sup>[6]</sup>

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 gold particles produced are spherical in shape with a diameter of 15 – 20 nm.<sup>[7]</sup> The UV/vis absorption spectrum of the Au colloidal solution has a strong absorption band at about 530 nm.

The AgCl photoanodes were prepared by electrochemical oxidation of a silver layer deposited on a glass support with a conducting gold layer. Photoelectrochemical experiments were done in a flow photoreactor system. Layers were exposed to successive illumination and dark periods of 100 min and 25 min duration each. In Figure 1a the oxygen production and the anodic photocurrent vs time for an AgCl electrode without gold colloids are shown for several light and dark cycles. The photoanode shows a O<sub>2</sub> production starting at around 200 nmol h<sup>-1</sup> and finally reaching a sustained O<sub>2</sub> production of 140 nmol h<sup>-1</sup> and a photocurrent around 4 μA. The slight decrease of oxygen production in Figure 1a is not due to lower photoactivity but to inferior mechanical stability of the layer after several illumination periods.

A number of experiments were also carried out with gold colloids sedimented on AgCl layers. We observed that small traces of Au colloids greatly influenced the photoelectrochemical activity. Gold colloids were sedimented on the AgCl layer by dipping it overnight into a colloidal solution. The results in Figure 1b show that AgCl layers modified with gold have a remarkably higher oxygen production and photocurrent. After a slight decrease during the first part of the experiment, a steady

O<sub>2</sub> production around 500 nmol h<sup>-1</sup> and a photocurrent around 14 μA can be observed. The oxygen production and the photocurrent were increased by a factor of about 3, as compared to layers without gold colloids.

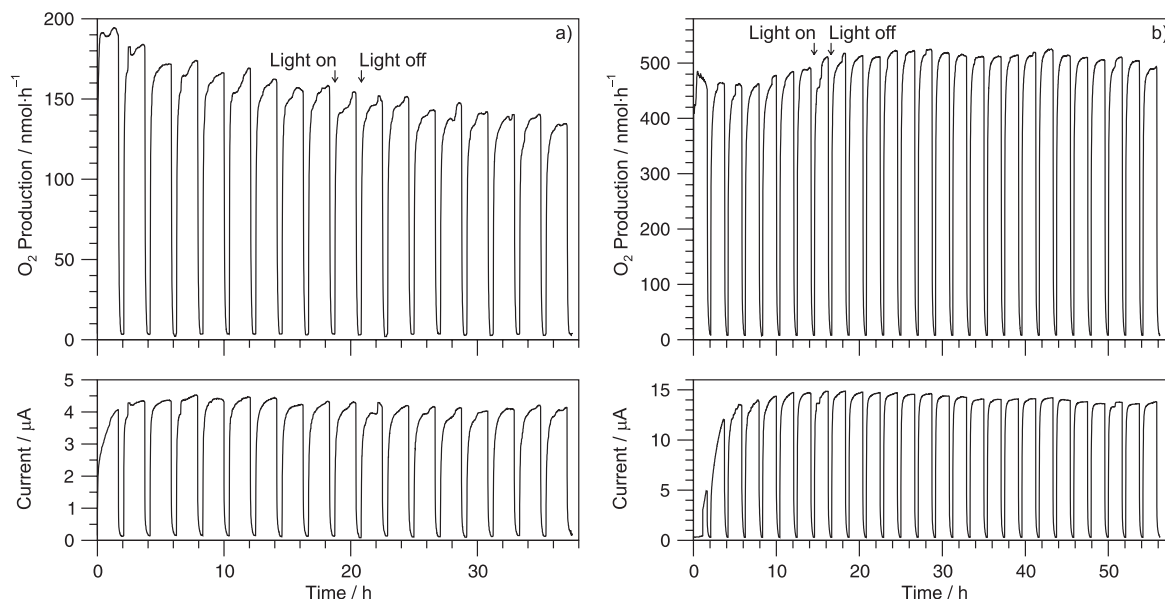


Figure 1. O<sub>2</sub> production and anodic photocurrent vs. time for an AgCl electrode without Au colloids, a), and modified with Au colloids, b), for several light and dark cycles.

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 led to photoelectrochemical water splitting to O<sub>2</sub> and H<sub>2</sub>. For AgCl photoanodes modified with gold colloids an increased photocurrent, and consequently a higher O<sub>2</sub> and H<sub>2</sub> production were observed.<sup>[8]</sup> Currently, we are investigating the effect of zeolite A as a back support for the AgCl layer in photoelectrochemical water oxidation experiments. First results will also be presented.

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