

# Energy-level Assessment for Small Silver Clusters in AgBr Emulsion from Combined Experimental Data of Light Absorption, Spectral Sensitivity, and Photobleaching

*Mitsuo Kawasaki and Yoshiaki Oku*  
*Division of Molecular Engineering, Kyoto University*  
*Yoshida, Kyoto 606-01, Japan*

## Abstract

A series of spectroscopic data concerning light absorption, spectral sensitivity, and photobleaching of reduction sensitized AgBr emulsions is presented. With some limitations, combination of these experimental data allows reasonable positioning of the electronic energy levels associated with reduction sensitization centers, representative of small silver clusters in AgX emulsions.

## Introduction

It seems that quantitative description of the fundamental photographic processes in silver halide emulsion is still far to reach. Convincing information may be lacking even with respect to the most basic electronic properties — the energy levels relative to the band edges of AgX — of a series of small silver clusters in AgX emulsion relevant to the process of latent image formation. The difficulty stems mainly from the extremely small size and small concentration at which such silver clusters are generally considered to function in photographic systems. However, the situation may be a little different in the case of reduction sensitization centers. They must be very small in size, but have been suggested to be present in regular sensitized emulsions in a concentration large enough to allow their absorption spectra to be obtained by e.g., diffuse reflectance spectroscopy [1-3]. Availability of such direct spectroscopic data also makes cluster characterization easier and more reliable. In this context, we present in this paper a series of spectroscopic information concerning light absorption, spectral sensitivity, and photobleaching of reduction sensitized AgBr emulsions, and discuss how and with what limitations these data can be combined to locate the reasonable energy levels associated with reduction sensitization centers, typical small silver clusters of photographic interest.

## Experimental

The AgBr emulsion consists of monodisperse 0.45 $\mu$ m octahedral grains, sensitized by dimethylamine borane (DMAB) in the concentration range 0–1.0 mg/mol-Ag at 70°C for 40 min. The emulsion has been coated on a clear support at 1.0 g/m<sup>2</sup> silver coverage.

The light absorption spectra of reduction sensitization centers were measured in a diffuse transmission mode by using a stack of ten sample films at maximum and a spectrometer specially designed for the purpose. In this measurement, the quantity proportional to the product of the concentration and absorption coefficient of the absorbing species is simply given by the diffuse absorbance,  $-\log T/T_0$ , where  $T_0$  and  $T$  represent the diffuse transmittances measured for unsensitized and sensitized samples, respectively.

The photobleaching (photoionization-induced type) experiment followed the method described elsewhere [4], but involved here samples in which a desensitizing dye, 1,1'-diethyl-2,2'-tricyanobenzene, was adsorbed as an effective electron acceptor to improve the bleaching efficiency. The merit of this dye is in that its comparatively high oxidation potential minimizes hole injection from dyes excited by the bleaching exposure, thus preventing the hole-induced type of bleaching from interfering with the photoionization-induced process.

The spectral sensitivity, or long-wavelength sensitivity, was measured by using the same apparatus as used for the photobleaching experiment, thereby the long-wavelength sensitivity threshold, invariant with exposure time, was determined for sufficiently extended irradiations with a total photon flux reaching the order of 10<sup>18</sup>/cm<sup>2</sup>.

## Results and Discussion

**Absorption Spectra:** Fig.1 shows a typical absorption spectrum taken for the DMAB sensitized emulsion coating and its changes upon repeated data acquisitions with relatively heavy blue exposures in between. The absorption peak of the reduction sensitization centers was found at ~455 nm for all the samples measured by our diffuse

transmittance method. This is substantially shorter than  $\sim 475$  nm, which has been reported for similar reduction sensitization centers in liquid phase emulsions based on the diffuse reflectance spectroscopy method [1-3]. More importantly, Fig.1 shows that the intensity decrease of the  $\sim 455$  nm absorption band by blue exposure is accompanied by the growth of a relatively broad new absorption band around  $\sim 580$  nm with a clear isosbestic point at  $\sim 480$  nm. This broad absorption band represents the plasmon excitation of print-out silver particles, which are at least a few nm in size and thus consisting of hundreds or even thousands of Ag atoms. Moreover, the appearance of the isosbestic point indicates that these print-out silver particles grow at the expense of reduction sensitization centers in a fixed mass ratio of print-out silver to reduction sensitization centers consumed. This not only provides a strong spectroscopic evidence for the hole-removing role of reduction sensitization centers, but also suggests that quite a significant number of reduction sensitization centers (presumably dimer species) are present on a single grain surface.

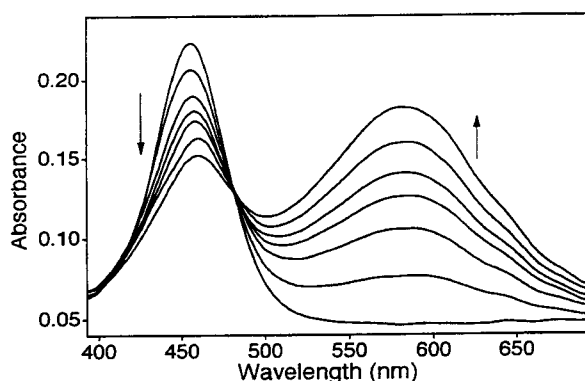


Figure 1. Typical absorption spectrum of reduction sensitization centers produced by dimethylamine borane (DMAB), and its changes upon repeated data acquisition with blue exposure in between. Measured by diffuse transmittance method for the high-level (1.0mg/mol-Ag) DMAB sensitized sample.

**Spectral Sensitivity and Photobleaching:** The light absorption at  $\sim 455$  nm, as detected directly by the diffuse transmittance spectroscopy, represents an intramolecular HOMO-LUMO transition associated with reduction sensitization centers. This is never the only allowed transition, however, for centers that can interact strongly with the AgBr grain surface. Weak as it is, transition may also occur from the HOMO level into the conduction band continuum of the host AgBr grain. This is what we refer to as the photoionization process, and the corresponding lowest excitation energy may be estimated from the long-wavelength sensitivity threshold or from the threshold for the photoionization-induced bleaching. Ironically, it is this much weaker transition that gives better insight into the location of the HOMO levels associated with reduction sensitization centers.

Fig.2 shows typical long-wavelength sensitivity data obtained for samples sensitized at the lowest [Fig.2(a)] and the highest [Fig.2(b)] DMAB concentration. In Fig.2(a), the

sensitivity threshold for sufficiently extended irradiations can be located at  $\sim 1.9$  eV ( $\sim 650$  nm). This was common to all the samples given low and moderate DMAB sensitizations. In contrast, at the highest level of sensitization the threshold moved further to longer wavelength and reached  $\sim 1.6$  eV. Thus at least two different centers seem to be produced by the DMAB sensitization depending on the sensitization level, even though we could observe only single absorption band with respect to the direct HOMO-LUMO transition as mentioned already.

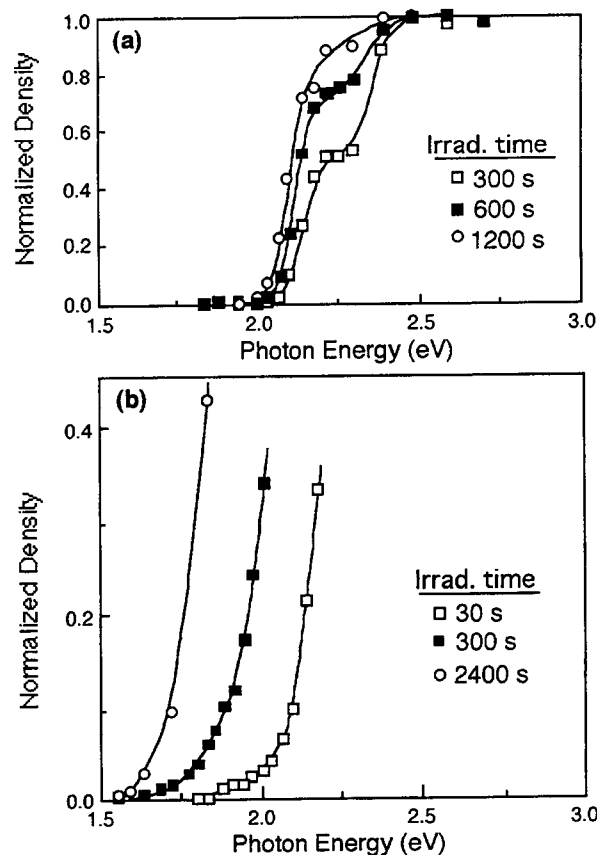


Figure 2. Long-wavelength sensitivity data obtained for (a) lowest (0.1 mg/mol-Ag) and (b) highest (1.0 mg/mol-Ag) level DMAB sensitized samples. The photon flux is  $3-4 \times 10^{14} \text{ cm}^{-2} \text{ s}^{-1}$ .

Fortunately, the above-noted two kinds of centers can be detected separately by the following methods. As shown in Fig.3, extended development for up to 80 min in an M-AA-1 surface developer gradually and markedly increased the fog density only for the high-level DMAB sensitized samples. This suggests that the centers produced additionally in such a high level of DMAB sensitization have indeed an electron-trapping property, so as to be detected as the extended-development-induced fog. As for the other type of center, dominant in population at relatively low levels of DMAB sensitization, gold latensification serves as the most powerful detection method, as even the lowest-level DMAB sensitized sample is completely fogged by gold latensification in the standard development condition.

The photobleaching experiment becomes feasible for any centers of interest, once their respective detection methods are established. The photobleaching spectra measured for the reduction sensitization centers produced at the lowest and the highest DMAB concentrations are as shown in Fig.4(a) and (b), respectively. Here the change of gold-latensification-induced fog [Fig.4(a)] or extended-development-induced fog [Fig.4(b)] density is plotted as a function of photon energy of the bleaching exposure. The bleaching thresholds found in these spectra,  $\sim 1.9$  eV in Fig.4(a) and  $\sim 1.6$  eV in Fig.4(b), agree well with the spectral sensitivity thresholds for each sample observed in Fig.2. This proves that both the long-wavelength sensitivity and the photobleaching studied here are caused indeed by the photoionizing transition from the HOMO levels associated with the reduction sensitization centers to the conduction band continuum of AgBr.

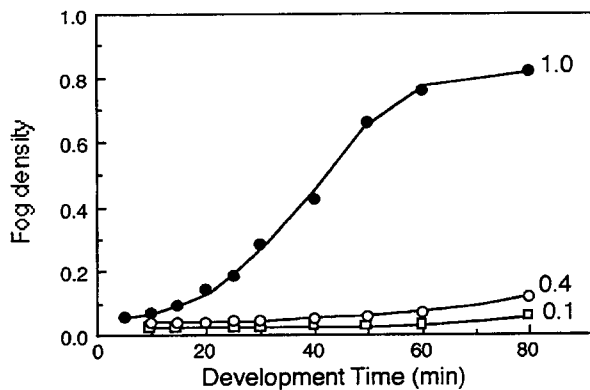


Figure 3 Fog density as a function of development time for samples sensitized at different DMAB concentrations indicated by the numbers in mg/mol-Ag.

**Energy Level Consideration:** In order to correlate the experimental data, obtained by the optical methods, to the specific energy levels of reduction sensitization centers, it is helpful to refer first to the hypothetical potential energy diagram shown in Fig.5. Here the two potential curves represent the total energies of a small silver cluster ( $Ag_n$ ) and its ionized counterpart ( $Ag_n^+$ ) on the AgBr grain surface. Thus the coordinate here represents the ionic polarization of the AgBr matrix rather than the internal cluster coordinate. The point being made in this diagram is that the total energy of a charged cluster is significantly altered by the highly polarizable medium, the corresponding potential minimum being considerably shifted along the polarization coordinate. The HOMO level of  $Ag_n$  relative to the bottom of the conduction band is defined by the energy required to remove an electron 'adiabatically' to the bottom of the conduction band, as illustrated in Fig.5 by a conventional energy level diagram aligned with the potential energy curves. Note that the difference between this adiabatic ionization energy and the vertical ionization energy (indicated by a dotted arrow) becomes much greater for clusters in polarizable media than for isolated clusters.

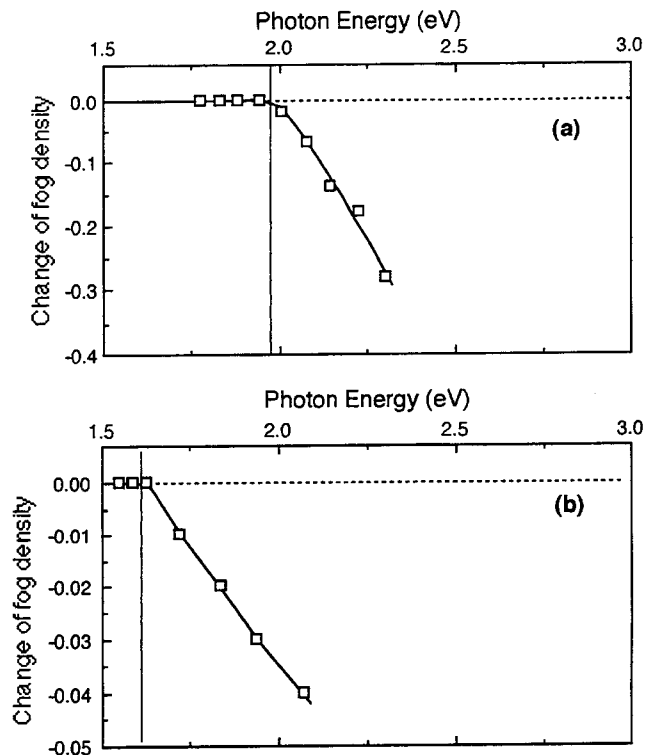


Figure 4. Photobleaching spectra of reduction sensitization centers obtained for (a) lowest (0.1 mg/mol-Ag) and (b) highest (1.0 mg/mol-Ag) level DMAB sensitized samples. Change of (a) gold-latensification-induced fog or extended-development-induced fog is plotted as a function of photon energy of bleaching exposure with a total photon flux of  $\sim 10^{18} \text{ cm}^{-2}$ .

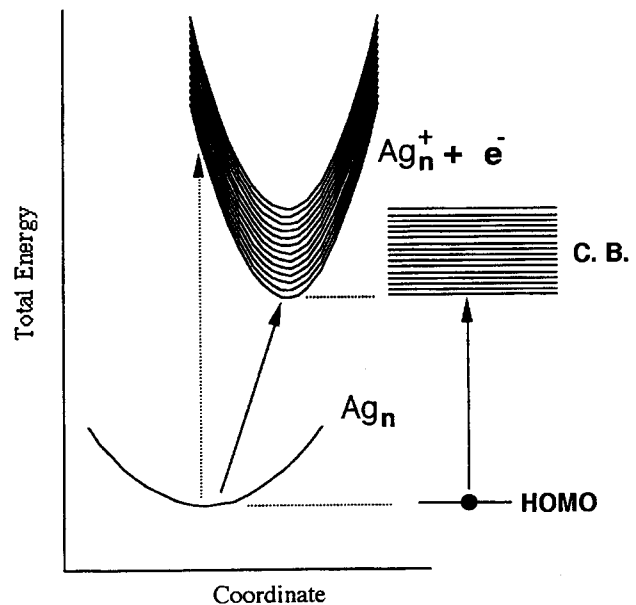


Figure 5 Potential energy diagram for a small silver cluster and its ionized counterpart on AgX grain surface. The coordinate represents ionic polarization of AgX matrix.

The spectral sensitivity threshold and the photobleaching threshold measured in this work correspond to the lower limit of photon energy necessary to cause the photoionization event. Thus the reported values,  $\sim 1.9$  eV and  $\sim 1.6$  eV, can be identified practically with the adiabatic ionization energies, and hence with the HOMO energies relative to the bottom of the conduction band. It should be also noted that the latter value of  $\sim 1.6$  eV, as measured for the high-level DMAB sensitized samples, is almost identical with that previously associated with the photoproduct two-atom subimage centers. This implies that subimage centers and reduction sensitization centers with electron trapping properties could be essentially identical with each other.

It should be stressed again that the HOMO level of any small center on the AgBr grain surface is highly sensitive to the extent to which the ionized counterpart is stabilized by the polarization effect (see Fig. 5). For example, suppose that there are two centers, one neutral and the other carrying a partial positive charge in their ground states, but otherwise identical with each other. At first sight, the partial positive charge associated with the latter center may appear to lower its HOMO level as compared with the neutral cluster. A simple electrostatic calculation allows us to predict, however, that the stabilization of the ionized counterpart due to the polarization of the surrounding medium can become so greater for the latter center as to cause the opposite situation where the HOMO level of a positively charged cluster is rather above that of a neutral cluster. This example may explain why the HOMO level associated with the reduction sensitization centers with electron trapping properties is located higher than that of hole trapping analogues ( $\sim 1.6$  eV versus  $\sim 2$  eV below the conduction band edge).

Once the HOMO level is fixed as described above, the direct HOMO-LUMO transition observed at  $\sim 455$  nm allows the corresponding (but non-adiabatic) LUMO level to be located well above the bottom of the conduction band. This intramolecular transition does not change the net charge of the cluster, so that the LUMO level estimated in this way may be approximately valid also in the adiabatic sense, particularly if the intramolecular cluster coordinate corresponding to the potential minimum is not much altered between the ground and excited states. Even so, this level is of little photographic significance, because it can be quite different from the level to which a photoelectron may be trapped. The position of this real electron-trapping level must be defined by the energy released when an extra electron is added from the conduction band to the given center. The net charge of the cluster is thus altered between the initial and final states, and the polarization effect immediately comes up again. For direct determination of the locations of such electron-trapping levels, one needs to be somehow able to measure either optical or thermal excitation spectra of the trapped electrons into the conduction band continuum.

**Comparison with Non-optical Methods:** The ionized states of small silver clusters in AgX emulsion, produced by e.g., trapping electrons (reduction) or positive holes (oxidation), rapidly undergo the subsequent ionic step to grow or decay to a larger or smaller cluster. As a result, the electrochemical methods, which work best for reversible redox couples, are difficult to apply to extract the correct position of e.g., the HOMO levels of small silver clusters. To do so, one needs to virtually freeze the ionic process and realize at least approximately or temporarily on the time scale of measurement a simple electron-transfer equilibrium between the given size of cluster and its ionized counterpart. Care should be taken not to confuse this simple electron-transfer equilibrium with a composite redox equilibrium between two silver clusters having different sizes; the latter involves silver ions as the essential species to maintain the equilibrium. The necessity of the optical methods involved in this circumstance, and the fundamental physics involved in the photoionization measurement, as suggested in Fig. 5, ensures that the method allows correct positioning of the electronic energy levels associated with small silver clusters in AgX emulsion.

## References

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