

Quantum-Sized Silver, Silver Chloride and Silver Sulfide Clusters

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Abstract

The amount of O_2 produced by the photocatalytical oxidation of water in an Ag/AgCl system can be increased by means of a structured surface. The photochemical activity of the system is extended from the near UV into the visible region of the spectrum by self sensitization. Quantum chemical calculations show that this process is caused by adsorbed silver clusters on the AgCl surface. The characteristics of the AgCl photoelectrode make its use in a photoelectrochemical water splitting device feasible. Clusters of semiconductor materials are interesting considering their use as a photocathode in such a device. In this context we present the synthesis and properties of luminescent quantum-sized silver sulfide clusters in the cavities of zeolite A.

Introduction

Ever since the invention of silver halide photography by Talbot in 1839, silver halides have been the object of countless studies which have helped to understand and greatly improve the photographic process. This process is based on the formation of silver clusters when the halide is illuminated with UV/vis light. We will show that these clusters are also of fundamental importance in the photocatalytic oxidation of water to oxygen on thin nanostructured AgCl layers which we have reported.¹ A better theoretical understanding of the Ag/AgCl system is important if we are to realize it as a photoanode in a water splitting device. This has motivated us to undertake a number of theoretical investigations of the system, in particular the electronic structure of AgCl clusters and the influence of silver ions adsorbed on its surface. We have also investigated the spectroscopic characteristics of quantum-sized silver sulfide clusters as a function of their size. A tunable band gap in this semiconductor material would make it very attractive for solar energy conversion.

Photoelectrochemical Water Splitting with AgCl as Photoanode?

Thin nanostructured AgCl layers photocatalytically oxidize water to O_2 under appropriate conditions.¹ The photoactivity of AgCl extends from the UV into the visible light region in a process known as self sensitization, which is due to the formation of silver clusters during the photoreaction (see Figure 1). A comparison with the energetic position of the semiconductor band gap of AgCl² shows that the silver clusters have empty energy levels below the conduction band of AgCl. Their presence allows a new electronic transition from the AgCl valence band to the empty silver cluster energy levels. This transition requires less energy than an AgCl valence-conduction band transition and can be induced by visible light. Meanwhile the holes formed oxidize water via a multistep process whose key steps involve the photocatalytic formation and the catalytic decomposition of hypochloric acid.¹

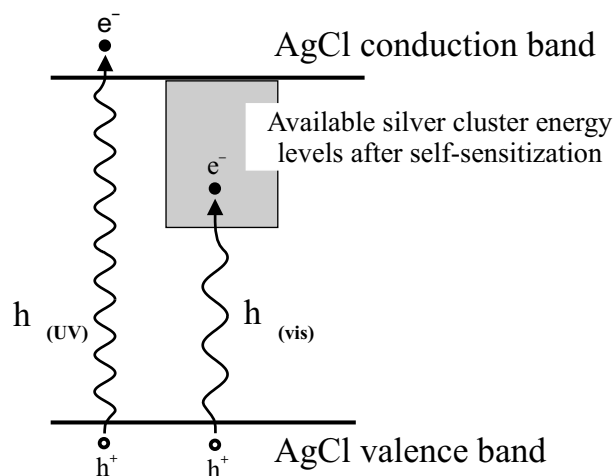


Figure 1. Energy level diagram illustrating the self sensitization of AgCl. The photochemical activity is extended from the near UV into the visible range of the spectrum upon near UV illumination.

The aforementioned silver is reoxidized almost quantitatively, and simultaneously to the water oxidation photoreaction, by applying an anodic bias to the AgCl electrode. This results in a strong photocurrent which correlates very nicely with the O₂ signals (see Figure 2). Moreover, the electrode displays a remarkable stability as evidenced by the sustained O₂ production and reoxidation photocurrent.

The amount of O₂ produced by the Ag/AgCl system depends on the illuminated surface area of the catalyst which can be increased by means of a structured surface. For this purpose, glass titerplates with square holes of about 1.5 x 1.5 mm² and a well depth of approximately 2.5 mm were used.

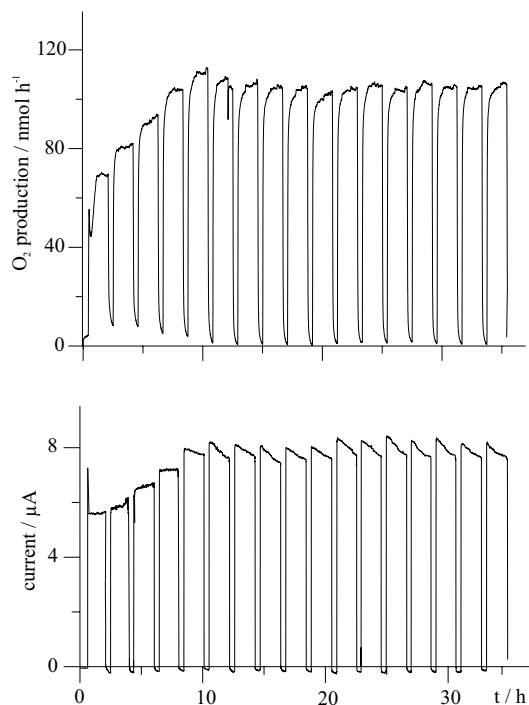


Figure 2. Chronoamperometry of an electrochemically prepared AgCl electrode (substrate: SnO₂:F coated glass, 1cm²) modified with a thin gold layer (100 Å), at 0.0 V vs. Hg/Hg₂SO₄, with illumination and dark periods. The O₂ production rate and the photocurrent (anodic current drawn upwards) are plotted vs. time. During the period shown the reoxidation was 72 % and the number of turnovers of AgCl was 11. The light intensity from a Xe arc lamp at the AgCl electrode was approximately 50 mWcm⁻².

Experiments were carried out in an apparatus consisting of two separate compartments connected through a salt bridge. One compartment was used for the AgCl photoanode and the other for a Pt counter electrode. With the structured glass support the area of the catalyst can roughly be increased by a factor of 4. Once the preparation and experimental conditions are optimized for the new support material of the Ag/AgCl photoanode, we expect that the amount of O₂ produced will increase by about the same factor.

The good photoactivity and stability of the AgCl photoelectrode makes its use as the photoanode in a photoelectrochemical water splitting device feasible. Suitable semiconductors for use as a photocathode will be selected according to their band edge positions relative to the band edge positions of the photoanode.

AgCl Surface States and AgCl/Ag Metal Contacts

AgCl Clusters - Surface States. We have investigated the influence of adsorbed Ag⁺(H₂O)₂ on the electronic structure of (AgCl)₁₀₈, a cluster of equal side length, by means of molecular orbital calculations.³ The energy level diagram shown in the middle of Figure 3 represents the situation where the Ag⁺(aq) is opposite from a middle surface cluster silver. The single Ag 5s-orbital of Ag⁺(aq) is striking. It rises quickly when Ag⁺(aq) is shifted above a Cl⁻. The next four higher levels are fully localized on the silver corner atoms. These Surface States (SURS) reduce the HOMO/LUMO gap by about 1 eV, even when no Ag⁺ is adsorbed. The HOMO derives from surface Cl⁻ 3p-orbitals. In this model the initial step for self sensitization is a charge transfer from a Cl⁻ on the cluster surface to the adsorbed solvated silver ion.

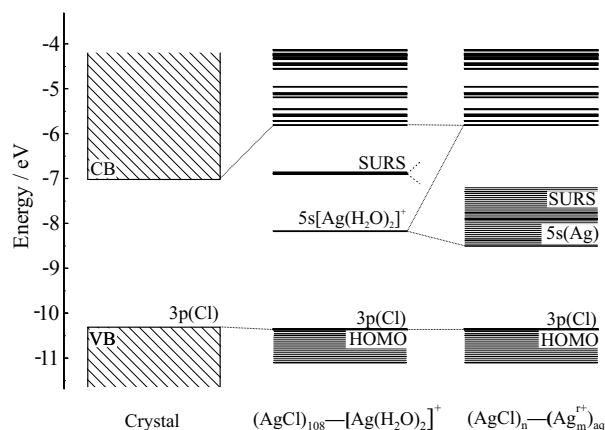


Figure 3. Comparison of the electronic structure of an infinite AgCl crystal, a cluster with one [Ag(H₂O)₂]⁺ adsorbed on its surface and one with several of them adsorbed, some of them already reduced and therefore represented as (Ag_{m+r})⁺aq with r ≤ m. The crystal band gap and (AgCl)_n—(Ag_{m+r})⁺aq values correspond to experimental values.⁴

We observed that when an Ag(H₂O)₂⁺ is placed on all six faces of the (AgCl)₁₀₈ the oscillator strength of the first electronic transition, which is of 5s(Ag)←3p(Cl) CT type, rises more than six times with respect to (AgCl)₁₀₈—[Ag(H₂O)₂]⁺ due to the cooperation between the adsorbed silver species.⁴ It is likely that these CT transitions are responsible for the well established increased

photochemical activity of nanocrystalline AgCl materials in presence of an excess of silver ions.^{1,5,6}

AgCl/Ag Metal Contacts. The Ag/AgCl cluster system illustrated in Figure 4 was investigated. To recognize the alteration of electron density, several Ag/AgCl cluster positions including the equilibrium position shown in Figure 4 were calculated.

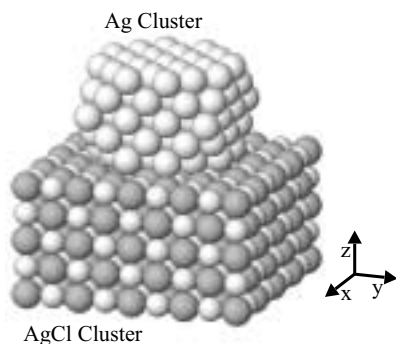


Figure 4. Typical size and shape of an Ag/AgCl cluster system we have investigated.

In the LUMO region we observe levels where electron density is transferred from Ag to AgCl and other levels with the reverse properties. Analysis of the electron density along the z-axis shows that directly at the junction a negative charge on the AgCl side (layer 6) and a similar positive charge on the Ag side is observed (Figure 5). Compared to the two separated systems, there are only major electron density changes in the layers 6, 7 and 8. The silver cluster is negatively charged at the surface and positively charged in the bulk. Details of the charge distribution of AgCl clusters are reported in ref 4.

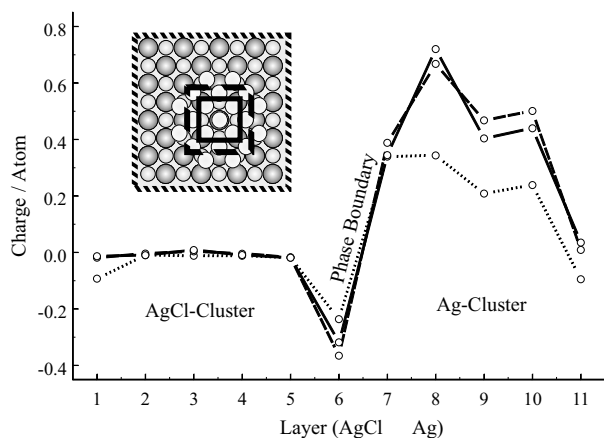


Figure 5. Charge distribution in an Ag/AgCl cluster system. The layers along the z-axis are numbered. Number 1 is at the origin of the coordinate system. The dotted line shows the situation when all atoms are taken into account, the dashed and solid lines represent the two lengthwise incisions marked in the inset.

The newly formed states, which we observe on the layers 4 to 6, correspond to the so-called metal induced gap states

(MIGS). They are responsible for the negative charge on the AgCl side of the phase boundary.

Quantum-Sized Silver Sulfide Clusters

The low-temperature phase of bulk silver sulfide (α -Ag₂S or acanthite, stable up to 450 K) is a semiconductor with a monoclinic structure and a band gap of approximately 1 eV at room temperature.⁷ The synthesis and the properties of nanoparticles of silver sulfide have recently attracted much interest.⁸ By using the well defined cavities of zeolites, which provide a convenient environment for preparing clusters with a narrow size distribution or cluster arrays,⁹ we developed a method of synthesizing quantum-sized silver sulfide clusters. The preparation method is based on the observation that Ag⁺-loaded zeolite A can be reversibly activated at room temperature.¹⁰ Its reaction with H₂S leads to the formation of silver sulfide clusters in the cavities of the zeolite.¹¹ To our knowledge, these are the first silver sulfide species for which luminescence in the visible range of the spectrum could be observed.

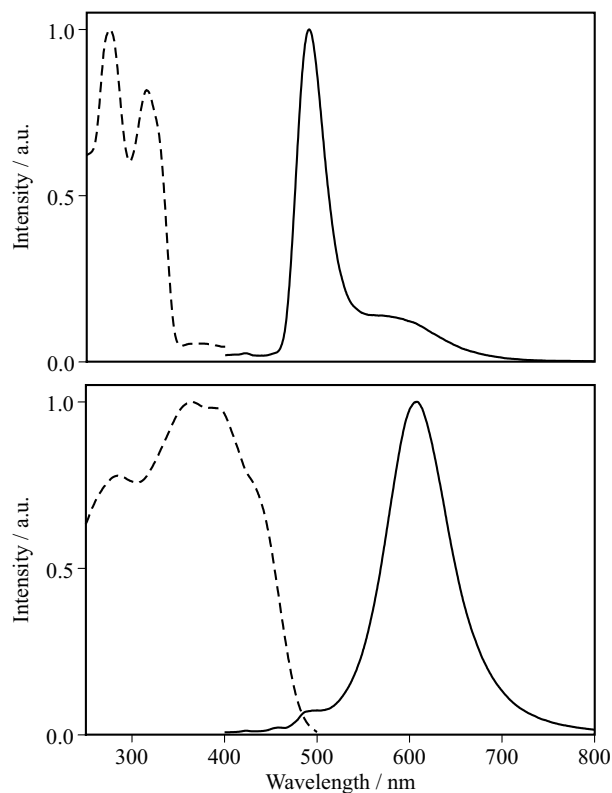


Figure 6. Luminescence spectra (solid lines, excitation at 280 nm) and excitation spectra (dashed lines) of Ag₂S-CaA-0.01 (top) and Ag₂S-CaA-2 (bottom) measured at 80 K.

The cluster size and therefore the band gap can be varied by adjusting the initial amount of silver ions present inside the zeolite. Considering the dimensions of the largest cavity in zeolite A (the so-called α -cage), it can be assumed that the

largest possible cluster does not exceed a diameter of approximately 15 Å. Interactions between clusters in adjacent α -cages might play an important role for high silver sulfide loading densities. The color of the silver sulfide–zeolite A composites ($\text{Ag}_2\text{S}-\text{NaA}-x$ or $\text{Ag}_2\text{S}-\text{CaA}-x$, where x denotes the number of silver ions per α -cage) ranges from colorless ($0.01 < x < 0.5$) to yellow-green ($0.5 < x < 2$) to brown ($x > 2$). A low silver sulfide content is characterized by a blue-green emission and distinct absorption bands, while samples with medium silver sulfide content show an orange-colored emission and a continuous absorption (see Figure 6). Further increasing the silver sulfide content ($x > 2$) results in a bathochromic shift of this characteristic emission.

Time-resolved luminescence measurements give lifetimes in the order of microseconds (at 115 K). The decays are multiexponential owing to a distribution of the silver sulfide clusters over different sites and/or a narrow size distribution.

Conclusions

The investigated Ag/AgCl system is a candidate for the oxidative part of a water splitting device. By increasing the illuminated surface area of the catalyst by means of a structured glass support the light absorbed and thus the amount of photocatalytically produced O_2 can be increased. For testing the water splitting ability of the Ag/AgCl photoanode, experiments with suitable semiconductors for use as a photocathode are carried out.

We found that adsorbed $\text{Ag}_m^{\text{tr}}(\text{aq})$ species on the surface of AgCl are responsible for the self sensitization. The band gap of AgCl decreases substantially by the presence of $\text{Ag}^+(\text{aq})$ 5s-states. The potential energy of a Ag cluster on a AgCl surface is lower compared to a separated system. The boundary between the Ag cluster and the AgCl surface shows predominantly a negative charge on the AgCl side and a positive charge on the Ag side.

Zeolite A is a convenient host material for silver sulfide nanoparticles. The cluster size and thus the spectroscopic

behavior of the silver sulfide clusters can be varied by adjusting the preparation conditions. The silver sulfide–zeolite A composites are luminescent in the visible region of the spectrum. The emission ranges from blue, to yellow, to orange, to red depending on the size of the clusters. The zeolite co-cations (e.g. H^+ , Na^+ , Ca^{2+}) influence the spectroscopic properties as well as the preparation conditions.

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