

Diffuse Transmittance Spectroscopy of Diatomic Ag Nuclei on AgBr Microcrystals

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A diffuse transmittance spectroscopy method that utilizes a large-area photodetector in contact with the sample is a simple and useful method to probe a weak light absorption by molecular species incorporated in a strongly scattering medium. The method successfully uncovered the electronic transition centered at 455 nm involving what are identified as diatomic Ag nuclei (Ag_2), which were size-selectively formed on a $0.45\ \mu\text{m}$ octahedral AgBr microcrystal in a photographic emulsion in a surprisingly high density (many thousands on each microcrystal surface) through a heterogeneous chemical reduction. The estimated oscillator strength for the 455 nm absorption, 0.5 ± 0.1 , compares favorably to the theoretical prediction (0.64) reported for the lowest-energy electronic transition of an isolated Ag_2 molecule, which is known to be centered at 435 nm. A possible mechanism underlying the remarkable size selectivity in the chemistry of Ag_2 formation on AgBr is also discussed in conjunction with a hypothetical (111) surface structure of the octahedral AgBr grain.

Introduction

The metal cluster science owes much of its recent advancement to the rapid technological development for mass-selected production and/or probing of a variety of simple metal clusters in interaction-free environments. The unique size dependence of their physical properties has thus extensively been investigated for a number of different metals. As a result, it is now firmly established that the so-called “electronic shell structure” is an unequivocal nature of the delocalized valence electrons, which may persist up to very large cluster sizes of the order of 1000 atoms.^{1,2}

Interactions with other materials become the integral element, however, for metal clusters in more practical environments in which they function, e.g., as chemical catalysts. Much of the physics and chemistry of metal clusters in such more complexed systems has thus far been little understood and continues to be a most challenging subject in the field. The traditional silver halide imaging system, in which extremely small-sized Ag clusters comprising much less than 10 atoms play the critical roles,³ is a particularly interesting example from this viewpoint.

In the long past far ahead of the evolution of the metal cluster science, there was already the common recognition that the light absorption by AgX microcrystals leads to the formation of extremely small Ag nuclei (thus called latent images) on the grain surface and that these Ag nuclei serve as an efficient catalyst for the reduction (photographic development) of the whole AgX grain to a macroscopic silver particle. It was not until around the late 1970s, however, that the majority of photographic scientists became aware of some strong linkage between their traditional imaging science and the more modern metal cluster science. The triggering works were those that were spurred by the very fundamental question that at what size of Ag clusters they become able to catalyze the photographic development. Despite the considerably different experimental approaches taken by different groups,^{4–8} the conclusions were

very similar and unanimously pointed to the critical size of four silver atoms. Furthermore, to account for the invariance of this critical size over some significant range of reduction potential (–100 to –400 mV vs saturated Ag/AgCl) of the developing solution, the importance of an odd–even alternation in the redox properties of small Ag clusters was addressed for the first time in the context of photographic development.⁶

Direct information about the physical and chemical properties of such small Ag clusters on AgX surfaces is nevertheless so limited that the understanding of the silver halide imaging process on an atomic level is still not within easy reach. One of the major problems has been the fact that the net concentration at which these clusters practically function in the imaging process is generally so small that the standard methods for probing molecular species in other systems seldom seemed useful. An extremely high-intensity irradiation or alternatively very extended irradiation of AgX microcrystals of course increases the concentration and the total mass of the photolytic Ag clusters, but only to end up losing the slightest room of control over the cluster size distribution. Feasibility of size-selected production and/or detection is the minimal requirement for whatever system of metal clusters to be studied in a straightforward manner.

An apparent exception recently came to our attention, however, in that a series of AgBr emulsions that were subject to controlled reduction treatments with some typical reducing agents (the process known as reduction sensitization⁹) have been shown to exhibit a well-defined absorption peak in the visible region ($\sim 475\ \text{nm}$) when examined by the diffuse reflectance spectroscopy method.^{10–12} The primary products of this sensitizing process have been deemed to be also some small Ag clusters but with properties considerably different from those associated with the photolytic counterparts.¹³ More importantly, it is clear that nothing but an unusually high density of essentially monosized clusters can give rise to such a well-defined absorption band detectable by the conventional spectroscopy method. In other words, there must be some unique size-controlling mechanism operating in the process of reduction

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sensitization, as opposed to the photolytic Ag cluster formation. The above-noted diffuse reflectance studies did not clearly address this potentially more critical aspect of reduction sensitization. It should be also noted that a series low-temperature (6 K) luminescence spectra for similar reduction-sensitized AgBr emulsions, quite recently examined by Marchetti and co-workers,¹⁴ have uncovered a couple of emission bands, which they assigned, together with the corresponding excitation spectra peaked at 442 nm, to Ag₂ dimers formed as a result of the reduction treatments. Marchetti and co-workers have also provided some limited information about the direct absorption spectra, the low-temperature absorption peak being located at ~ 440 nm in agreement with the excitation spectra. They have made a little perplexing statement, however, that a very weak low-temperature absorption could be discerned also between 470 and 480 nm at the higher level of reduction sensitization, thereby suggesting that the ~ 475 nm absorption band in the aforementioned room-temperature reflectance spectra could be associated with rather heavily reduction-sensitized AgBr grains, not necessarily with Ag₂ dimers.

Thus, the main purpose of this paper is to illuminate more quantitatively the origin and the nature of the unique room-temperature absorption band associated with reduction-sensitized AgBr emulsions, in careful comparison with the known absorption spectra of simple Ag clusters in the gas phase or trapped in low-temperature noble-gas matrices. For this purpose we have constructed a model spectrometer that allows the desired absorption spectra to be obtained in a diffuse transmission mode for arbitrary emulsion coatings met in practice. This method has an obvious advantage over diffuse reflectance spectroscopy, in that the latter requires the measured reflectance data to be analyzed by the so-called Kubelka–Munk equation¹⁵ (valid only for ideal scattering layers with infinite thickness) and hence a special care about the sample. There is no such constraint for interpretation of the diffuse transmittance data, and a careful spectrometer calibration allows us to discuss the experimental data even more quantitatively. Our results uncover a well-defined room-temperature absorption band for reduction-sensitized octahedral AgBr emulsions centered at ~ 455 nm, which is apparently closer to the low-temperature peak (442 nm) reported by Marchetti and co-workers¹⁴ than to the room-temperature reflectance peak (~ 475 nm) reported by other groups.^{10–12} The experimental results obtained in the present work can be associated with indeed a surprisingly high density of diatomic Ag nuclei (Ag₂) that selectively form on the AgBr grain surface through a heterogeneous chemical reduction. A possible mechanism allowing such a highly selective Ag₂ formation on (111) surfaces of AgBr is also proposed.

Experimental Section

Materials. The series of AgBr emulsions sensitized with dimethylamine borane (DMAB) were kindly prepared at Kodak by a controlled double-jet method following the procedure specified in ref 16 and supplied as coated on a clear acetate film support. The AgBr emulsion consists of monodispersed octahedral AgBr microcrystals with the mean edge length of 0.45 μm . Each coating has a coverage of 1.0 g/m² in silver (10^{-2} mol of AgBr/m²) and 2.0 g/m² in a gelatin binder. The corresponding coating thickness is ~ 3 μm , in which the AgBr grains are dispersed in the estimated number density per unit area, $6.4 \times 10^8/\text{cm}^2$. The reduction treatment with DMAB was applied in the stage of liquid emulsion before coating at pH 5.6 and pAg 8.2, to which DMAB was mixed at concentrations ranging from 0.1 to 1.0 mg/mol of AgBr (1.7–17 μM /mol of

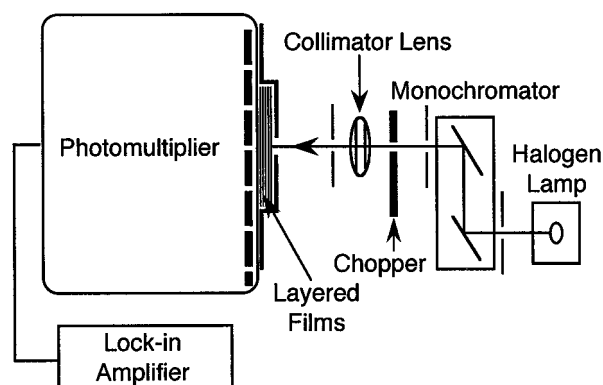


Figure 1. Experimental setup for diffuse transmittance measurement.

AgBr), the whole mixture then being digested at 70 °C for 40 min, long enough for the reaction to complete.¹⁷ In contrast to this wet mode of reduction sensitization, another type of reduction sensitization was allowed to occur in a dry H₂ atmosphere. Here a primitive emulsion coating (3.5×30 cm²) placed in a cylindrical vacuum chamber (5.8 cm in inner diameter and 33 cm long, made of stainless steel) was evacuated by a turbomolecular pump (Shimazu Co., UHV-50) for ~ 14 h in advance. The chamber was then filled with 1 atm of 99.99% H₂ gas (Sumitomo Seika Co.), which was warmed to ~ 50 °C by using a heating tape wound round the outer surface of the cylindrical chamber. The dry coating was stored therein for 1–5 h.

Diffuse Transmittance Measurement. Figure 1 shows the experimental setup for the diffuse transmittance measurement. The model spectrometer consists of the built-in components (halogen lamp, monochromator, collimator lens, and chopper) of a spectro-ellipsometer (Mizojiri Kogaku Co., type DV-36S), combined with an end-on photomultiplier tube (Hamamatsu Co., type R375) with a large aperture size ~ 50 mm in diameter and an autophase lock-in amplifier (NF Circuit Design Block Co., model LI-574). A stack of sample coatings (3.5×2.5 cm²) was directly attached to the window of the end-on photomultiplier tube. The incident monochromatic beam to the sample was adjusted to have a spot size of 5 mm in diameter. This optical geometry allows the majority of the diffuse transmitted light to be successfully captured by the photomultiplier. Also, the use of the stacked (typically 10-fold resulting in the total sample thickness ~ 2.5 mm including the film base) film samples greatly compensated for the weakness of the absorption masked by the strong light scattering due to the AgBr grains. Automatic wavelength scan and data acquisition are not presently feasible in this system, so the measurement was made point-by-point at 5 nm intervals by manual adjustment of the monochromator. The data were then subject to interpolation in a personal computer to get a smoothed spectrum. The resulting spectral resolution was still better than 5 nm, as checked by the transmittance spectra taken for a series of interference filters with 15–18 nm bandwidth at half-maximum.

Spectrometer Calibration. The light scattering in the emulsion coating is controlled by the large number of AgBr grains regardless of the presence of a small amount of extra light-absorbing species. Furthermore, the scattering is so strong that the effective light path lengths across the sample are expected to become approximately equal for all the diffuse transmitted photons at the given thickness of the sample. In this condition, given that the diffuse transmittances measured for samples with and without a small concentration of extra light-absorbing species are T and T_0 , respectively, the absorption

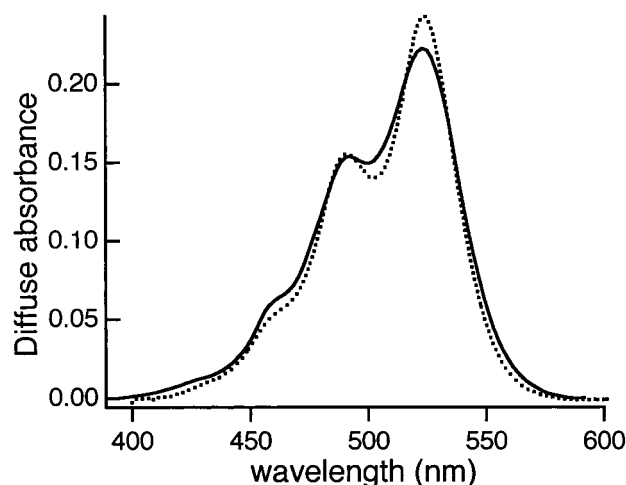


Figure 2. Diffuse absorbance spectrum (solid curve) measured for a stack of 10 equivalent sample coatings so weakly dyed with simple cyanine to allow the dye molecules to be incorporated exclusively as monomers into the emulsion layer. For reference the dotted curve duplicates the shape of the absorption spectrum of monomer solution of simple cyanine, scaled to yield total peak area equal to that of the solid curve.

coefficient of the extra absorbing species can be simply scaled linearly to the diffuse absorbance, as defined by $\log T_0/T$. In practice, this relationship can be verified by mixing in the emulsion a reference light-absorbing species with a known absorption spectrum. Also, by comparing the diffuse absorbance measured for this reference species with the absorbance of the same species but in a scattering-free medium, one can quantitatively estimate the extent to which the scattering affects the effective light path length in the emulsion coating. For this purpose, we have chosen a simple cyanine dye, 1,1'-diethyl-2,2'-cyanine bromide (used as received from Nippon Kankō Shikiso Co.), dissolved in a mixed solvent of singly distilled water and ethanol (Nacalai Tesque, Inc., guaranteed reagent grade) of 1:1 volume ratio to the concentration of 1–25 μM . The emulsion coating was bathed in this solution for 10 min at 20 °C, quickly rinsed by water, and dried; thereby, the dye molecules could be incorporated into the emulsion layer mostly as monomers and partly as dimers or higher aggregates depending on the dye concentration.

Desensitizing Dye. The photoinduced Ag cluster formation in emulsion grains is strongly suppressed by adsorption of what are known as desensitizing dyes,¹⁸ which are capable of removing photoelectrons from the conduction band of silver halide. In one of the experiments reported in this paper we have used a sample dyed with a typical desensitizing dye, phenosafranine (purchased from Nippon Kankō Shikiso, Co.). The dyeing procedure was similar to that described above for the simple cyanine and involved 10^{-4} M dye solution in the mixed water and ethanol solvent additionally containing 10^{-3} M KBr.

Results and Discussion

Spectrometer Calibration. The solid curve in Figure 2 shows a diffuse absorbance spectrum measured for a sample that was so weakly dyed (by using 1 μM dye solution) with simple cyanine that the dye molecules were incorporated into the emulsion layer exclusively as monomers. The spectrum here was obtained by stacking 10 equivalent coatings together in front of the photomultiplier, but the peak diffuse absorbance is still only slightly larger than 0.2 because of the low dye content.

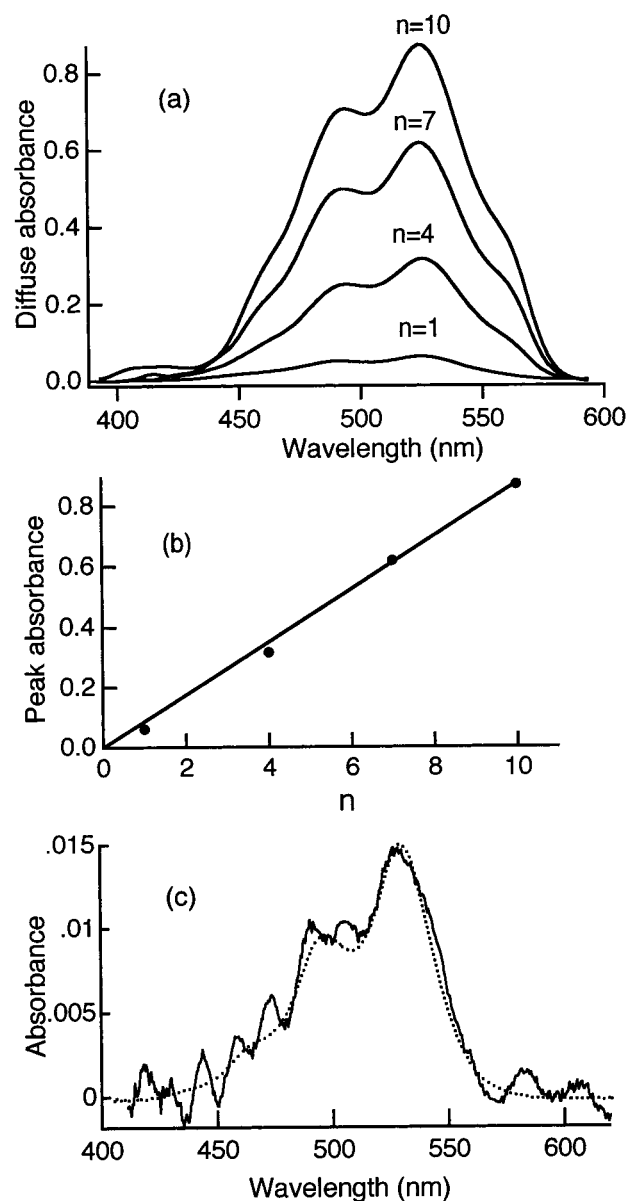


Figure 3. (a) Series of diffuse absorbance spectra taken for samples also dyed with simple cyanine but with a considerably higher dye content than that in Figure 2, as a function of the number (n) of coatings layered in the sample stack. Comparison with Figure 2 gives clear indication of partial aggregation of dyes. (b) Relationship between the peak absorbance at ~ 525 nm in (a) and the number (n) of sample coatings stacked together. (c) Dye absorption spectrum (solid curve) of the same coating as used in (a) but after processing with a gelatin-hardening acidic fixer; thereby, the AgBr grains rapidly dissolve, leaving all dye molecules in a scattering-free gelatin matrix. The spectrum can be fitted by that of monomeric dye solution (dotted curve) and no longer retains the aggregate bands.

For comparison, the dotted curve in Figure 2 duplicates the shape of the absorption spectrum of the same dye in its monomer solution in the mixed water/ethanol solvent, its vertical scale being adjusted so as to give an equal peak area to that of the solid curve. Except for a noticeable peak broadening in the solid curve, which we attribute to a matrix effect, the two curves reasonably agree with each other. Figure 2 thus gives support for the assumed linearity in the relationship between the diffuse absorbance and the absorption coefficient of the extra absorbing species.

Additional support for this simple relationship comes also from Figure 3a, which shows a series of diffuse absorbance

spectra taken also for a dyed sample but with a considerably higher dye content (bathed in 10 μM dye solution) as a function of the number of coatings layered in the sample stack. Partial aggregation of the dyes incorporated in the emulsion layer is now clearly visible in the spectra. It can be seen that all the spectra have identical shapes regardless of the number of coatings, and as shown in Figure 3b, the peak diffuse absorbance at 525 nm increases approximately linearly with the number of coatings stacked together. In other words, the diffuse absorbance measured in our optical configuration approximately satisfies Lambert's law for the scattering samples, being rationalized only when the diffuse absorbance is correlated linearly to the absorption coefficient.

It is clear that the strong light scattering by the AgBr grains substantially increases the effective light path length in the emulsion coating. To determine how this effective path length differs from the geometrical thickness of the emulsion coating, we need a reference absorption spectrum for the same amount of dyes in unit area but dispersed in a nonscattering medium. We have obtained this reference spectrum by processing the dyed coating with a gelatin-hardening acidic fixer;¹⁹ thereby, the AgBr grains are rapidly dissolved out to the solution leaving all the dye molecules behind in the residual, nonscattering, gelatin matrix. That no appreciable amount of dyes escaped into the fixer was confirmed by spectrophotometric analysis of the solution after the above treatment. The dye molecules were so strongly held in the emulsion layer that the opposite method in which we attempted to extract the dye molecules into an ethanolic solvent did not prove to be promising. A typical example of the spectra measured in this way is shown in Figure 3c. The spectra were affected more or less strongly by the interference effect associated with the thin gelatin layer but could be reasonably fitted by the spectrum taken for a monomeric dye solution, thus no longer retaining the aggregate bands. Therefore, quantitative comparison between parts a and c of Figure 3 has to be done in terms of the integrated (over the frequency or wavenumber) absorbance. For example, the peak diffuse absorbance per single coating, corresponding to the slope of the straight line in Figure 3b, is already 5.7 times as large as the peak absorbance in Figure 3c measured in the scattering-free condition. The comparison in terms of the integrated absorbance increases this factor to 7.5 ± 0.5 . Thus, the increase in the effective path length in the emulsion coating due to the scattering by the AgBr grains turns out to be quite significant.

Spectroscopy of Diatomic Ag Nuclei. Figure 4a shows a series of diffuse absorbance spectra measured for the DMAB-sensitized samples as a function of the initial DMAB concentration. Here again all the spectra were obtained for a stack of 10 equivalent sample coatings. A well-defined absorption peak centered at 455 nm is clearly resolved with a full width at half-maximum (fwhm) of ~ 50 nm or ~ 0.35 eV. Both the peak position and the peak width are virtually invariant in the whole range of the initial DMAB concentration, suggesting that the light absorption stems from a certain monomeric species produced by the reaction involving DMAB. In addition, Figure 4b shows that the peak intensity increases in proportion to the initial DMAB concentration. Given that the sensitizing reaction completes at all levels of the initial DMAB concentration, thereby forming only one particular kind of light-absorbing species, the linear relationship between the peak intensity and the initial DMAB concentration is only a natural consequence of the law of mass action. It should be also stressed that the lowest initial DMAB concentration of 0.1 mg/mol of AgBr corresponds to so weak a reduction sensitization that the

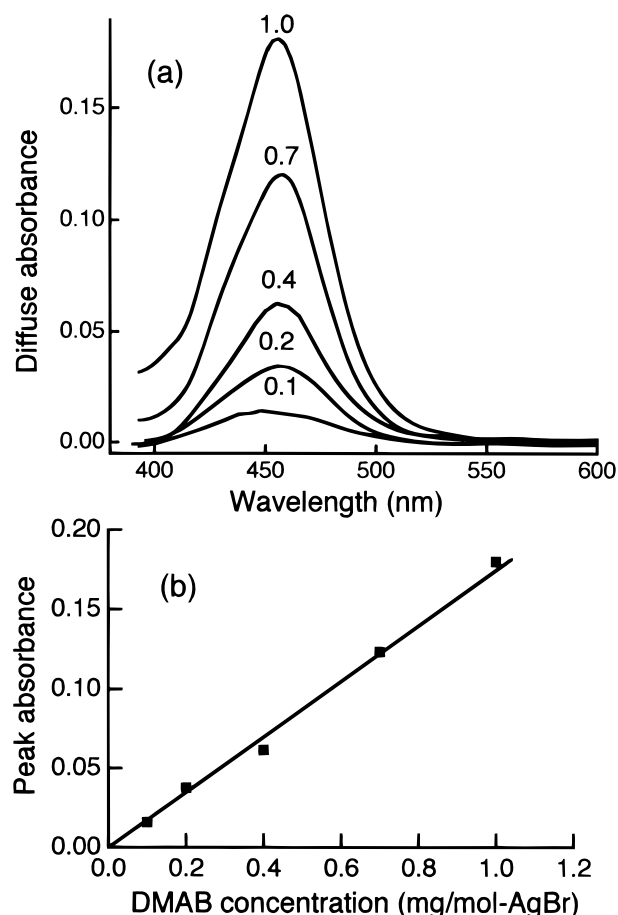


Figure 4. (a) Series of diffuse absorbance spectra taken for DMAB-sensitized samples, all being taken by using a stack of 10 equivalent sample coatings, as a function of the initial DMAB concentration. (b) Approximately linear relationship between the peak absorbance at ~ 455 nm and the initial DMAB concentration.

corresponding photographic sensitivity increased only by a factor of 1.3 as compared to that of the primitive emulsion. Thus, the 455 nm absorption band observed here is never a feature associated with only heavily reduction-sensitized samples.

The identity of the species responsible for the 455 nm absorption can be narrowed down further by examining another series of diffuse absorbance spectra taken for the H_2 -sensitized samples, as shown in Figure 5. Note that this important form of reduction sensitization in a dry condition was not examined in the previous diffuse reflectance studies^{10–12} involving thick liquid layers of AgBr emulsion. In Figure 5 it can be seen that the same 455 nm absorption band as produced by the DMAB sensitization is closely reproduced, despite the considerable difference in the reaction mode (wet versus dry) and in the form of reducing agent (DMAB versus molecular hydrogen). Here the peak intensity increases linearly with the reaction time (Figure 5b), which is another reasonable relationship considering that the reducing agent in this case is present in much excess in the form of 1 atm of pure H_2 gas.

In the case of H_2 sensitization, possible reduction products that potentially give rise to the visible light absorption are more limited than in the case of DMAB sensitization and must be either small Ag clusters or some reduced form of gelatin. The latter possibility is easily ruled out, however, by noting a couple of rather trivial observations. First, a similar H_2 treatment but of a plain gelatin layer produced no such visible absorption. Second, when the AgBr grains were fixed out from the sensitized emulsion coating, the 455 nm absorption disappeared concur-

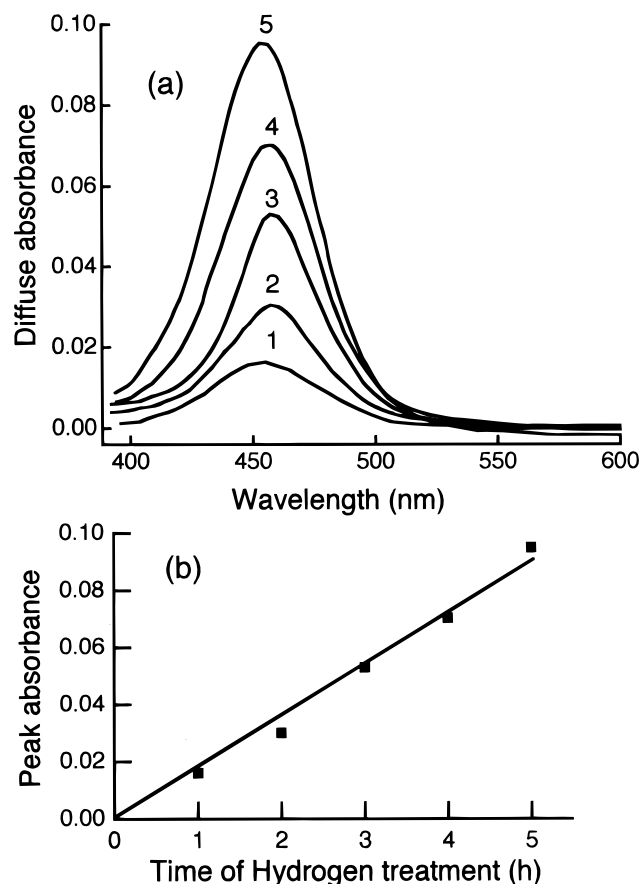


Figure 5. As in Figure 4 but for H_2 -sensitized samples, as a function of the time of hydrogen treatment.

rently, indicating that the absorbing species are so small and so closely associated with the AgBr grains that they are easily carried away together with the dissolving AgBr. An extremely small Ag cluster deposited on the AgBr grain surface best accounts for this behavior.

That the reduction sensitization of AgBr emulsion leads to the formation of only one size of Ag cluster, most likely the Ag_2 dimer, has been given much support by other groups already.^{10,11,14} In view of the crucial importance of this fact, however, it seems that we are also required to provide some supporting argument of our own. First of all, as will be discussed later in more detail, the observed range of diffuse absorbance can be rationalized only if such small Ag clusters are present on each grain surface at the level of number density far exceeding 10^3 /grain. Nevertheless, all the reduction-sensitized coatings studied here proved to remain almost intact upon the standard photographic development. This means that none of these Ag clusters have yet attained the size necessary to initiate or catalyze the development. Of course, the electronic properties of Ag clusters on the AgBr grain surface depend not only on the cluster size but also on what particular sites of the grain surface they are located at, as demonstrated, for example, by the comprehensive theoretical calculation by Baetzold²⁰ for the size range of Ag– Ag_4 . Thus, the standard development criterion that Ag_4 is the critical size may not necessarily be applicable to the case of chemically produced Ag clusters. However, it should be also noted that Ag_4 has been shown to be the most likely critical size to initiate development not only for the photolytic Ag clusters on $AgBr^{5-7}$ but also for those physically deposited on $AgBr^8$ and even on SiO_2 substrate.⁴ Thus, it seems that chemically produced Ag clusters may also initiate development at their size comparable to, if not identical

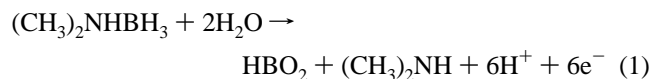
with, Ag_4 . Considering that presence of just one such cluster on the grain surface is sufficient to initiate development, it is highly unlikely that Ag_4 and larger clusters represent some significant fraction of the many thousands of Ag clusters produced on each grain surface.

On the smaller side, it is well established that atomic Ag centers are so unstable that they decompose thermally into a conduction electron and an interstitial silver ion on the time scale of at most a few seconds at room temperature.²¹ It has also been suggested in our previous experimental work⁶ that three-atom Ag clusters (Ag_3), the first odd-numbered cluster in the small Ag_n series, are considerably less stable than diatomic nuclei (Ag_2) in a redox environment. This stability order is also consistent with the greater dissociation energy (1.6 eV) of Ag_2^{22} than that (0.96 eV) of Ag_3^{23} and may also be understood in the framework of the simple electronic shell model,^{1,2} because the first shell closing with spin-paired electrons occurs at the diatomic size. It thus appears that Ag_2 is virtually the only possible species that can be produced in so large a number density as noted above without activating the AgBr grains for the photographic development. We therefore conclude that the 455 nm absorption band represents one of the characteristic electronic transitions associated with chemically produced diatomic Ag nuclei on the AgBr grain surface.

Then the observed absorption peak wavelength of 455 nm may be compared to those assigned to the Ag_2 molecule in the gas phase (435 nm)^{24,25} and in a low-temperature Kr or Xe matrix (390 nm),²⁶ corresponding to the lowest-energy electronic transition between the 5s-derived $2\sigma_g$ (highest occupied) and $2\sigma_u$ (lowest unoccupied) molecular orbitals. The corresponding data reported for the low-temperature Ar matrix (412/388 nm²⁶ or 443/388 nm²⁷) are a little more complicated because of the apparent splitting of the absorption band, due to the multiple trapping sites for the Ag_2 molecules in the Ar matrix. In any case the present result exhibits a considerable amount of red shift by 20–60 nm (0.13–0.47 eV) as compared to the transition energies for the gas-phase and matrix-isolated Ag_2 molecules. This is, however, not particularly surprising considering that our diatomic Ag nuclei are adsorbed on the ionic crystal, which comprises homonuclear Ag^+ cations plus Br^- anions with relatively large electronic polarizabilities. Besides, we also have to make allowance for a potential increase in the internuclear distance by adsorption, which obviously causes a smaller energy gap between the $2\sigma_g$ and the $2\sigma_u$ molecular orbitals. For instance, according to the SCF-X α -SW calculation by Ozin and co-workers,²⁸ less than 15% increase in the internuclear distance would fully account for the observed amount of red shift.

The position of the 455 nm absorption band also seems to be in reasonable agreement with the peak position (442 nm) in the excitation spectra of the low-temperature luminescence studied by Marchetti and co-workers,¹⁴ considering the large difference in temperature. As mentioned earlier, concerning the appreciably longer wavelength (~ 475 nm) peak found in the diffuse reflectance studies,^{10–12} Marchetti and co-workers suggested that it could be associated with rather heavily reduction-sensitized samples, not necessarily with Ag_2 dimers.¹⁴ In light of our present result, however, we would rather suggest that liquid layers and coated ones may offer different dielectric environments for the Ag_2 molecules at room temperature, the former causing a further red shift in the transition energy. At least in the work of Hailstone and co-workers^{11,12} the ~ 475 nm absorption signal was so well-defined in a wide range of sensitizer concentrations that it is hard to assign the signal to any clusters other than Ag_2 molecules.

An even more useful comparison with the gas-phase or matrix-isolated Ag_2 molecules is with respect to the oscillator strength. There have been experimentally no reliable data for this quantity, but according to the molecular orbital calculation just quoted above,²⁸ the $2\sigma_g \rightarrow 2\sigma_u$ transition carries about one-third (0.64) of the total oscillator strength of 2.0, associated with the paired electrons in the highest occupied $2\sigma_g$ orbital. The other two-thirds account for the stronger transition into the upper-lying $2\pi_u$ state, appearing in the ultraviolet region around 270 nm for which we had no experimental access in the present measurement. In the present case, however, we can estimate the experimental oscillator strength for the 455 nm absorption from Figure 4, under the assumption that each DMAB molecule can release six electrons according to the following scheme.^{29–31}



Furthermore, if all the electrons released by the above reaction are consumed to reduce silver ions to the Ag_2 molecules, the corresponding number of Ag_2 amounts to 4.5×10^4 for each AgBr grain (or $5.1 \times 10^{-11} \text{ mol/cm}^2$) in the case of the highest DMAB concentration of 1.0 mg/mol of AgBr. Note that this number of Ag_2 molecules corresponds to about 1% of the total number of ions on the (111) surfaces of a $0.45 \mu\text{m}$ octahedral AgBr grain, which is calculated to be 4.2×10^6 . From this concentration of Ag_2 molecules and from the integrated absorption strength for the spectra shown in Figure 4, we estimate the net oscillator strength of the 455 nm absorption to be 0.5 ± 0.1 , the error arising from both the uncertainty in the integrated peak area and that in the factor (7.5 ± 0.5) of scattering-induced magnification in the effective light path length. Since we have assumed the maximum yield for the formation of Ag_2 molecules by DMAB, the calculated oscillator strength could rather be a lower limit. Even so, it seems that the value ~ 0.5 compares very favorably with 0.64,²⁸ as theoretically calculated for the isolated Ag_2 molecule. Thus, in terms of both the absorption peak wavelength and the oscillator strength, there are no inconsistencies for the identification that the 455 nm absorption stems from the lowest-energy electronic transition involving the Ag_2 molecules adsorbed on the AgBr grain surface.

Photobleaching of Diatomic Ag Nuclei. That our Ag_2 nuclei are not simply trapped in the emulsion layer but really adsorbed on the AgBr grain surface can be shown more explicitly in terms of the photobleaching of the 455 nm absorption band, being closely correlated with the photoinduced Ag cluster formation. The series of diffuse absorbance spectra shown in Figure 6 were obtained by repeated data acquisition for a DMAB-sensitized sample (initial DMAB concentration, 0.7 mg/mol of AgBr) with a relatively heavy 395 nm exposure at the photon flux of $\sim 7 \times 10^{13}/\text{min}$ for 3–60 min between two successive scans. The change of the spectrum was gradually slowed, requiring significantly longer 395 nm exposure in later stage to cause a noticeable change. The 395 nm exposure has a negligible overlap with the 455 nm molecular absorption and causes relatively strong intrinsic transition in AgBr producing free electrons and positive holes. In Figure 6, a new broad absorption that grows at around ~ 600 nm no wonder represents the surface plasmon excitation associated with the photolytic Ag clusters. Figure 6 shows that this plasmon band grows at the expense of the 455 nm absorption with a clear isosbestic point at ~ 480 nm. The occurrence of an isosbestic point for the combination of plasmon and molecular absorptions is particularly impressive and suggests that the photolytic Ag

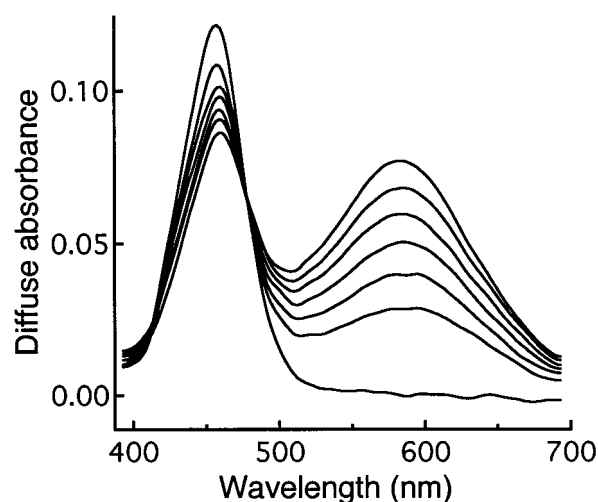


Figure 6. Change of diffuse absorption spectrum of DMAB-sensitized sample (initial DMAB concentration 0.7 mg/mol of AgBr) by relatively heavy 395 nm exposure of the sample at photon flux of $\sim 7 \times 10^{13}/\text{min}$ for a total of 3, 8, 18, 38, 78, and 138 min. Bleaching of the 455 nm absorption band and gradual growth of plasmon absorption band due to photolytic Ag clusters occur concurrently with a clear isosbestic point at ~ 480 nm.

clusters grow at the expense of the Ag_2 nuclei in a fixed mass ratio, satisfying a sort of mass action law. This relationship can be best rationalized by the scheme that the Ag_2 nuclei preferentially (and irreversibly) react with positive holes generated by the intrinsic absorption of the host AgBr grains, and the equal number of photoelectrons thus made free from recombination are subsequently consumed for the growth of the photolytic Ag clusters. Since there are many thousands of Ag_2 nuclei on each grain surface as estimated already, sufficiently large Ag clusters to exhibit the surface plasmon excitation can indeed grow according to this scheme. That small Ag clusters produced by reduction sensitization preferentially trap holes is an idea given a number of experimental supports already,^{9,11} but Figure 6 adds much more to this idea because such a close mass relationship between the formation of photolytic Ag clusters and the bleach of chemically produced Ag clusters has not been proved before.

Additional support for this hole-removing function of the Ag_2 nuclei is shown in Figure 7. Here the series of spectra were taken repeatedly in the similar exposure condition as in Figure 6 but for another sample dyed with phenosafranine in advance. To mask the strong overlapping absorption due to the phenosafranine dye, the spectra here are drawn in a differential scale. Phenosafranine is known as a typical desensitizing dye that irreversibly traps photoelectrons from the host AgBr grain, thereby strongly counteracting the formation of photolytic Ag clusters. As a result, growth of distinct plasmon absorption as seen in Figure 6 is no longer visible in Figure 7, but the 455 nm absorption of the Ag_2 nuclei is steadily bleached due to the reaction with positive holes.

Origin of Size Selectivity. The Ag_2 nuclei produced by the chemical reduction of AgBr grains by DMAB or molecular hydrogen have to be discriminated in at least two important aspects from another kind of diatomic species that must form in the early stage of the photoinduced Ag cluster formation and subsequently grows to be large enough to initiate or catalyze the photographic development. First, the chemically produced Ag_2 nuclei, because of their strong reactivity with positive holes as shown above, cannot play such precursory roles in the imaging process. Second, the fact that many thousands of Ag_2

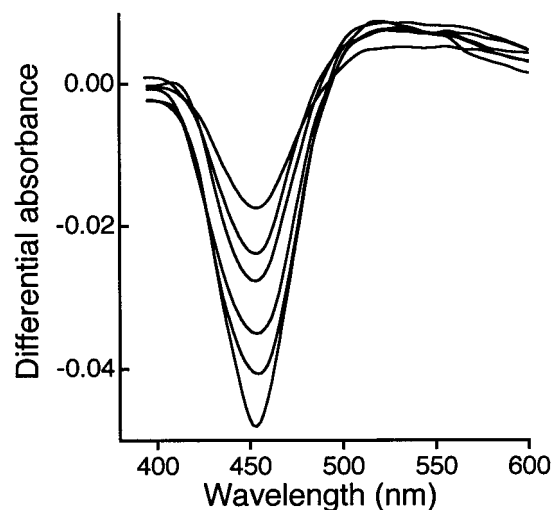


Figure 7. As in Figure 6 but for DMAB-sensitized sample (initial DMAB concentration 0.7 mg/mol of AgBr) dyed with phenosafranine (desensitizing dye) in advance, drawn in differential scale to mask the strong overlapping absorption signal due to phenosafranine dyes. The 455 nm absorption band is steadily bleached while growth of plasmon band is strongly suppressed.

nuclei can be size-selectively produced on a single AgBr grain surface in the chemical reduction mode is diametrically opposed to the concentration principle applied to the imaging process. It is known that optimally sensitized AgBr grains become developable by absorption of less than 10 photons/grain.¹⁶ This is impossible unless virtually all the corresponding photoelectrons are concentrated to produce a single photolytic Ag cluster somewhere on the grain surface.

The difference apparently stems from the different sources of electrons; photoelectrons versus reducing agents having no ability to inject electrons into the conduction band of AgBr. In the case of reduction sensitization, therefore, the formation of the diatomic Ag nuclei is considered to occur through a heterogeneous surface reaction between the Ag^+ ions on the grain surface and the reducing agents. In this context, it should be also noted that the formation of the Ag_2 nuclei proceeds far more efficiently on the octahedral AgBr grains with (111) crystal surfaces than for cubic AgBr grains with (100) surfaces. We have also obtained a series of coated layers of DMAB-sensitized cubic AgBr emulsions with approximately the same grain volume as that for the octahedral sample but failed to detect any absorption signal associated with Ag_2 molecules even after the samples had been additionally subject to the hydrogen treatment. Note that Marchetti and co-workers¹⁴ have also failed to detect the low-temperature emission bands associated with Ag_2 molecules in the case of AgBr microcrystals having only (100) surfaces.

An ideal (111) surface of AgBr, which consists of only Ag^+ or Br^- ions arranged with a hexagonal symmetry, is unlikely to occur in the real system. In their earlier model Hamilton and Brady thus proposed an incomplete (111) surface, where Ag^+ ions half in number of those in a complete (111) plane form a hexagonal superstructure on the (111) lattice of Br^- ions.³² In this way all the (111) surfaces become equivalent, the total charge neutrality being maintained at the same time. On the other hand, for the octahedral AgBr emulsion grains precipitated under relatively high pAg above ~ 8.0 the grain surface is naturally expected to become rich in Br^- , though the excess negative charge has to be eventually balanced by some counter charge, which does not necessarily have to be associated with Ag^+ ions. There are then two alternative ways to realize

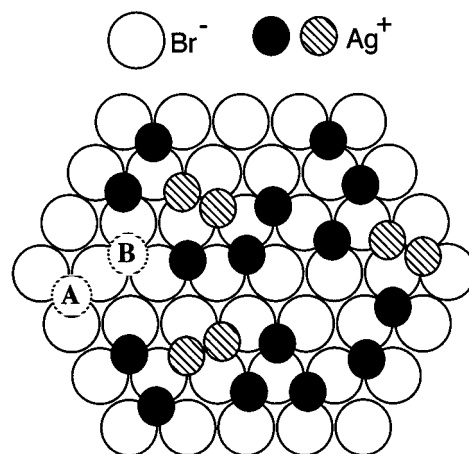


Figure 8. Structural model of the (111) surface of octahedral AgBr microcrystal, more realistic at higher temperature. Ag^+ ions that are short in number to complete an ideal (111) lattice are distributed with no special order over the two equivalent groups of 3-fold hollow sites (labeled A and B) of the underlying (111) lattice of Br^- ions. Close pairs of Ag^+ ions that may occur in this configuration; possible candidates to be reductively transformed to Ag_2 molecules are shown by hatched circles.

the net excess of Br^- ions relative to Ag^+ ions. One is to modify the incomplete (111) plane of Ag^+ ions in the outermost position, so as to reduce the number of Ag^+ ions to less than a half of that in a complete (111) plane. Alternatively, one may put in the outermost position an incomplete (111) plane of Br^- ions, instead of Ag^+ ions, more than half in number of those in a complete (111) lattice. We prefer the former model here because it seems extremely difficult to allow an effective heterogeneous chemical reduction of surface Ag^+ ions when none of them can be found in an incomplete (111) lattice.

It should be noted that, in such an incomplete (111) lattice of Ag^+ ions far less in number than required to complete an ideal (111) plane, there seems no particular reason for the Ag^+ ions to arrange in such a high structural order as assumed by Hamilton and Brady, particularly inside the emulsion layer rich in various adsorbates. Figure 8 depicts an alternative model of the (111) surface with a more disordered arrangement of Ag^+ ions. The point is that they still predominantly occupy the 3-fold hollow sites of the underlying (111) lattice of Br^- ions, but there is no preference as to which one of the two equivalent groups of the hollow sites (labeled A and B in Figure 8) is taken by Ag^+ ions that are too short in number to make up a complete (111) lattice. In other words, one may find a number of stacking faults in such an incomplete (111) plane on the grain surface. In this circumstance (particularly at the elevated temperatures at which the actual sensitizing reactions proceed), one may also note the possibility of occurrence of such a close pair of Ag^+ ions as separated from each other by ~ 2.3 Å, which is the nearest distance between the two adjacent hollow sites and incidentally close to the internuclear distance ($2.5\text{--}2.8$ Å)²⁸ expected for an Ag_2 molecule. In Figure 8 these Ag^+ ions are discriminated by hatched circles from others that are represented by closed circles. Of course, such a pairing of Ag^+ ions should not be an energetically favored process, thus allowed only locally and/or temporarily if any. Clustering of more than two Ag^+ ions is even more disfavored and may be disregarded.

Correct evaluation of the required energy for the cation pairing would be most helpful to judge the validity of the proposed structural model, but the inherent complexity associated with the grain surface presently allows only an order-of-magnitude estimate at best. In this respect it should be noted

first that the required energy in question is never associated with the process involving just a couple of Ag^+ ions initially separated by an infinite distance. As can be inferred from Figure 8, even in such an incomplete (111) plane there are still a significant number of Ag^+ ions regardless of occurrence of the pairing event. More specifically, the nearest-neighbor distance between Ag^+ ions in their complete (111) plane is obviously equal to the primitive lattice spacing, 4.08 Å. Even if the total number of Ag^+ ions is reduced to about a half to make an incomplete (111) plane, the corresponding average nearest distance, increased by a factor of $\sqrt{2}$, is still as small as 5.8 Å. The resulting large repulsive Coulomb interactions among these Ag^+ ions are compensated primarily by the negative charge background due to the underlying (111) lattice of Br^- ions, thus each Ag^+ ion experiencing a net attractive Madelung potential. The energy required to form one single pair of Ag^+ ions in this situation cannot be determined by the interaction just between the paired ions but should be defined by the net change in the collective Coulomb interactions involving all the nearby Ag^+ ions. The net repulsive interaction will increase as a result of the cation pairing only ~ 2.3 Å apart, but its magnitude will probably be no greater than several electronvolts. Moreover, this energy has to be corrected for another important effect, i.e., a counteracting dielectric stabilization. The cation pairing causes some higher localization of positive charge, which in turn induces a new dielectric polarization of the surrounding ions. The polarization energy acquired here is analogous to the hydration energy of ions, which in the case of simple spherical ions in a homogeneous dielectric medium is given by the square of the ion charge divided by twice the ionic radius if the dielectric constant of the surrounding medium is sufficiently greater than unity (all in cgs units).³³ Though the exact polarization energy in our far more complexed context involving the grain surface is not very clear, it may possibly reach a few to several electronvolts for a center with an effective local positive charge of unity and an effective radius of ~ 2 Å. Note that the effective dielectric constant at the grain surface, approximated by half of that in bulk AgBr, is still much greater than unity. If so, the overall energy required to form a pair of Ag^+ ions, as illustrated in Figure 8, has a fair chance to go down to the order of 1 eV or even less. For 1 eV, e.g., the Boltzmann factor at 50–70 °C (the temperatures for our sensitizing treatments) takes a value of the order of 10^{-15} . Thus, for a typical frequency factor of $\sim 10^{12} \text{ s}^{-1}$ and, besides, in the presence of $\sim 10^6$ Ag^+ ions on each grain surface, the cation pairing may occur frequently over the time scale of our sensitizing treatments, about an hour to several hours.

The occurrence of such a close pair of Ag^+ ions on the grain surface, though yet speculative, opens a way for the selective Ag_2 formation by their virtually simultaneous reduction (or ones in rapid succession) to a single Ag_2 molecule, with the levels deep enough to receive two electrons from the reducing agents. The alternative, step-by-step, reduction mechanism allowing the formation of atomic silver centers as intermediates never seems to rationalize the size-selective formation of many thousands of Ag_2 molecules on a single grain surface without growth of a higher aggregate. The proposed reduction mechanism naturally requires a two-electron donor as the reducing agent. This condition is met by molecular hydrogen. On the other hand, the chemistry of DMAB is still not very well understood, our knowing only that six electrons can be released at maximum. We presume, however, that the two-electron-donating reaction also prevails in this case, thereby the six electrons being consumed in three independent steps to produce three Ag_2

molecules. It is hoped that, including the validity of the proposed mechanism, the unique heterogeneous reaction involving the AgBr grain surface could be illuminated further on an atomistic level.

Summary and Conclusions

A diffuse transmittance spectroscopy that utilizes a large-area photodetector in contact with a scattering sample has been proved to be a simple and reliable method to study a weak absorption of the species embedded in a highly scattering medium. The method was successfully applied to illuminate the unique spectroscopic and photochemical properties of the diatomic Ag nuclei produced on AgBr microcrystals.

For both kinds of octahedral AgBr grains subjected to a wet mode of reduction with dimethylamine borane (DMAB) and to a dry mode of reduction with molecular hydrogen, a common absorption band centered at 455 nm was clearly resolved with the intensity proportional to the initial DMAB concentration or to the time of hydrogen treatment. Only diatomic Ag nuclei, being selectively produced in number density of the order of 10^4 per each AgBr grain, reasonably accounts for this molecular absorption. Though noticeably red-shifted by 20–60 nm, the peak absorption wavelength is indeed comparable to those assigned to the lowest-energy $2\sigma_g \rightarrow 2\sigma_u$ transition of the gas-phase or matrix-isolated Ag_2 molecules. The estimated oscillator strength for the 455 nm absorption band, ~ 0.5 , also compares favorably to that (0.64) theoretically calculated for an isolated Ag_2 molecule. It has also been shown that the 455 nm absorption band is easily photobleached because these Ag_2 molecules adsorbed on the AgBr grain surface preferentially react with positive holes. Moreover, the photolytic Ag clusters grow at the expense of the Ag_2 nuclei in a fixed mass ratio, satisfying a sort of mass action law.

The size-selective formation of many thousands of Ag_2 nuclei on a single grain surface requires a special mechanism of heterogeneous chemical reduction. We have proposed that close pairs of Ag^+ ions can occur on the octahedral AgBr grain surface where Ag^+ ions form an incomplete (111) plane above that of halide ions and that these paired ions are reduced simultaneously or in rapid succession to a neutral Ag_2 molecule by receiving two electrons from multivalent reducing agents.

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