Spectroscopic Studies of Chemically Produced Silver Clusters

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Abstract

The reducing agent thiourea dioxide was used to produce silver clusters chemically in AgBr emulsion. These silver clusters were detected with sensitometry, microwave photoconductivity and diffuse reflectance spectroscopy at photographically revelant sensitizer concentrations. Spectroscopy was also used to monitor the photochemical reactions of these silver clusters. As the sensitizer concentration increased, the photochemical behavior of silver clusters was different. Lower sensitizer concentrations produced R centers ; a substantial decrease in the specific absorption of silver clusters was observed upon band-gap exposure, suggesting that these clusters interacted with photogenerated holes and were destroyed. Whereas, with higher concentrations of sensitizer, absorption of silver clusters, after a first slight diminution, kept stable even for longer exposure times, suggesting that some clusters did not interact with holes. These could be considered as electron-trapping clusters, corresponding to the P centers discussed above. Thus, two distinct silver clusters in terms of their electronic properties were produced with high sensitizer concentrations. These results provide firm experimental evidence for the electron-trapping and hole-trapping functions ascribed earlier to these clusters.

Introduction

Properties of silver clusters are of great importance to the performance of silver halide materials, since they constitute latent image and latent subimage centers in the photographic process[1]. However, chemically produced silver clusters at the surface of silver halide have photochemical[2] and development[3] properties different from those of photoproduced clusters. In particular, it has been suggested that they are two kinds of chemically produced silver clusters on AgBr emulsion grains[4] : one type of these centers, which do not influence the photoconductivity of the grains (i.e the photoelectrons concentration), was assigned to a R center acting as a *positive hole trap*, whereas the other type, which lower the photoconductivity, was assigned to a P center acting as *an electron trap*.

Although this above-stated hypothesis is attractive and important for the understanding of the mechanism of photographic sensitivity, it is based on very few experimental evidence. This work has been undertaken to obtain further experimental evidence for electronic properties of the silver clusters (R or P centers) by applying a new technique to emulsion systems in which silver clusters clearly play important roles.

Recently, Tani and Murofushi[4] have developed a new technique for characterizing chemically silver clusters. They have shown that diffuse reflectance spectroscopy[5] of thick emulsion layers can be used to detect the absorption spectra of silver clusters - either chemically produced or photo-produced. Thus, by applying combined experiments with spectrocopy and photobleaching[6] to reduction-sensitized emulsions, R and P centers have been detected. The study focuses on the spectroscopic and photochemical properties of chemically produced clusters and the correlation of these properties with their effects on sensitometry and micowave photoconductivity.

Experimental

Photographic emulsion used in our work was performed of 0.68 μm (main edge length) octahedral AgBr grains suspended in aqueous gelatin solution, and prepared by controlled double jet method. Reduction sensitization was accomplished by digesting the emulsion with reduction sensitizers for 60 minutes at 60°C (pAg = 8.1, pH = 4.8). The reduction sensitizer used was thiourea dioxide (TUD). The emulsions were coated, dried, exposed for 10^{-2} second on Sch. Sensitometer, and developped in MAA-2. Photoconductivity of emulsions was measured by means of 9-GHz microwave apparatus, in which each sample was excited by a light pulse of 355 nm from a Nd-Yag laser with a third harmonic. Absorption spectra of reduction sensitized emulsion were obtained by measuring the reflectance of thick layers of the emulsion in the liquid state, with reference to unexposed unsensitized emulsion, by means of a SHIMADZU UV-3101-PC spectrophotometer with an integrating sphere.

The photobleaching experiments were conduced by exposing emulsions in cuvette to a 25 $\mu W/cm^2$ Xenon lignt source for seconds using a 405-nm interference filter (26 nm half band-width). The reflectance spectrum of an

unexposed sample was substracted from that of each of the exposed samples to obtain the photobleach characteristics. This procedure was performed one sample at a time, i.e., the sample was taken to the spectrophotometer after it was exposed.

To study chemically produced clusters in the absence of the photoproduced clusters, a strong electron-trapping agent (byproduct of bipirydinium) was needed. It was added to the emulsion before exposure to prevent the formation of a latent image. Samples were then immediately studied.

Results and Discussion

Fig.1 shows photosensitivity and fog density of reduction sensitized octahedral AgBr emulsion grains as a function of amount of TUD used.

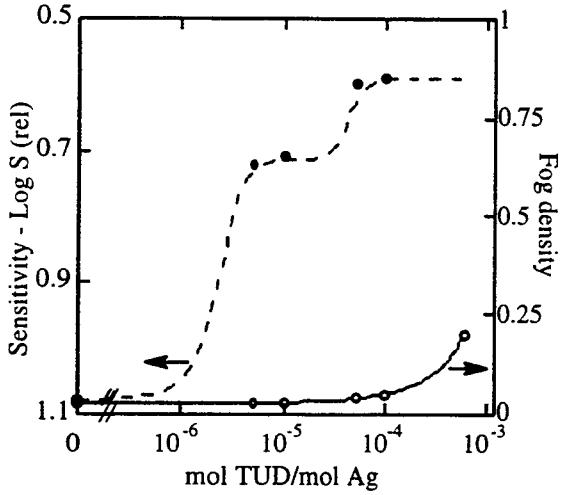

Figure 1. Change of sensitivity and fog level as a function of TUD concentration.

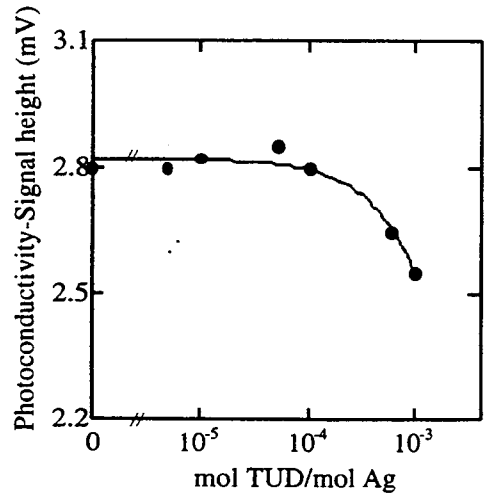

Figure 2. Change of photoconductivity as a function of TUD concentration.

With increasing amount of sensitizer, the increase in photographic sensitivity takes place in two steps and was followed by the formation of fog centers as typically[4] observed. Fig.2 shows photoconductivity signal measured on the previous samples at low temperature (80K). The sensitivity increase in the first step was not associated with the decrease in the photoconductivity, whereas the sensitivity increase in the second step was followed by the decrease in the photoconductivity. By considering that electric carriers in the microwave photoconductivity are photoelectrons, it is considered that the sensitivity increase in the first step was caused by R centers acting as hole traps and the sensitivity increase in the second step was caused by P centers acting as electrons. This is consistent with earlier results observed by Tani[4] on 0,2 μm AgBr grains. To confirm these electron-trapping and hole-trapping functions ascribed to clusters, photobleaching experiments were investigated.

Fig.3 shows the diffuse reflectance spectra of thick liquid layers of reduction sensitized emulsions corresponding to the TUD levels used in Fig.1.

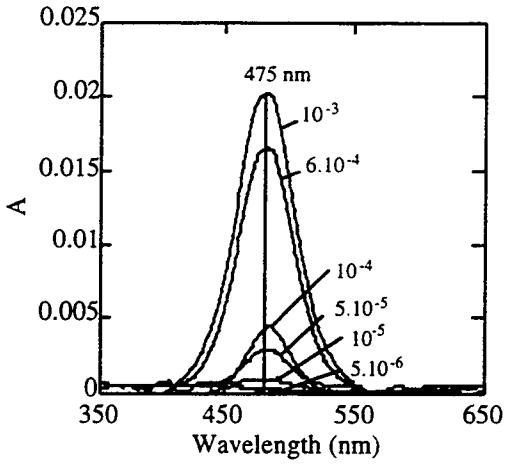

Figure 3. Absorption spectra for TUD sensitized emulsions. The peak intensity increases with the amount of TUD used.

Reduction sensitization produces a main absorption band peaked at about 475 nm which increases with the amount of TUD. The wavelength of the absorbance maximum slightly blue-shifted as the TUD level increases. Photochemical reactions on each sample have been carried out with a strong electron trapping agent (byproduct of bipyridinium) adsorbed on microcristals. This agent was added to the emulsion before exposure to prevent the formation of a latent image. Two examples of these results are given in Figs.4 and 5, for low and high sensitizer concentrations respectively.

-Low sensitizer concentrations :

Fig.4 shows the absorbance evolution when a sample sensitized with low amount of TUD was exposed to 405 nm light for the indicated times. As exposure times increase, we observe that the 475 nm peak decreases in intensity and entirely disappears at longer exposure times. By taking into account the fact that photocarriers in photobleaching experiment are photoholes, this suggests that all clusters prboduced interact with photoholes, and are destroyed. This result confirms that silver clusters acting as R centers are responsible for the sensitivity increase observed in Fig.1.

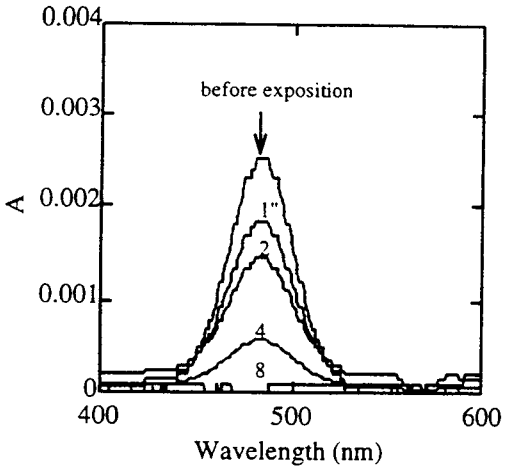

Figure 4. Absorption of TUD (5.10^{-5} mol/molAg) sensitized emulsion exposed for indicated times (s).

-High sensitizer concentrations :

Photobleaching experiments were also repeated for samples sensitized with higher amount of sensitizer (corresponding to the second step of sensitivity increase). In this case, at short exposure time, we observe that the 475 nm peak first decreases in intensity and sligthly red-shifted ; but, on prolonged exposures, it keeps stable and an additional absorption appears at 600 nm (Fig.5). This additionnal absorption at 600 nm is characteristic of photoproduced clusters[6]. Their formation is due to the too low concentration of reducing agent (byproduct of bipyridinium) used in experiment or/and to electron dynamic change. Thus, after exposure, when the totality of the bipyridinium agent has reacted, the photoelectrons excess present in the matrix can react with silver ions and produce latent image centers. Apart from photoproduced silver clusters, the evolution of clusters absorbance suggests that some clusters do not interact with holes. These could be electron-trapping clusters, corresponding to P centers. Thus, two kinds of clusters would be produced at high sensitizer levels : those

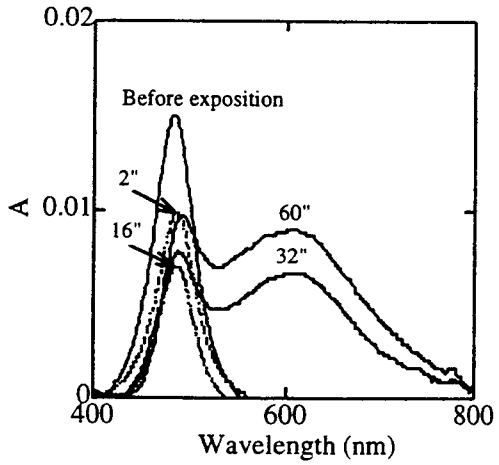

Figure 5. Absorption of TUD ($6x10^{-4}$ mol/mol Ag) sensitized emulsion exposed for indicated times (s).

which are bleachable (holes traps), and those which are unbleachable (electrons traps).

We now know that two kinds of silver clusters give rise to the 475 nm absorption. Low sensitizer concentrations produce R centers ; whereas, high sensitizer concentrations produce R centers and P centers ; both are formed as the sensitizer concentration increases. In comparing these data with those for microwave photoconductivity in Fig.2, we see that spectroscopic and photoconductimetric results are correlated and complementar. In particular, at high concentration, spectroscopic detection of the photochemical reaction demonstrates the presence of bleachable clusters undetectable by photoconductivity.

A closer study of spectra observed in Fig.5 was also made in order to check stability of silver clusters after exposition. Results for samples exposed at short exposure times (2, 16 s) keep stable : no change in clusters spectra is observed after exposition (no represented). This suggests that silver clusters photobleached were stable and that the photochemical reaction of silver clusters was fast. However, for samples exposed at longer exposure times (i.e when the latent image appears -600 nm-), silver clusters spectra change with time (Fig.6).

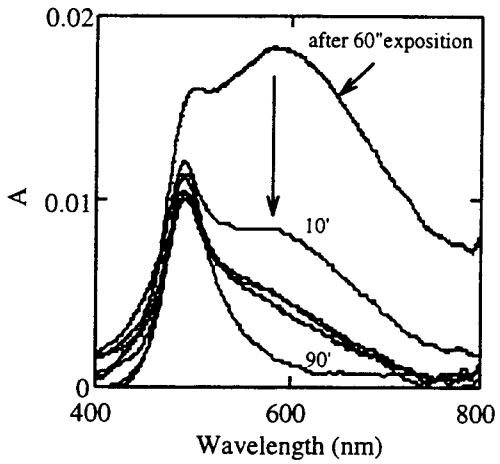

Figure 6. Evolution with time of TUD ($6x10^{-4}$mol/mol Ag) sensitized emulsion exposed for 60 seconds.

Photoproduced silver clusters absorption decreases and entirely disappears whereas a weak additional absorption around 475 nm appears. This may have for origin a slow reaction of photoproduced silver clusters with photoholes. If we consider that these clusters are $Ag_{4,5}$ or 6 (since they are developpable), they may transform by oxidation to smaller clusters presenting an absorption close to that of chemically produced silver clusters. Contrarly to photoproduced silver clusters, these latter are no oxydable. This may be due to a difference in capture cross-section for the hole, which may be related to possible charge differences between these two types of clusters. Exact identification of these clusters is unknown, so that more work would be needed to confirm the effect observed otherwise.

Conclusion

Spectroscopic data seem to be consistent with the photoconductimetric data, suggesting tnat only one kind of silver clusters is produced during chemical sensitization with low amount of reducing agent. They are photo-bleachable, indicating that they are irreversible hole traps (R center). However, for high concentration, it seems there are two kinds of chemically produced silver clusters - those which are bleachable with short exposure time and those that are unbleachable even with long exposure time. This suggests the presence of both hole traps (R center) and electron traps (P center) under conditions.

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