

A Study of Size-Selection and Ionic Deposition of Silver Sulfide Sensitization Clusters on AgBr Microcrystals

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Abstract

Silver sulfide cluster cations: $\text{Ag}(\text{Ag}_2\text{S})_n^+$, $n=1-6$ were generated by laser ablation of silver and sulfur powder, and mass-selected, decelerated to deposit onto substrates containing mono-dispersed binder-free cubic AgBr microcrystals. After exposure to light the samples were developed in a photographic developer. The fraction of the developed grains were measured and plotted versus the counting coordinate in the samples. The results show that the development fractions were increased after deposition of $\text{Ag}(\text{Ag}_2\text{S})_n^+$ with $n=1-3$ and decreased after deposition of $\text{Ag}(\text{Ag}_2\text{S})_n^+$ with $n=4-6$ with a maxima when $n=2$ and 3.

Introduction

The study of the formation, nature and function of chemical sensitization cluster has been the attention of a good many of researchers for a long time. The views of the stated problem among different researchers are quite far from common agreement, this is because of all these problems are related to the practical components and the surface charge of Ag_2S (or Ag) clusters and these problems could be solved and gradually clarified only when the cluster chemistry, especially the determination and test methods of clusters, develops and advances to a atomic level, at least to a nanometer particle or molecule level. The information on the relationship between the size/charge of individual chemical sensitization clusters and their catalytic activity toward formation of latent image cluster, hence toward development of exposed silver halide emulsion microcrystals may inject insight to clarify the chemical nature and function of chemical sensitization clusters and to distinguish the photo-sensitive clusters from fog aggregates.

We reported the formation of binary silver sulfide clusters^{1,2)} and the reaction of silver sulfide cluster anions with bromine atoms³⁾ with the aid of laser ablation and time-of-flight mass spectroscopy. Being as a continuation of this systematic research we introduced here some silver sulfides generation by deposition on surface of silver bromide microcrystals and their catalytic activity toward photographic development.

Experimental and Results

Experiments were performed on a home-made tandem time-of-flight mass spectrometer (TOF MS) which has been described in detail previously⁴⁾. Briefly, a disk of silver and sulfur powder mixture was ablated with the focused second harmonic of an Nd: YAG laser (532 nm, 5-20 mJ/pulse). The repetition rate was 10 Hz. The solid sample was kept in a holder in a vacuum chamber at 10^{-4} Pa. The cluster ions produced were extracted and accelerated with a pulsed voltage of 1200 V, and then drifted in a field-free region for 3.5 m, where deflection and focusing systems were installed to decrease the dispersion of cluster ions and intensify the detected signals. The cluster ions were detected with two microchannel plates in series. At the end of the field-free region, a mass gate operated by a pulsed voltage was installed for selecting cluster ions by mass. The mass-selected cluster ions were decelerated (<100 eV) and photolyzed with a UV laser beam (248 nm). The fragmented ions and the remaining parent ions were detected and analyzed with the second stage TOF MS whose accelerate voltage was 4100V, field-free flight length was 1.5m. The second stage TOF MS was perpendicular to the first stage TOF MS, its detector was another dual microchannel plate and was fixed at the end of the second stage flight region.

The signals were preamplified and recorded with a transient recorder (10 MHz), then stored to a computer.

Table 1: Fraction of developed grains of 6 specimens deposited with $Ag(Ag_2S)_n^+$, $n=1\sim6$, respectively.

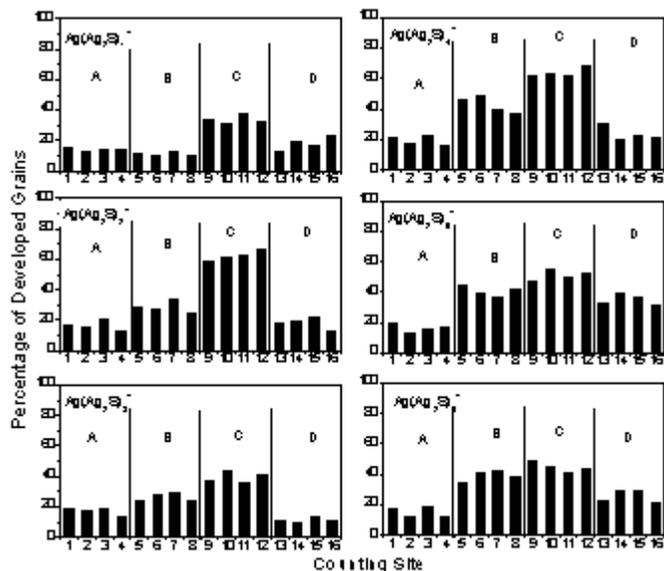


Figure 1: Development fraction versus counting coordinate. From top to bottom are the results of specimens deposited by $Ag(Ag_2S)_n^+$, $n=1\sim6$, respectively. At the left hand side of point A was undeveloped and unexposed, B was undeveloped and exposed, C was deposited and exposed and D was deposited and unexposed.

Region	1	2	3	4	5	6
A	15.0	17.1	18.7	21.0	19.8	17.8
	12.8	15.6	17.0	17.8	13.7	12.3
	13.5	20.9	18.9	23.2	15.2	18.9
	13.6	13.2	13.8	15.6	16.9	11.8
B	11.9	28.3	24.6	46.7	44.2	34.2
	10.6	27.5	27.9	48.7	39.8	40.3
	12.3	33.4	28.6	39.3	36.3	41.9
	10.35	24.5	24.3	36.9	42.5	38.0
C	34.05	57.9	37.3	62.1	47.2	48.9
	30.75	61.5	43.3	62.9	54.5	45.4
	37.05	62.4	35.8	61.4	49.4	41.3
	31.95	66.0	40.5	68.3	52.2	43.2
D	13.1	17.5	11.5	30.0	32.7	23.2
	19.4	19.5	9.2	20.5	39.6	28.8
	16.7	22.5	14.2	23.2	36.3	29.5
	22.55	12.3	10.5	20.6	31.0	21.3

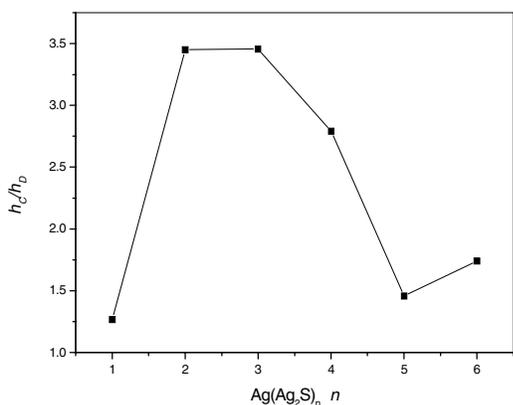


Figure 2: h_C/h_D versus size of $Ag(Ag_2S)_n^+$, $n=1\sim6$

Experiments were carried out just like that undertaken by Fayet et al⁵¹. AgBr was synthesized in a dark room with solutions of $AgNO_3$ and KBr of photographic grade. The grains had a cubic shape of edge length $0.8 \mu m$ and were enzymatically freed from the surrounding matrix and distributed as a monolayer of cubic AgBr on substrate of ITO glass (AgBr/ITO). The silver sulfide cluster cations were generated by laser ablation of Ag and S powder and mass-selected by pulsed negative voltage⁶¹. By applying a decelerating voltage, the energy of the selected clusters were reduced from 1150 eV to 5 eV, and soft-landed on the substrate of AgBr/ITO.

In order to distinguish signal from noise, when deposited, the first half of the substrates of ITO glass (1.5cmx6.0cm) was covered by conductive glass plate, and the second half was deposited by the cluster cations. The first half was divided into 2 parts designated as part A and B. A was undeveloped and unexposed, B was undeveloped and exposed region. The second half was also divided into 2 parts designated as part C and D, C was deposited and exposed and D was deposited and unexposed region. It is obvious that part C corresponds sensitivity and part D corresponds fog. The each specimen was developed for 30 seconds in D19b developer and investigated under the light microscope. Noting that the underdeveloped grain is

transparent and the developed grain is black, then the development fraction (h) of different field of view can be determined. The value of development fraction, the higher of the relative catalytic activity, hence the relative sensitivity. In each field of view the number of developed grains and the total number of grains (over one hundred per field of view) were counted. Then the development fraction of the grains was determined. According to this procedure, we measured the photographic activity of silver sulfide cluster cations: $\text{Ag}(\text{Ag}_2\text{S})_n^+$, $n=1\sim 6$. The results are shown in Fig.1-2 and summarized in Table 1.

The relative sensitivities of the $\text{Ag}(\text{Ag}_2\text{S})_n^+$ clusters with different sizes (different n values), and the relationship between the sensitivity and cluster size were obtained. It was found (Fig.2) that the all the clusters in this series are of catalytic activity, they can sensitize the silver bromide. The cluster with $n=1$ has begun to show sensitivitive activity, the sensitizing activity is strongest while $n=2,3$, its ratio of h_c/h_d is the highest (see Fig.2). The sensitizing activity decreases when $n=4$, and alter slightly when $n>4$. It was also found that the specimens with deposited clusters with n up to 5 Ag_2S units have higher fog, and tend to increase.

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Biography

Xiang Zhao received his B.S.degree in Chemistry from Northwest University in Xi'an, China, in 1992, a master's degree in Physical Chemistry from the same university in 1996 and a Ph.D. in Physical Chemistry from the Institute of Photographic Chemistry, Chinese Academy of Sciences in 1999. During 1996-1999 he studied the sensitive clusters on the silver halide grain surface by cluster technology. Now he is focusing his study field on the cluster-molecular reactions in the gas phase.