Chemically Produced Silver Electron or Hole Trapping?

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Introduction

The role of chemically produced silver clusters created during reduction sensitization continues to be an active topic of discussion. These clusters appear to behave as either electron or hole traps, depending upon size, location, charge, etc. To distinguish between these two properties some researchers have relied on low-temperature photoconductivity where a decrease in signal height is interpreted as electron trapping induced by at least some of the chemically produced clusters.[1] Other researchers have utilized emulsions which have some ability to form internal image.[2,3] Desensitization of the internal image is interpreted as electron trapping by the surface silver clusters created by reduction sensitization. In this paper we illustrate the advantages of internal-image-forming emulsions as model systems for studying the electronic properties of the chemically produced silver clusters.

Experimental

Core-shell emulsions were prepared by first precipitating 0.45 μm AgBr octahedra in a manner described elsewhere.[3] This "core" was sensitized with thiosulfate at 70°C for 40 min. The levels chosen were 0, 0.25X, 1.0X, and 4X, where X is the optimum thiosulfate level. These four cores where then shelled to a final edge length of 0.70 μm. The surface of these core-shell emulsions were sensitized with either dimethlyamineborane (DMAB) at 60°C for 30 min or with a high-pH treatment at 70°C for 40 min.

Emulsions were coated on clear acetate base in an unhardened format and without any keeping addenda. Exposures were done on an EG&G sensitometer with unfiltered light. Internal development was revealed by first bleaching any surface image with a ferricyanide bleach described by Sutherns,[4] followed by development in D-19 containing 0.1 g KI/l for 25 min. Surface image was revealed by development in EAA-1 developer.[5] All processing was carried out at 20°C with nitrogen-burst agitation. Speeds were measured at the midpoint of the D-log E curve, halfway between D_{min} and D_{max}.

Computer Simulation

To help in interpretation of the sensitometric results, computer simulation was utilized. The simulation is based on the N&G model[6] and the simulation scheme itself is based on the Monte Carlo approach.[7] The core-shell system is simulated by placing electron traps on a core that has a diameter that is 0.75 of the core-shell diameter. Varying the trap density at the core simulates the effect of thiosulfate level on internal speed. Surface reduction sensitization is modeled as a hole removal process, the pseudo first-order rate constant being varied to simulate the effect of different concentrations of reduction sensitizer. Electron trapping by the surface silver clusters is modeled by placing electron-trapping "clusters" at specific sites.

Results and Discussion

The effect of surface DMAB sensitization on the internal image of the 4X internally sensitized emulsion is shown in Fig. 1 for a 10^{-2} s exposure. These data show that DMAB increases internal speed by up to 0.65 log E. These emulsions show no surface image and surface fog is low for all DMAB levels except the highest one where the fog is somewhat less than half the D_{max} of the internal image. Figure 2 is a plot similar to Fig. 1 except that high pH was used to carry out the surface reduction sensitization. Again, internal speed is increased up to 0.5 log E by this surface treatment. No surface image or surface fog was observed at any of the pH values used.

Internal speed increases for 10^{-5} s exposure were 1.0 log E or greater for both sensitizing reagents, suggesting this shorter exposure time might provide a more sensitive condition for testing the sensitometric effects of surface reduction sensitization. The higher speed increases observed at this shorter exposure time are mainly due to a slower nonreduction sensitized control. The shorter exposure time enhances HIRF and the reduction sensitization decreases it.

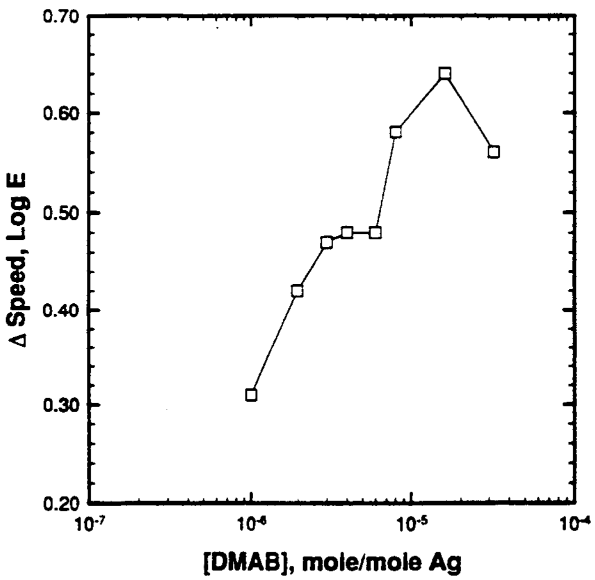

Fig. 1. Internal speed increase relative to the nonreduction sensitized control vs DMAB concentration. Exposure time is 10^{-2} s.

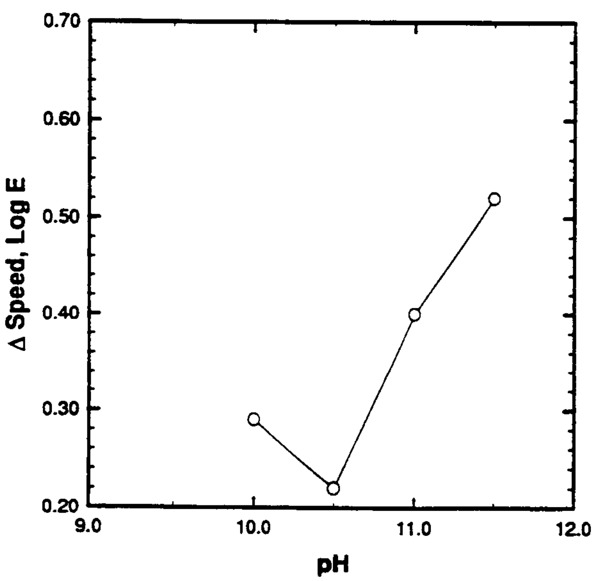

Fig. 2. Same as in Fig. 1 except for high-pH sensitization.

These sensitometric results strongly suggest that the chemically produced silver clusters at the grain surface are trapping and destroying holes and thereby enhancing the efficiency of internal image formation. If the surface silver clusters were electron trapping they should promote surface image formation and compete with internal image sites for available photoelectrons. However, a more realistic situation would be one in which some surface silver clusters are hole trapping and some are electron trapping, in which case it would not be straightforward to predict the effect on internal speed.

To help clarify this situation we utilized computer simulation. The hole removal rate constant was adjusted to give an internal speed increase comparable to that observed experimentally. Then, one electron trapping silver cluster was placed at a specific site on the surface and the simulation run again. The internal speed increase was reduced in this case, and at low values for the hole removal rate constant there was even a desensitization of the internal image.

These simulations demonstrate how powerful electron trapping silver clusters can be in directing the location of the latent image. Just one such cluster at the surface can compete with thousands of reversible electron traps at the core of the core-shell structure. This happens because only growth is required at the electron trapping clusters, whereas both nucleation and growth are required at the internal sites.

Although internal speed increases were observed with just one electron-trapping silver cluster at the surface, the simulations also indicate that the surface speed should be substantially faster than the internal speed in such situations. As indicated above, we could detect no surface image in our reduction sensitized core-shell emulsions. The simulation results suggest that no electron-trapping silver clusters are being produced under our experimental conditions. One exception to this conclusion is the smaller internal speed increase seen at this highest DMAB level (Fig. 1). This effect is attributed to the fact that a significant fraction of the grains are fogged at this concentration. These fog grains contain at least one fog center which is expected to be electron trapping and should influence the internal speed in the manner observed.

Conclusions

The core-shell system described in this work is an ideal model system for studying the electronic properties of chemically produced silver clusters. Both DMAB and high-pH sensitization produce clusters which trap and destroy holes. No electron-trapping clusters, other than fog centers, could be detected. Computer simulation predicted sensitometric properties of electron- vs hole-trapping silver clusters that were invaluable in the interpretation of experimental data.

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