

Preparation of Gold Clusters Dispersed in Gelatin Layer in Using Photographic Film (4) : Effect of Emulsion Characteristics

Ken'ichi KUGE, Michiko ARISAWA, Ken'ichi KIMIJIMA, Tadayuki SHINOZAWA, Naokazu AOKI, Akira HASEGAWA
Department of Information and Imaging Sciences, Faculty of Engineering, Chiba University
Chiba/Japan

Abstract

Gold clusters are noted as a nonlinear optical material. We have reported the preparation of gold clusters dispersed in gelatin layer by utilizing the photosensitivity of silver halide photography. As the latent image specks act as a catalyst for redox reactions, gold ions are reduced and deposited on the latent image specks when the exposed film is immersed in gold(I)thiocyanate complex solution for several or tens of days. After fixation gold clusters dispersed in gelatin layer remains. The film produced by this method was purple owing to the plasmon absorption by gold clusters. We prepared here the gold clusters from photographic films with different sensitivity, and compared the characteristics of cluster by absorption spectrum and size distribution. The absorption peak was blue-shifted and sharpened, and the cluster size decreased and dispersed narrowly along with the decrease of film sensitivity. The relationship between the characteristics of gold clusters and latent image specks was suggested.

Introduction

Gold clusters have nonlinear optical effects and are noted as a material for light switch or optical modulator.[1-6] There have been reported many formulas for the preparation of gold clusters.[4-6] However, majority of preparation are dealt in liquid phase and those researches exerted large efforts to prevent coagulation of clusters. Moreover, gold clusters need to disperse in adequate binder and make it filmy state, for instance, in order to apply it as a device. There are also considerable reports to prepare a layer with dispersed clusters.[7-10]

We have reported a new method to prepare a film dispersed with gold clusters by making use of photosensitivity of photographic films.[11-14] In this method, film with dispersed gold clusters in gelatin layer is prepared directly.

The latent image specks act as a catalyst of redox reaction. Development is a reduction of silver halide to silver catalyzed by them. The latent image specks also function as a catalyst of other redox reactions. Metallic gold clusters are deposited by reduction of gold(I)complex such as gold thiocyanate complex ion $\{Au(SCN)_2\}^-$, and this process was known as the gold development.[15,16] If the exposed film is immersed in the solution containing gold(I)thiocyanate complex ions, the latent image specks catalyze the reduction of gold ions which lead to subsequent deposition of gold atoms on the latent image specks.

Since the deposited gold atom clusters function as a catalyst as well, the deposition of gold atoms continues. When a film with deposited gold clusters is immersed in a fixer solution, silver halide grains are dissolved and gold clusters dispersed within gelatin layer will remain. After washing and drying, the gelatin layer with dispersed gold clusters are formed.

Layers prepared with present method has the following features. (a) As gold clusters are kept in gelatin layer, changes of the clusters such as coagulation or the like are not likely to occur after preparation. (b) Preparation of uniform layer with wide area is possible. (c) Since gold clusters are only produced in the exposed area, pattern forming of gold clusters is possible through exposure.

Previously we reported that the characteristics of photographic film altered the characteristics of gold cluster.[13] This associated us a relationship to the characteristics of latent image specks. So, we studied the effect of them to the preparation of gold clusters and considered this relationship.

Experimental

We used process film and electron microscopic film (Fuji Photographic Film Co.), and X-ray film (Konica Co.). We also used a coating of ultrafine grain emulsion (0.06 μm). Characteristics of those samples are shown in Table 1. The order of sensitivity is the same as the order of grain size. These films were exposed uniformly with white light for 1 second or 10^{-3} second.

Gold developer by Birch and others was used for gold deposition solution.[15] Formula of the gold developer is shown in Table 2. Gold deposition was carried out by immersing a strip of exposed film at 20°C for five to twenties of days. After deposition was complete, samples for optical density measurement were washed with water and immersed in F-5 fixer for 5 minutes. After fixation samples were washed with water and dried. Then absorption spectrum was measured in a film state.

For measurement of cluster size, first of all, dilute gelatin solution with suspended silver halide grains was prepared by dissolving gelatin layer in warm water. The solution was dropped to grid for electron microscope and dried. And then the grid and all was immersed in sodium thiosulfate solution to dissolve and remove silver halide. Then, a thin layer of gelatin containing gold clusters was obtained. This layer was observed with an electron microscope, and distribution of cluster size was determined from electron microphotographs.

Table 1 Characteristics of the sample film

Sample	Symbol	Grain size (nm)	Sensitivity (1/H)
Ultrafine grain emulsion	UF	60	0.0025
Electron microscopic film	EM	150-300	0.91
Process film	PR	400-500	4.5
X-ray film	XR	500-1000	35

Table 2 Formula of gold developer

Reagent	Concentration (mol / l)	Amount (ml)
KSCN	1.23	5
$NaAuCl_4$ $2H_2O$	0.021	5
KBr	1.68	5
Water to make 1 l		

Experimental Results

Effect of exposure intensity to the absorption spectrum for PR film is shown in Fig. 1. It shows the increase of absorption peak with the immersion period for both exposure periods of 1 and 10^{-3} sec. The increase saturated over 15 days of immersion period for the 1 sec exposure. In all cases, the plasmon absorption of gold clusters having a maximum around 550-570 nm was observed. The peaks were sharp and blue-shifted at high intensity exposure, even though the maximum of absorption was larger than that at the low intensity exposure.

Effect of exposure intensity to the size distribution for each film is shown in Fig. 2 for 1 sec and in Fig. 3 for 10^{-3} sec exposure. This also represent that the cluster size is small and the size distribution is narrow at high intensity exposure. This difference is notable for the emulsion with smaller grains or lower sensitivity.

Those results are summarized in Table 2. Generally, along with the decrease of film sensitivity the absorption peak was shifted to short wavelength and the peak width was narrowed. On the same time, the cluster size decreased and the size distribution was also narrowed.

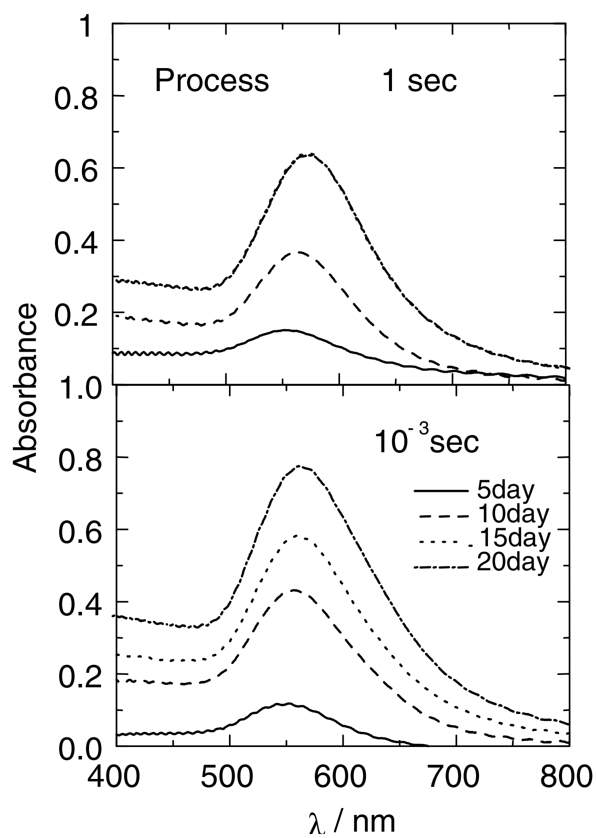

Figure 1. Effect of exposure intensity to absorption spectrum of gelatin layer with dispersed gold clusters prepared from PR film at different immersion periods. Top : 1 sec exposure, bottom : 10^{-3} sec exposure.

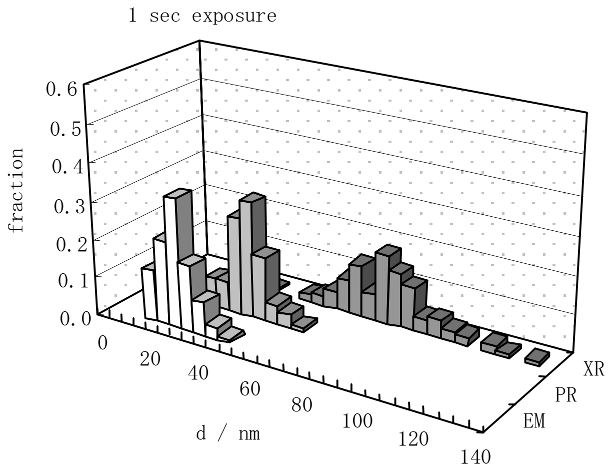

Figure 2. Size distribution of gold clusters prepared from different photographic films. Exposure period was 1 sec and immersion period was 15 days.

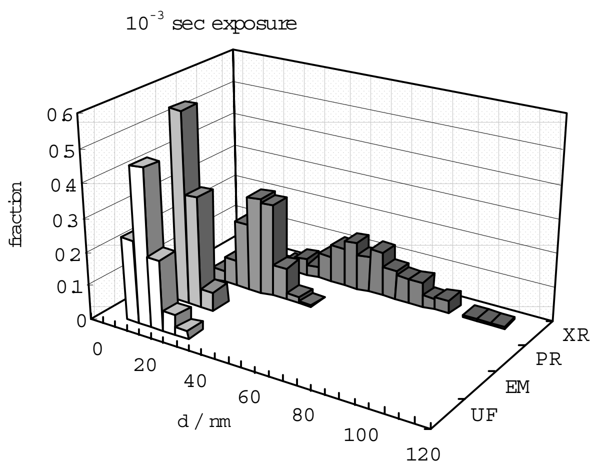

Figure 3. Size distribution of gold clusters prepared from different photographic films. Exposure period was 10 $^{-3}$ sec and immersion period was 15 days (UF:14 days).

Table 3 Characteristics of the gelatin layer with dispersed gold clusters for each exposure period. Immersion period : 15 days (UF : 14 days)

Sample	Optical Characteristics		Cluster Characteristics	
	Peak wave-length (nm)	Half width (nm)	Cluster size (nm)	Standard deveat-ion (nm)
1 sec exposure				
EM	549	124	23	6.1
PR	559	58	36	7.6
XR	582	189	78	16
10^{-3} sec exposure				
UF	543	43	13	3.6
EM	545	66	15	3.4
PR	558	63	28	5.2
XR	578	180	59	16

Discussion

It is well-known that optical characteristics of gold cluster, such as plasmon absorption, depends on the cluster size. Dependence of cluster size was calculated in using Mie's theory by many authors, and every calculation indicated the red shift and broadening of the absorption peak with the increase of cluster size.[17] The result of absorption spectrum in Table 2 suggested that the cluster size was small and the size distribution was narrow at high intensity exposure. This was also indicated from the result of size distribution. The smaller and narrowly-dispersed clusters were formed at the high intensity exposure.

Moreover, the result here indicated that the cluster size depended on the size of silver halide emulsion grains. As the sensitivity of emulsion depends on the gain size, the cluster size also depends on the sensitivity of photographic films. The film having high sensitivity showed the large cluster size and red-shifted absorption. As exposure value given to the films was almost same at the same intensity, size of latent image speck would be large in the film with high sensitivity.

This suggests that the size of gold cluster depends on the size of latent image specks. The large latent image speck would have large ability to catalyze the reduction of gold ions, and form large clusters.

The latent image specks act as a catalyst for reduction reactions. The development is one of the redox reaction and it is well-known that the development rate is lower when the latent image specks are smaller size.[18] As the gold deposition is another kind of reduction reaction, the size of specks will also affect to the deposition rate and so to the cluster size.

At the high intensity exposure the dispersion of latent image specks proceeds and this causes the formation of many specks with smaller size, which would form the small and many clusters.

Because control of the cluster size is indispensable to reveal the fine nonlinear optical effects, the size of latent image speck is an important factor to prepare the gold clusters. In order to use the gold cluster for the optical devices the monodispersed clusters must be dispersed in the layer with high density. So, it is important to clarify the relationship. Fortunately, we have many knowledge of latent image formation process and it may be possible to apply this knowledge to the preparation of gold clusters of same size with high density.

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