Surface Chemistry of Silver Halide Microcrystals

Rolf Steiger*

Abstract. Experimental techniques to study the surface properties of silver halide crystals in the µm range, dispersed in gelatin, are discussed. The adsorption of sensitizing cyanine dyes and the properties of the adsorbed sensitizers on such silver-halide particles are studied by various surface techniques yielding complementary information necessary for a quantitative description of the spectral sensitization process.

Introduction

The surface of silver-halide (AgHal) microcrystals, dispersed in gelatin ("photographic emulsions"), plays a dominant role in the formation of developable latent images consisting of silver clusters which contain only a few Ag-atoms. After development of latent images by a reducing agent (e.g. hydroquinone), macroscopic silver particles ("photographic images") are formed with an autocatalytic amplification factor of ca. 10⁸. The quantum yield which determines the photolytic formation of these latent images is strongly influenced by recombination processes between photoelectrons and photoholes. Surface states play a dominant role in such reactions. If sensitizing dyes are present on AgHal surfaces, the recombination centre for electrons and holes is located near the dye chromophore. The quantitative description of sensitizer molecules which have been organized by the Langmuir-Blodgett technique at the surface of evaporated AgHal layers has helped to understand electron-hole recombination [1][2]. By extrapolation of these results to the case of spectral sensitizers adsorbed on AgHal microcrystal surfaces, the quantum yield for latent image formation was increased by modifying the AgHal surface in the nm range [3].

Results

The physical properties of AgHal surfaces on nm scales have been studied by atomic force microscopy (AFM). Structural features like steps and terraces, distortions, epitaxial growth, and surface reconstruction (Fig. 1) have been revealed [4] on AgHal crystals with dimensions in the µm range (Fig. 2). For electrostatic reasons, the [111] surface of AgBr (NaCl-type lattice) should undergo substantial surface reconstruction, because it is composed of ions of the same sign. AFM has revealed this surface reconstruction (Fig. 1).

The topographic distribution of surface ions has been characterized by secondary-ion mass spectroscopy (SIMS) in the imaging mode (Fig. 3) using incident Ga⁺ ions leading to very high lateral resolution [5][6]. Surface heterojunctions between I⁻ and Br⁻ ions in mixed AgHal microcrystals facilitate the charge separation between photoelectrons and photoholes (Fig. 4). Iodide ions in AgBr crystals...
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The physical properties of AgHal surfaces on nm scales have been studied by atomic force microscopy (AFM). Structural features like steps and terraces, dislocations, epitaxial growth, and surface reconstructions (Fig. 1) have been revealed on AgHal crystals with dimensions in the μm range (Fig. 2). For electrostatic reasons, the [111] surface of AgBr (NaCl-type lattice) should undergo substantial surface reconstruction, because it is composed of ions of the same sign. AFM has revealed this surface reconstruction (Fig. 1).

The topographic distribution of surface ions has been characterized by secondary-ion mass spectroscopy (SIMS) in the imaging mode (Fig. 3) using incident Ga⁺ ions leading to very high lateral resolution [5][6]. Surface heterojunctions between I⁻ and Br⁻ ions in mixed AgHal microcrystals facilitate the charge separation between photoelectrons and photoholes (Fig. 4). Iodide ions in AgBr crystals...
act as hole traps. The partial replacement of Br\textsuperscript{-} surface ions by I\textsuperscript{-} has been studied \cite{4} by photoelectron spectroscopy (ESCA) and AUGER electron spectroscopy using incident X-rays (X-AES). The ESCA-binding energy and the difference in the kinetic energy between photoelectrons (ESCA) and AUGER electrons (AUGER parameter, Table) show that the Ag-I binding energy depends on the concentration of surface iodide. At surface iodide concentrations \( \leq 1.6 \) monolayers, a silver iodide species with a higher binding energy between the Ag and the I\textsuperscript{-} ion than in AgI is observed (Table). The electronegativity of the Ag\textsuperscript{+} ion in this Ag-I species is increased as compared with Ag\textsuperscript{+} in AgI. Imaging SIMS \cite{7} has revealed that surface I\textsuperscript{-} is preferably formed along the edges and corners of the cubic AgI\textsubscript{2} microcrystals used in these experiments (Fig. 5). After Ga-ion depth erosion, this discrete I\textsuperscript{-} distribution disappears, which proves that the postulated geometry along the crystal periphery really occurs. Surface I\textsuperscript{-} is a strong nucleating agent for the formation of highly aggregated cyanine sensitizers \cite{7}. This was shown by diffuse reflectance spectroscopy and by microcalorimetry (Fig. 6). While such cooperative dye aggregates (J-aggregates) are formed on iodide-containing AgBr surfaces at dye coverage \( \leq 0.4 \) monolayers, only monomers and dimers were observed on pure AgBr surfaces by diffuse reflectance spectroscopy and by microcalorimetry. For iodide coverages \( > 0.6 \) monolayers, the Ag-I binding energy and the difference in the kinetic energy between photoelectrons and AUGER electrons indicate a higher binding energy for iodide than for bromide species (Table). This corresponds to a higher binding energy for the Ag-I species than for the AgBr surface species. The higher electronegativity of Ag-I with respect to AgBr is also confirmed by the enhanced electron density at the Ag-I bond as indicated by the increased iodide concentration in the inner shell of the AgBr crystal (Fig. 3). The outer bromide-rich shell due to the deposition of pure AgBr at the crystal surface is clearly shown. Indicated scale: 0.5 \( \mu m \).

| mol\%-iodide added to AgBr | Surface iodide concentration (monolayers) | ESCA binding energy \( E_{3d_{5/2}} \text{AgI} \) [eV] | AUGER parameter [eV] | Surface iodide species formed |
|---------------------------|-------------------------------------------|---------------------------------|----------------------|-----------------------------|
| \( > 0.6 \)               | \( > 1.6 \)                                | \( 251.1 \pm 0.1 \)            | \( 1137.4 \pm 0.1 \) | AgI                         |
| \( \leq 0.6 \)            | \( \leq 1.6 \)                             | \( 251.6 \pm 0.1 \)            | \( 1138.6 \pm 0.1 \) | Ag-I with higher electronegativity |

Fig. 2. AFM Micrograph of a tabular AgBr microcrystal which also contains an epitaxial triangular growth hill on top of the [111] face. The scanned area is 6.5 x 6.5 \( \mu m \). Mean surface roughness of flat areas: ca. 0.5-2 nm.

Fig. 3. Imaging SIMS scan of the AgBr crystal of Fig. 4. Br\textsuperscript{-} ion distribution: blue; I\textsuperscript{-} ion distribution: red. Increased iodide concentration in the inner shell. The outer bromide-rich shell due to the deposition of pure AgBr at the crystal surface is clearly shown. Indicated scale: 0.5 \( \mu m \).

Fig. 4. Computer design of a thin, tabular AgBr crystal with iodide-rich inner shell and AgBr core, as suggested from crystallisation conditions.


Fig. 6. Integral heat of adsorption of an adsorbed oxacarbocyanine sensitizer (15% surface coverage) vs. iodide concentration in 0.47 lm cubic AgBr microcrystals. Inserts: diffuse reflectance spectra (after Kubelka-Munk correction) of the adsorbed sensitizer on pure AgBr crystals (left) and on AgBr crystals containing 1 mol-% bulk iodide (right). Only monomers (508 nm) and a small amount of dimers (484 nm) are adsorbed on pure AgBr, while cooperative J-aggregates absorbing at 554 nm are predominantly formed using 1% iodide (corresponding to an overall surface coverage of 2.6 monolayers of AgI).

Fig. 7. Imaging SIMS picture showing the distribution of F-atoms of a fluoro-cyanine dye (insert in Fig. 7) adsorbed at the surface of cubic AgBr microcrystals of pure AgBr (edge length: 1.25 lm, 80% surface coverage). Only 6 F-atoms are present in the dye molecule containing 80% iodide (assuming a homogenous distribution at the surface) [9]. However, has shown that the J-aggregated cyanine is predominantly adsorbed along the AgBr-grain periphery (Fig. 7).

Discussion

Experiments as those discussed above have also provided a more detailed understanding on the mechanisms of spectral sensitization. Electron-hole recombination occurring at the excited sensitizer chromophore could be decreased in practice by appropriate organisation of sensitizer molecules along surface structures like steps and terraces of atomic dimensions at AgHal microcrystal surfaces [10]. By incorporating such surface-modified, micro-engineered AgHal crystals into color photographic materials (Hifochrome Classic films used for copying color slides), the exposure time of these products could be reduced by a factor of 10 under certain conditions.

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