Gold and silver metal nanoparticle-modified AgCl photocatalyst for water oxidation to O₂

V R Reddy, A Currao and G Calzaferri
Department of Chemistry and Biochemistry, University of Bern, Freiestrasse 3, 3012 Bern, Switzerland
Email: currao@iac.unibe.ch

Abstract. Nanostructured AgCl layer acts as photocatalyst for water oxidation in the presence of a small excess of Ag⁺ in solution. 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. Anodic polarization reoxidizes the produced silver species. Experiments were carried out with spherical gold as well as spherical and prismatic silver nanoparticle modified AgCl layers. We observed that traces of these nanoparticles greatly influenced the photoelectrochemical activity. With spherical gold nanoparticle modification, the O₂ production and the photocurrent increased by a factor of about 3, as compared to layers without gold colloids. Also spherical and prismatic silver nanoparticles led to an increased O₂ production and photocurrent.

1. Introduction
At the dawn of the 21st century, the area of nanoscience and nanotechnology, the art of manipulating mater on the atomic scale, became a versatile platform of modern research at the interface of chemistry, physics, materials and biomedical sciences [1]. In particular, metal nanoparticles of gold and silver are at the forefront of the nanotechnology wave because of their wide range of applications in areas such as catalysis [2], nano-electronics [3], medical diagnostics and biological imaging [4]. Ease of chemical synthesis and absence of toxicity as compared to some other nanomaterials is an advantage [5]. Michael Faraday was the first scientist who made gold colloids, around 1857 [6]. Synthesis has been much simplified by the pioneering work of Turkevich [7] and Frens [8]. A strong visible absorption, called surface plasmon absorption, appears when the size of the metal nanoparticles decreases to the nanometer length scale [9].

Gold nanoparticles have a profound impact on a variety of scientific disciplines such as catalysis [10], drug activity enhancement [11], DNA detection and decease diagnosis [12], surface-enhanced plasmon sensing [13], and for the construction of nano devices such as light emitting diodes and solar cells [14]. The properties of gold particles at the nano scale (1 to 100 nm) remarkably differ from those of the bulk counter part. As a result, nano gold show colors ranging from ruby red to blue, green and orange etc., depending on the size and shape of the particles [15]. It also shows remarkable catalytic activity, whereas bulk gold is known to be catalytically inert [16].

Gold nanoparticles can be synthesized by reduction of HAuCl₄ solution with sodium citrate or sodium borohydride in different media. The citrate and borohydride reduction are considered to be classical and convenient methods due to their simplicity. Addition of stabilizing agent increases the stability of the nanoparticles against, e.g., coalescence. The citrate reduced Au colloidal solution has a
red wine colour with an absorption in the visible region with maxima around 530 nm. The particle size is 15 to 20 nm [7]. The borohydride reduced gold particles have an average size of 5 nm and the absorption maximum is 520 nm [8]. The absorption maximum difference in the citrate and in the borohydride reduced particles is due to the different particle size. For non-spherically shaped gold nanoparticles like gold rods there are two absorption maxima. The absorption at 520 nm and 800 nm are due to transverse and longitudinal surface plasmon resonance, respectively. The nanorods are about 50 nm long and 10 nm wide [17].

Many papers have been published on controlling size and shape of nanoparticles in both organic and aqueous media [18]. Functionalization of gold nanoparticles with organic molecules has been carried out via phase transfer catalysis. SH and NH$_2$ functional groups of organic molecules are well known to bind to the surface of inorganic Au nanoparticles [19]. Immunoassays for resource poor settings have recently been developed by Whitesides based on Au nanoparticle optical sensitivity [20]. Gold nanoparticles can also exhibit enantioselectivity upon bound to chiral molecules. This marvelous strategy can be used for chiral discrimination and separation of enantiomers and production of desired ones [21]. Attempts were made for assembling and patterning well ordered one-, two- and three-dimensional arrays of metal nanoparticles [22]. Gold nanoparticles have also been capped with antibodies such as vancomycin and ciprofloxacin to enhance the antibacterial activity of the drugs [11]. Kamat explored extensively the photochemistry of chromophore-functionalized Au clusters [23]. Gold has been widely used for sensitization in photography. Gold incorporation into latent-image specks increases the stability and reduces the critical size of Ag/Au clusters in the process of latent image formation [24]. Photographic films have been used in the preparation of patterned gold clusters [25].

On the other hand, silver colloids also show interesting properties depending on size and shape. Synthesis of silver particles can be accomplished by following the methods used for gold colloids by replacing the gold salt with silver nitrate. The final colour of Ag colloids is pale yellow. In the case of citrate reduction the absorption maximum is 420 nm, for the borohydride reduction it is 390 nm. The citrate reduced colloids are 60 to 80 nm in size, and the borohydride reduced colloids are around 20 nm in size. Spherical silver nanoparticles change their shape from spheres to nano-prisms under illumination of a colloidal solution [26]. It is possible to grow silver prisms thermally in the dark [27]. Silver nanoprism have two absorption maxima, one is at 500 nm and the other one is at 800 nm.

Silver nanoparticles with different size and shape can be prepared in various ways such as such as glucose reduction in the silver mirror reaction [28] and PVA reduction [29]. The synthesis of mono-dispersed silver nanocubes in water [30] and the growth of silver wire arrays electrochemically [31] were also reported. For several centuries it has been known that silver can be used as an antibacterial agent. Recently, it has been demonstrated that silver nanoparticles show antibacterial activity [32,33]. Enhanced luminescence of dyes on aggregated silver nanoparticles was also reported [34].

Nanostructured AgCl layer acts as photocatalyst for water oxidation in the presence of a small excess of Ag⁺ in solution. 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. Anodic polarization reoxidizes the produced silver species [35]. AgCl layers modified with Au colloids were used in water oxidation [36] and water splitting experiments [37]. Herein, we present photoelectrochemical water oxidation experiments with gold and silver colloid modified AgCl photoanodes and compare their photoactivity.

2. Experimental Section

2.1. AgCl Photoanodes

For water oxidation experiments glass support disks with a diameter of 20 mm and a thickness of 2 mm were used. The surface of the support was roughed by sandblasting. A 50 nm thick Au layer was deposited as a conducting layer on the whole support. For the silver deposition, a cover ring was placed on the support, covering 3.5 mm of the outer edge, which would be used for back contacting the electrode. On the central part of the support, a 150 nm Ag layer was deposited (12 mm diameter).
Deposition of gold and silver layers were carried out by physical vapor deposition in a high vacuum coating system (Bal-Tec, MED 020). The AgCl layers were prepared by electrochemical oxidation of the silver layer in 0.2 M KCl (Merck) aqueous solution at pH ≈ 2, with a computer-controlled potentiostat (EG&G, model 273A). The nanostructure of the layer is quite homogeneous with well-defined particles between 300 and 800 nm in diameter. The layers have pores and gaps of different size and shape between the particles. The diameter of small cavities ranges from 20 to 50 nm (See figure 4 in ref. 36).

2.2. AgCl Layers Modified with Au and Ag Colloids
Gold and silver colloidal solutions were used to sensitize AgCl photoanodes. The colloids were sedimented on the AgCl layer by immersing it into 5 mL of colloidal solution overnight. The next day, the layer was allowed to dry at room temperature. Au and Ag colloid modified AgCl photoanodes were used for water oxidation experiments.

Gold Colloids by Citrate Reduction: Gold colloids were synthesized by the Turkevich method [7]. 1 mL of a 5 mM tetrachloroauric (III) acid solution (HAuCl₄·3H₂O, Merck) was transferred in a flask and diluted by adding 18 mL of water. The solution was heated until it began to boil. Then 1 mL of a 0.5 % (17 mM) trisodium citrate solution (C₆H₅Na₃O₇·2H₂O, Fluka) was added while stirring rapidly. The heating was continued until the color changed to pale purple. The flask was then removed from the heating element and stirring was continued until the solution cooled to room temperature. The solution was topped with water up to 20 mL to account for boiling losses.

Gold Colloids by NaBH₄ Reduction: In this procedure, sodium citrate is replaced with sodium borohydride, which is a stronger reducing agent. 10 mL of an ice-cold 2 mM NaBH₄ (Fluka) was added dropwise to 10 mL of 0.5 mM HAuCl₄ under stirring. The solution was further stirred for about 15 minutes until the colour changed to pink [8].

Silver Colloids by Citrate Reduction: An aqueous solution of silver nitrate (0.1 mM, 25 mL), trisodium citrate (30 mM, 1.5 mL), polyvinylpyrrolidine (molecular weight M₉ ≈ 29 000 g/mol, 0.7 mM, 1.5 mL), and hydrogen peroxide (30 wt. %, 60 µL) were combined and vigorously stirred at room temperature. To this mixture, 10 to 50 µL of 100 mM sodium borohydride solution was rapidly injected, generating a colloidal solution that was pale yellow. After 30 min, the solution darkened to deep yellow, indicating the formation of small silver nanoparticles. After a few seconds, the colour of the solution continued to change from yellow to purple. The final color depends on the amount of NaBH₄ used [27].

3. Results and Discussions

Gold-Colloid-Modified AgCl Photocatalyst
Photoelectrochemical water oxidation experiments were carried out with AgCl layers without Au colloids and with layers modified with Au colloids. For details on the experimental setup see references 36 and 37. Layers were exposed to successive illumination and dark periods of 100 min and 25 min duration, respectively. In figure 1.1a the O₂ 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 an O₂ production starting at around 200 nmol/h and finally reaching a sustained O₂ production of 140 nmol/h and a photocurrent of around 4 µA. The slight decrease of O₂ production shown in figure 1a is not due to lower photoactivity but to inferior mechanical stability of the layer.

A number of experiments were also carried out with gold colloid modified AgCl layers. We observed that traces of Au colloids greatly influenced the photoelectrochemical activity. The results in figure 1b show that AgCl layers modified with gold have a remarkably higher O₂ production and photocurrent than unmodified AgCl. After a slight decrease during the first part of the experiment, a
steady O₂ production of 500 nmol/h and a photocurrent of 14 µA was observed. The O₂ production and the photocurrent were increased by a factor of about three, and in some best cases even up to a factor of four, as compared to layers without gold colloids. This led us to use gold modified AgCl layers as photoanodes in water splitting experiments (see ref. 37).

Figure 1. O₂ production and anodic photocurrent vs. time for AgCl photoanodes, a) without Au colloids, b) modified with Au colloids.

For our present work, the synthesis of gold nanoparticles has been mainly accomplished following the Turkevich method. We also used colloids prepared by the borohydride reduction method. Although the size of the gold spheres considerably differs based on the synthesis procedure adopted, we do not observe a significant difference in the O₂ production and photocurrent. In situ characterization of AgCl electrodes was carried out with UV/Vis diffuse reflectance spectroscopy. Silver chloride photoanodes modified with Au colloids were compared with AgCl layers without colloids (see figure 5 ref 37). Silver chloride layers modified with gold colloids show throughout the experiment a higher absorbance of about 20% over layers without colloids.

The sensitization mechanism of the adsorbed gold colloids is assumed to be closely related to the self-sensitization of the AgCl layer. Silver cluster levels, as well as AgCl surface states and metal-induced gap states from Ag/AgCl cluster composites are present in the bandgap region of AgCl [39]. We assume that a photoelectrical interaction between levels from gold colloids and levels due to the self-sensitization of AgCl in the bandgap region is responsible for the spectral sensitization with gold colloids. This is supported by the diffuse reflectance spectroscopy measurements. However, the increase in layer absorbance is not proportional to the observed oxygen production and photocurrent increment. It has been shown that gold deposited on TiO₂ nanoparticles promotes the charge transfer process at the semiconductor/electrolyte interface, improving the photocatalytic oxidation capability of the semiconductor [40]. The hole transfer in the oxidation process is improved because the metal nanoparticles on the semiconductor accept greater amounts of electrons. The improvement of photoelectrochemical performance is explained by the inhibition of charge recombination of photoinduced electrons and holes [41]. Considerable efforts have also been devoted towards modification of semiconductors such as CdS [42] and Fe₂O₃ [43] with gold colloids. The increased photocurrent was attributed to enhanced charge separation due to gold nanoparticles accepting electrons upon illumination. A similar effect has also to be considered for our gold colloid modified AgCl photoanodes.

Silver-Colloid-Modified AgCl Photocatalyst
AgCl layers were modified with spherical and prismatic silver nanoparticles. The spherical particles we made according to the Turkevich method. Figure 2a shows the results of a photoelectrochemical
water oxidation experiment. The $O_2$ production is around 250 nmol/h and the photocurrent between 7 to 8 $\mu$A. Comparing these values with a AgCl layer without colloid modification, like in figure 1a, we see an increased $O_2$ production and photocurrent.

We have also modified AgCl photoanodes with silver nanoprisms made by the Mirkin method [27]. The results of a photoelectrochemical water oxidation experiment are shown in figure 2b. In the beginning, the $O_2$ production is around 320 nmol/h but decreases rapidly, reaching 160 nmol/h at the end of the experiment. The photocurrent is 7 $\mu$A at the beginning and 6 $\mu$A for the rest of the experiment. Here as well, we see an increased $O_2$ production and photocurrent as compared to non-modified AgCl layers.

![Figure 2](image)

**Figure 2.** $O_2$ production and anodic photocurrent vs. time for AgCl photoanodes modified with a) spherical silver colloids, b) prismatic silver colloids.

In the case of silver sphere and prism sensitization we have a slightly increased $O_2$ production and photocurrent as compared to non-modified AgCl layers. The smaller effect of Ag colloids on the performance of AgCl photoanodes is probably due to different electronic properties of the sedimented Ag nanoparticles. For the purpose of studying only the oxidation half reaction of the water splitting problem a potentiostat simulates the other half cell, in other words an anodic bias of 0.64 V is applied to the AgCl photoelectrode to reoxidize the reduced silver species. Therefore, it is possible that silver nanoparticles sedimented on the AgCl for sensitization purpose may get oxidized. It is well known that the redox potential of silver clusters becomes more negative with decreasing particle size [44]. Thus, the applied polarisation potential is sufficient to oxidize the sedimented Ag particles.

4. Conclusions

We presented results on water oxidation experiments carried out with gold and silver nanoparticle modified AgCl photoanodes. AgCl layers modified with spherical Au colloids have a remarkably higher photoactivity. The $O_2$ production and the photocurrent were increased by a factor of about three, and in some best cases even up to a factor of four, as compared to layers without gold colloids. In the case of silver sphere and silver prism modification of AgCl layers we have slightly increased $O_2$ production and photocurrent signals as compared to non-modified AgCl electrodes. The smaller effect of Ag colloids on the performance of AgCl photoanodes is probably due to different electronic properties of the colloids. Many examples in the literature show that nanoparticles can promote the charge transfer process at the semiconductor/electrolyte interface, improving the photocatalytic oxidation capability of the semiconductor. A similar effect has also to be considered for the gold and silver colloid modified AgCl photoanodes.

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