The Exchange of Fluorinated Dyes Between Different Types of Silver Halide Microcrystals Studied by Time of Flight Secondary Ion Mass Spectrometry (TOF-SIMS)

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Introduction

Time of Flight Secondary Ion Mass Spectrometry (TOF-SIMS) is a surface sensitive analytical technique that can be used for the characterization of inorganic as well as organic surface layers. Three types of information can be obtained by TOF-SIMS analysis: 1. It is possible to identify elements and molecules that are present at the surface, 2. TOF-SIMS allows studying the lateral distribution of these compounds and 3. in-depth distributions of elements can be studied.

In earlier studies at this laboratory TOF-SIMS was used to monitor the in-depth and lateral halide distributions of silver halide microcrystals. Now special attention is paid to the characterization and localization of organic carbocyanine dye layers adsorbed on the surface of silver halide microcrystals. The purpose of this study was to reveal differences in adsorption selectivity and exchange capacity of carbocyanine dyes as a function of crystal morphology. Two different types of crystal morphology were examined: cubic and octahedral silver bromide crystals.

Experimental

Instrumentation

The measurements were preformed on a TOF-SIMS IV Cameca instrument, equipped with a gallium liquid metal ion gun operating at 25 keV. The images were obtained by bombarding the sample surface by short pulses of primary ions (typical pulse length of 200 ns), the primary ion beam had a direct current between 80 and 100 pA. A lateral resolution of 65 nm could be obtained for elemental species, according to the 16%, 84% criterion (figure 1).

Products and Sample Preparation

In these experiments cubic and octahedral silver bromide crystals with a Möller diameter of 0.4 µm were examined.

The adsorption selectivity and exchange capacity of two different dyes was studied: a cationic dye and a zwitterionic dye. In figures 2a and 2b the structures of the dyes are represented. The secondary ion mass spectra of carbocyanine dyes adsorbed on silver halide microcrystals under Ga⁺ bombardment revealed no molecular information of the dyes. In order to permit the localization and identification of these dyes, it was necessary to label them. In these experiments fluorine was used as a label. Due to its high negative secondary ion yield, fluorine allows to image the organic dyes with a high lateral resolution and to

Figure 1. Left: Line scan across the surface of a single tabular Ag(Br, I) microcrystal. Right: Plot of the Br-ion intensity versus the distance.
retrieve them at the surface of silver halide microcrystals\textsuperscript{4, 5, 6}.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure2a.png}
\caption{Cationic fluorinated dye (dye 1)}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure2b.png}
\caption{Zwitterionic fluorinated dye (dye 2)}
\end{figure}

The dyes are dissolved, respectively in methanol (cationic dye) and in a mixture of methanol and phenoxy-ethanol (zwitterionic dye), to a concentration of 4g/L. Afterwards the solutions are added to the silver halide crystal emulsions. The mixture is then stirred for some time depending on the type of experiment. The studied emulsions are diluted with water. A drop of this solution is placed on a piece of polished silicon to transfer the crystals into the TOF-SIMS instrument. All manipulations and experiments are performed under appropriate darkroom conditions.

**Analysis Procedure**

The analysis of the samples occurs in two different steps. First secondary ion imaging is performed at low magnification. The beam is rastered over fields of 15 x 15 \(\mu\text{m}^2\). The purpose is to visualize the homogeneity of the dye distribution over the total crystal population. In a second step images with high lateral resolutions are collected. The primary ion beam is then rastered over fields of maximum 5.5 x 5.5 \(\mu\text{m}^2\). These high-resolution images make it possible to distinguish between cubic and octahedral silver halide crystals with a Möller diameter of 0.4 \(\mu\text{m}\).

**Results and Discussion**

**Adsorption selectivity of carbocyanine dyes for cubic and octahedral microcrystals**

In order to study the difference in adsorption selectivity for carbocyanine dyes between cubic and octahedral crystals, a mixture of the two emulsions was made in a 1/1 surface proportion. To this mixture enough dye solution was added, to reach a general surface coverage of 40%. The mixture was then stirred for 30 minutes at 50° C.

In the low-resolution images collected from this sample it can be clearly seen that the dye is not homogeneously distributed over the total crystal population. The cationic and the zwitterionic dye apparently give the same result. A homogeneous distribution was reached when the dye solution was added to an emulsion that contained only one type of silver bromide microcrystals. This indicates that the dye has a preference for adsorption on one of the two crystal morphologies.

The high-resolution images shown in figures 3a and 3b clearly indicate that there is a correlation between the fluorine image and the octahedral crystals. The cubic crystals on the left hand side of this field, on the other hand remain blank. The secondary ion images clearly indicate that the cationic as well as the zwitterionic dye adsorb preferentially on a (111) silver bromide surface.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure3a.png}
\caption{Cubic and octahedral crystals (50/50 mixture) + 40\% dye 1, high-resolution images (F and Br)}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure3b.png}
\caption{Cubic and octahedral crystals (50/50 mixture) + 40\% dye 2, high-resolution images (F and Br)}
\end{figure}

**Exchange of carbocyanine dyes between cubic and octahedral crystals in a gelatin matrix**

To test the exchange of dyes between cubic and octahedral microcrystals, an emulsion of cubic AgBr crystals covered with dye (80% theoretical surface coverage) was mixed with a blank emulsion of octahedral AgBr microcrystals in a 1/1 surface proportion. To permit
the dyes to exchange between the two crystal morphologies, the mixture was stirred for 4 hours at 50° C.

For the cationic dye both the low- and high - resolution images (fig 4a) show that the dye molecules are homogeneously distributed over the total crystal population. This indicates that the dye molecules desorb from the surface of the cubic silver halide crystals, but that they do not selectively adsorb on the surface of the octahedral crystals. It should be noted that the secondary ion images recorded from this sample show a diffuse fluorine image in which individual crystals can hardly be separated. This result can be explained by a lack of stability of the emulsion during the thermal treatment. UV –VIS measurements on the sample indicate that the dye itself is unaffected by the thermal treatment, the absorption maximum remains unchanged.

For the zwitterionic dye both the low- and high - resolution images (fig 4b) show that the dye molecules are heterogeneously distributed over the crystal population. Moreover in the high - resolution images it can be observed that the octahedral crystals are covered with zwitterionic dye molecules, while the cubic crystals have lost their coverage. For some cubic crystals rests of fluorine signals are observed at the edges. The results of this experiment indicate that the dye molecules desorb from the (100) surface of the cubic crystals and adsorb selectively on the (111) surface of the octahedral crystals. The dye molecules adsorbed on the edges of the cubic crystals are not desorbed during the thermal treatment.

Conclusions

The experiments on cubic and octahedral silver bromide crystals with a Møller diameter of 0.4 µm clearly show that the lateral resolution that can be achieved with Time of Flight Secondary Ion Mass Spectrometry is good enough to distinguish between these two types of crystals. Moreover TOF-SIMS also allows to detect and image organic dyes that are adsorbed on the surface of these silver halide microcrystals. In order to do so the dyes have to be labeled with a specific label (e.g. fluorine).

It is shown that TOF-SIMS allows to study the adsorption selectivity of fluorine labeled dyes as a function of crystal morphology and to observe the exchange of fluorine labeled dyes between different types of crystal morphology in a direct manner. The two dyes that were used in these experiments adsorb selectively on the (111) surface of octahedral crystals, moreover it is illustrated that the dyes can desorb from the (100) surface of cubic crystals and re-adsorb on the surface of octahedral crystals.

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References

Biography

Jens Lenaerts got his degree for master in science in 1998. He is doing his Ph.D. in analytical chemistry at the university of Antwerp in the center of Micro and Trace Analysis. His work is manly focused on the study of thin organic layers with time of flight secondary ion mass spectrometry.