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(Physique appliquée/*Applied physics*)

AGRÉGATS COMME PRÉCURSEURS DES NANO-OBJETS
CLUSTERS AS PRECURSORS OF NANO-OBJECTS

The role of silver clusters in photography

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Abstract The principle of silver photography is based on the photosensitivity of minute silver halide crystals. The light generates clusters of a few silver atoms on the crystals. Their ensemble constitutes the latent image of extremely weak intensity and invisible. The development consists of converting chemically into metal particles the crystals containing a cluster with a supercritical number of photoinduced silver atoms and of transforming catalytically the latent image into a visible picture. Crystal doping by a selective anti-oxidant scavenger permits one to avoid the loss of electrons, which otherwise recombine rapidly with holes, and to reach the integral quantum yield of atoms produced per photon absorbed. ***To cite this article: J. Belloni, C. R. Physique 3 (2002) 381–390.*** © 2002 Académie des sciences/Éditions scientifiques et médicales Elsevier SAS

Le rôle des clusters d'argent en photographie

Résumé Le principe de la photographie argentique est basée sur la photosensibilité de petits cristaux d'halogénure d'argent. La lumière génère des clusters de quelques atomes d'argent sur les cristaux. L'ensemble constitue l'image latente invisible d'intensité extrêmement faible. Le développement consiste à convertir chimiquement en particules d'argent métallique les cristaux contenant un cluster de nucléarité supercritique d'atomes d'argent photoinduits et à transformer catalytiquement l'image latente en une image visible. Le dopage des cristaux par un capteur sélectif anti-oxydant permet d'empêcher la perte des électrons, qui sinon se recombineraient rapidement avec les trous, et d'atteindre le rendement quantique intégral en atomes formés par photon absorbé. ***Pour citer cet article : J. Belloni, C. R. Physique 3 (2002) 381–390.*** © 2002 Académie des sciences/Éditions scientifiques et médicales Elsevier SAS

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La photographie argentique, noir et blanc ou couleur, repose sur la formation primaire par la lumière, dans des cristaux d'halogénure d'argent, de clusters d'argent dont le nombre d'agrégation n est de quelques atomes. Le développement à l'aide d'un révélateur donneur d'électrons permet de poursuivre la réduction des ions d'argent autour des clusters jusqu'à transformation totale du cristal en particule d'argent noire.

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Mais le phénomène ne se produit pas dans un cristal peu ou pas exposé (nombre d'agrégation sous-critique) en raison d'un seuil thermodynamique. Cette discrimination entre les cristaux produit le contraste de l'image. Grâce à des expériences de cinétique rapide simulant le développement photographique, la discrimination et l'existence du seuil ont pu être expliquées par la différence variable, positive ou négative, entre le potentiel de Fermi des clusters qui dépend de n et le potentiel du révélateur.

L'action primaire de la lumière consiste à produire dans le cristal autant de paires électron–trou (e^-–h^+) que de photons absorbés. Les électrons forment avec des ions Ag^+ les atomes du cluster. Toutefois, l'efficacité du processus est limitée par une recombinaison directe ou indirecte très importante des paires initiales (e^-–h^+). On a pu montrer comment l'addition, au moment de la précipitation du cristal, d'un dopant capable de capter sélectivement les trous pouvait accroître considérablement l'échappement des électrons et le rendement de production des atomes. Si le produit de cette capture est lui-même donneur d'électron, comme quand le dopant est l'ion formiate, le rendement atteint la valeur optimale de deux atomes par photon absorbé. Cette approche s'applique à tous les types d'émulsions argentiques.

1. Introduction

Photography, invented by Nicéphore Niépce in around 1820 [1,2], is a domain where the specificity of very small particles was early suspected, long before the detailed mechanisms of cluster reactions in the formation and in the development of the latent image were understood.

The most important concept on clusters first appeared in early sixties [3]. The theory is that an isolated atom, or a few atoms linked together in a cluster as in a molecule, possess discrete electron levels, introducing a *quantum-size effect*. It has been shown indeed that the thermodynamic properties of a metallic cluster vary with the number of atoms n which it contains, in solutions [4,5] or in the vapor phase [6–8]. The consequences for photography of these specific properties of clusters are explained here.

2. Principle of modern silver photography

Fundamentally, the actual basis of photography [9–15], black and white or color, utilizes the transformation caused in the photosensitive silver halide crystals by the influence of light reflected from the object. The photosensitive layer is constituted of a mosaic of tiny silver halide crystals surrounded by gelatine, each crystal of a few tenths of 1 µm in size, containing about 10^9 Ag^+X^- ion pairs. The crystal constitutes the smallest element of the silver image ($(2–10) \cdot 10^7$ elements in a 24×36 mm^2 film). The aim is to replace silver ions by silver atoms through the photophysical effect during the short *exposure* of the layer to the light in the camera [16]. The light effect printed on this layer results in one single cluster per crystal, generally located at the crystal edge, and containing only a few atoms, that is, much below the visibility threshold. Though the latent image obtained, which is the ensemble of crystals with clusters of variable atom numbers n (or nuclearities), is invisible, it reflects the different levels of illumination in the original scene as our eyes perceive it.

The next step of *development*, introduced by Daguerre in 1839 [17], provides an enormous amplification of the light effect, obtained through a catalytic chemical reaction, and also discriminates between crystals exposed and crystals weakly or not exposed. When the film is immersed into a bath containing the developer, which is an electron donor, only silver ions around clusters containing a number of atoms equal to or larger than a critical value n_c behave as electron acceptors. If so, the number of atoms of the cluster is increasing autocatalytically by one unit at each electron transfer from the donor (a silver cation associated with the cluster is neutralized, then a new cation is again included at the cluster surface and the sequence is repeated). The process stops when all the ions of the crystal bordered by the gelatine are reduced into silver metal. The gain is about 10^8 and the image becomes visible. From photometric measurements, the critical number of atoms required to catalyze the development was found to be of a few units (around $n_c = 3$ to 5 atoms/cluster) [18] and to decrease with the redox potential of the developer [19].

Then, the undeveloped crystals are eliminated by dissolution in the *fixing* step. Eventually, the negative photographic image results from the contrast between the variable density of the developed black grains of silver metal in the exposed parts and the transparency of the support. The positive image is obtained by exposing another film through the negative image used as a mask.

3. Silver cluster properties

The answer as to how the developer is capable of discriminating supercritical nuclearities among the cluster population lies in the latent image properties. The resolution of electron microscopy used in the past in attempts to study directly the initial steps of development on the crystal is by far not sufficient [9]. The recent advances result in fact indirectly from the improvement of techniques, allowing the study of small nuclearity clusters in other environments, namely gas phase and interface with solutions, or from simulations with theoretical models.

3.1. Cluster thermodynamics in the gas phase

Clusters in the gas phase are formed by gas aggregation sources. The sudden expansion of a population of metal atom vapor causes the coalescence of atoms into clusters and their size distribution after a given time-of-flight is determined by mass spectrometry. Under these conditions, various properties are studied. In particular, the ionization potential of silver clusters decreases at increasing nuclearity as a general trend, but also exhibits discontinuities due to the layered electron structures and fluctuations corresponding to changes in the numerical parity of the electrons [20,21]. Odd-numbered clusters are more stable against the loss of an electron than even-numbered ones (Fig. 1). These experimental results have been confirmed by theoretical calculations on the ionization potential of neutral silver clusters Ag_n and on the vertical electron detachment of negatively charged clusters Ag_n^- [22].

3.2. Mass-selected cluster deposition

An interesting approach was to prepare mass-selected silver clusters in the range of a few atoms by the molecular beam method and to deposit them on to the surface of AgBr microcrystals through soft landing, without excess energy, in order to avoid further dissociation or other side reactions [23,24]. The latent image produced by the photographic exposure process is therefore closely simulated, except that the cluster nuclearity is selected for each experiment and the same for all clusters (in contrast with the latent image where the cluster nuclearity depends on the number of photons absorbed by the crystal, that is on its location on the film). The AgBr crystals are then developed under conditions comparable with

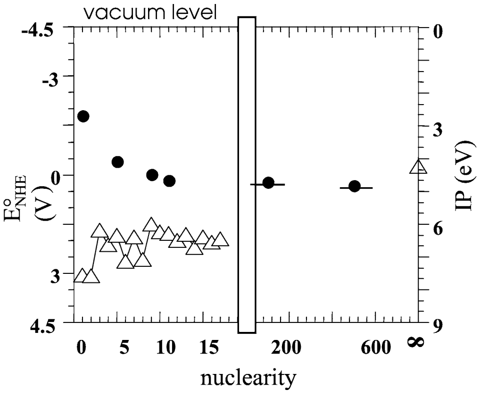


Figure 1. Nuclearity dependence of the silver cluster redox potential $E^\circ_{\mathrm{NHE}}(\mathrm{Ag}_n^+/\mathrm{Ag}_n)$ in water [31]. Comparison between E°_{NHE} (●, left ordinate scale) and the ionization potential *IP* of clusters in the gas phase (△, right ordinate scale) [20,21].

Figure 1. *Variation avec la nucléarité du potentiel redox d'agrégats d'argent* $E^\circ_{\mathrm{ENH}}(\mathrm{Ag}_n^+/\mathrm{Ag}_n)$ *dans l'eau* [31]. *Comparaison entre* E°_{ENH} (●, *ordonnées à gauche*) *et le potentiel d'ionisation des clusters dans le gaz* (△, *ordonnées à droite*) [20,21].

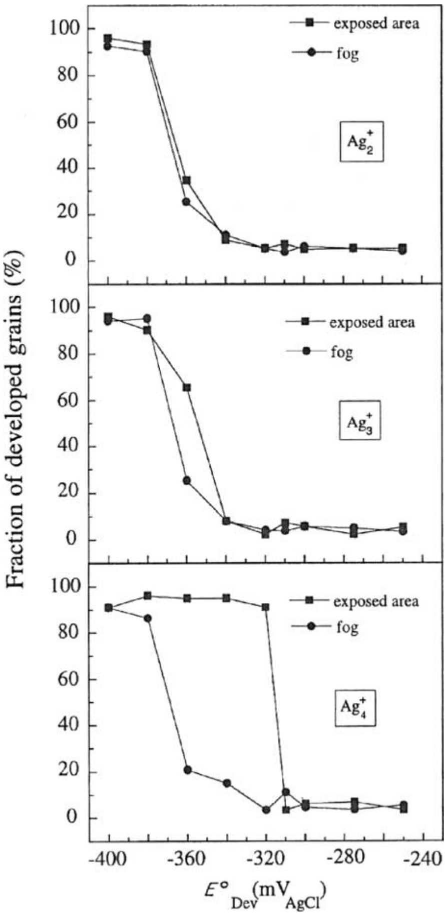


Figure 2. Dependence on the developer redox potential of the developability of AgBr crystals after deposition of mass-selected Ag$_n^+$ clusters [24].

Figure 2. *Variation de la fraction développable des cristaux de* AgBr *en fonction du potentiel redox du révélateur après dépôt de clusters* Ag$_n^+$ *selectionnés en nucléarité* [24].

photography. The developability is evaluated by counting in the electron micrograph of the substrate the fraction of crystals effectively reduced (Fig. 2). It was confirmed [24], according to conclusions accepted in photography [9], that only clusters above a critical nuclearity are indeed developed, and that this nuclearity decreases from 5 to 2 when the developer redox potential is more negative.

4. Solvated cluster growth and development

For over a century, numerous theoretical models have been proposed to explain how the supercritical clusters created by the light act as nuclei to catalyze development. The *phase* models [15,18,19] suggested that the primary photo-induced silver atoms remained dispersed within the silver bromide as in a supersaturated metastable phase, and could coalesce only when concentration produced by the developer was higher than a certain threshold value. However, the new phase had implicitly the properties of bulk silver and not of clusters. The *atomistic models* [25–28] took into account the specific character of clusters but isolated as in the gaseous phase. Since their ionizaton potential was decreasing at increasing n, the development would be expected to be restricted to subcritical clusters, in total disagreement with the facts [9]. Indeed, Trautweiler [29] suggested in his speculative model that the ionization potential of supercritical sizes should lie *above* that of the developer. However, the only data then available did not confirm this view.

Other results obtained in radiation-induced cluster studies suggested that atoms and small clusters in solution could be easily oxidized in contrast with the bulk metals [4], and that the trend of the potential nuclearity dependence could be inverted in solutions relative to the gas [30].

This nuclearity dependence of the cluster redox potential was determined by pulse radiolysis techniques [30]. A synchronized time-resolved optical absorption device is capable of measuring the fast kinetics of the transient species. The principle is to produce silver atoms by reaction in the solution of silver ions with the solvated electrons generated within the short electron pulse (typically a few nanoseconds). Because of the optical detection, the solutions are chosen insensitive to light and reducible only by the electron beam. The concentration of atoms is sufficient to allow the direct observation of their formation and coalescence (simulating the exposure step) and their reactions with an electron donor (simulating the development step). The molecule acting as a developer is also generated by the pulse from a suitable precursor and observed by its specific absorption spectrum. Actually, the electron transfer from the developer to a silver cluster Ag_n^+ is delayed as far as a certain nuclearity is not reached by coalescence, because the potential of the cluster, which in solution increases with n, should become more positive than that of the donor (or than the first potential for two-electron donors). As soon as $n \geqslant n_\mathrm{c}$ the developer concentration decays rapidly and simultaneously the silver cluster absorbance increases due to a new formation of atoms at the surface of supercritical nuclei up to the reduction of all silver ions. The kinetics indeed correspond to a coalescence of atoms and clusters after exposure combined with an autocatalytic growth of clusters by development (or repetitive sequence of Ag_n^+ neutralization and adsorption of another Ag^+). The quantitative analysis of kinetics of the reaction cascade processes is achieved through computer numerical simulation and provides turn-over rate constant and n_c values. When changing the electron donor, the critical nuclearity for which the transfer is thermodynamically possible increases with the donor potential in agreement with the contrast change observed by photographers. From the known redox potential of a series of donors, the nuclearity-dependent potential of silver clusters in water was derived (Fig. 1) [31].

The important feature of the results in Fig. 1 is that the redox potential in solution and the ionization potential of silver clusters in the vapour show opposing dependences on nuclearity. The difference ΔIP between IP and IP_solv is explained by the important free energy gained in the solvation of the positively charged cluster Ag_n^+ in solution, since that of the neutral species may be neglected, and since the cluster structure is supposed to be unchanged by ionization. For $n = 1$, $\Delta IP(\mathrm{Ag}_1) = \Delta E_\mathrm{solv}(\mathrm{Ag}^+) = 4.96$ eV. For larger n values, $\Delta IP(\mathrm{Ag}_n)$ decreases. Assuming the Born approximation for the polarization of the solvent by the charged cluster, the dependence on n of the solvation free energy ΔE_solv is given by

$$\Delta E_\mathrm{solv} = \frac{e^2}{2 \times 4\pi\varepsilon_0 r_n}\left(1 - \frac{1}{\varepsilon_\mathrm{s}}\right), \tag{1}$$

where r_n is the radius of the cluster of nuclearity n, e the electronic charge, ε_0 and ε_s the permittivity of the vacuum and of the solvent, respectively. Assuming that Ag_n is spherical, and using the same radius r_0 for both Ag^+ and Ag^0, the radius r_n may be expressed as $r_n = r_0 \times n^{1/3}$. The difference $\Delta IP(\mathrm{Ag}_n)$ between the experimental data in solution and those in the gas phase agrees fairly well with the value of ΔE_solv as a function of $n^{-1/3}$ according to the Born solvation model (Eq. (1)).

Though the environment of clusters is different in solutions and on AgBr crystals, the development occurs in both cases at the interface between the cluster and an aqueous solution and the various aspects of development revealed by the kinetic studies of solutions correspond with characteristics known to photographers. Therefore the same growth mechanism which was demonstrated for Ag_n^+ clusters in solution was proposed for cluster development in photography (Fig. 3) [30]. The discrimination induced by the developer is the consequence of a quantum-size effect on the silver nuclei redox potential (or on the Fermi potential or the ionization potential in solution) which at the aqueous interface does increase with n: the critical nuclearity n_c is determined by the threshold imposed by the first monoelectronic potential of the developer. Apart the development in photography, most nucleation and growth mechanisms based on a

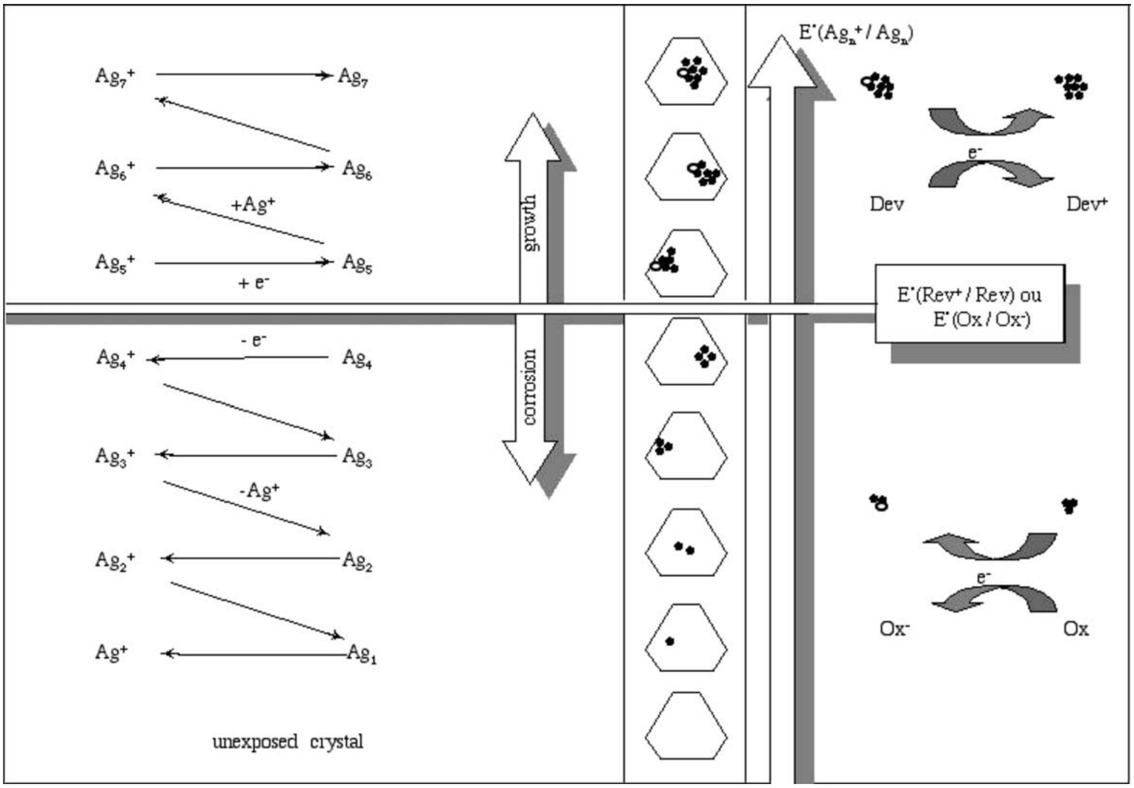


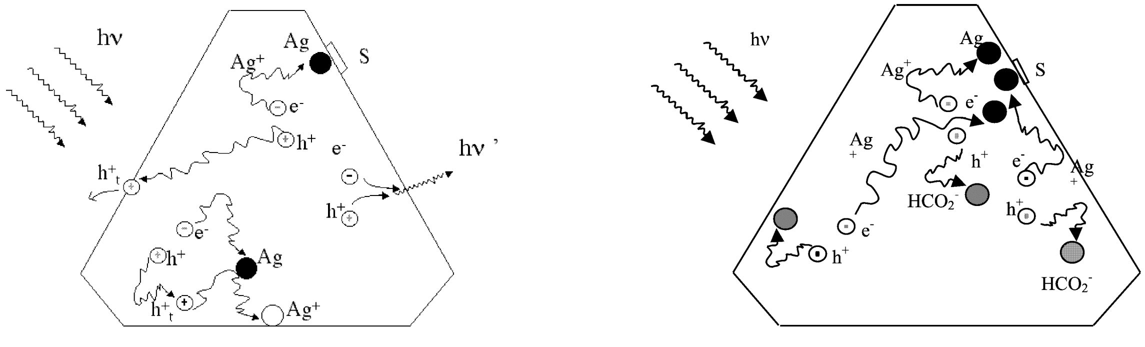
Figure 3. Photographic development mechanism. The redox potential of the latent image clusters, when in contact with a solution, increases with the number of atoms. Therefore a nuclearity threshold for development is created by the redox potential of the developer. Above the critical nuclearity, the potential $E^\circ(\mathrm{Ag}_n^+/\mathrm{Ag}_n)$ is higher than $E^\circ(\mathrm{Dev}^+/\mathrm{Dev})$ and alternate electron transfer toward Ag_n^+ and Ag^+ adsorption on Ag_n let grow the cluster autocatalytically. On the contrary, when $E^\circ(\mathrm{Ag}_n^+/\mathrm{Ag}_n)$ is lower than $E^\circ(\mathrm{Dev}^+/\mathrm{Dev})$, corrosion of subcritical clusters takes place by oxidizing molecules, such as Dev^+ [30].

Figure 3. *Mécanisme du développement photographique. Lorsque les clusters de l'image latente sont en contact avec une solution, leur potentiel redox croît avec le nombre d'atomes. Un seuil de nucléarité pour le développement est donc créé par le potentiel redox du révélateur. Au-dessus de la nucléarité critique, le potentiel* $E^\circ(\mathrm{Ag}_n^+/\mathrm{Ag}_n)$ *est supérieur à* $E^\circ(\mathrm{Dev}^+/\mathrm{Dev})$ *et le cluster grossit autocatalytiquement par alternance de transfert d'électron vers* Ag_n *et d'adsorption de* Ag^+ *sur* Ag_n. *Au contraire, quand* $E^\circ(\mathrm{Ag}_n^+/\mathrm{Ag}_n)$ *est inférieur à* $E^\circ(\mathrm{Dev}^+/\mathrm{Dev})$, *la corrosion des clusters sous-critiques prend place par des oxydants, tels que* Dev^+ [30].

chemical reduction are likewise controlled by the nuclearity dependence of the cluster redox potential and the electron donor potential [32].

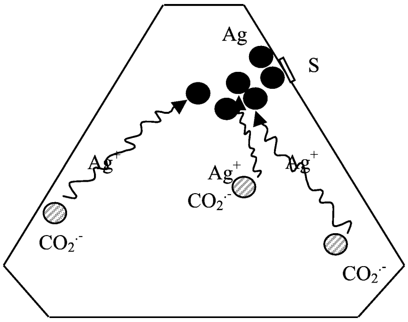
5. Latent image formation

According to the Gurney–Mott model [16], the primary light effect on AgBr is to produce as many electron–hole pairs (e^-–h^+) as photons absorbed. The hole corresponds to the electron vacancy created by the electron photoejection.[1] The electron reduces a silver cation into an atom, generally close to a sensitizer S adsorbed at the surface of AgBr (Fig. 4(a)). Then a cation adjacent to the atom and constituting a charged dimer is reduced by another electron, and so on, the result being a cluster of a few atoms. However, an important part of electrons are lost by direct recombination with the parent holes, before



(a)

(b)



(c)

Figure 4. Latent image formation. (a) Undoped AgBr crystal. (b) Formate doped crystal: hole scavenging step. (c) Formate doped crystal: reduction by formyl radical.

Figure 4. *Formation de l'image latente.* (a) *Cristal de* AgBr *non dopé.* (b) *Cristal dopé par le formiate : étape de capture du trou.* (c) *Cristal dopé par le formiate : réduction par le radical formyle.*

these diffuse to the surface where they are irreversibly scavenged by gelatine and additives. Holes are also able to oxidize the newly formed silver atoms, so counterbalancing somewhat the reduction by electrons (indirect recombination). If R is the fraction of initial pairs lost by both types of recombination, the effective quantum yield is

$$\Phi_{\mathrm{eff}} = \Phi_{\mathrm{theor}}(1 - R), \qquad (2)$$

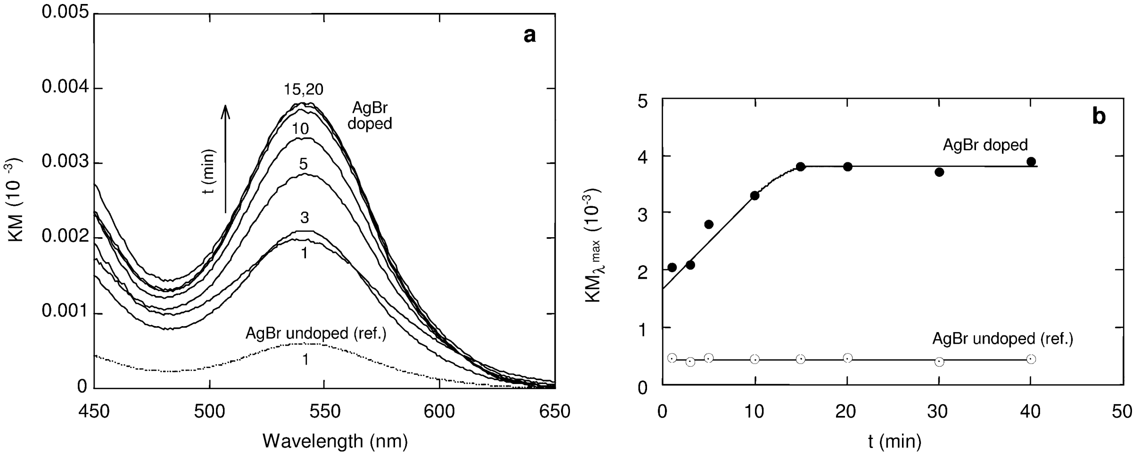
with $\Phi_{\mathrm{theor}} = 1$ pair/photon.

The yield is enhanced up to $\Phi_{\mathrm{eff}} = 0.10$–$0.30$ (the fraction R is thus 0.90–0.70) by enhancing the electron trapping in specific surface sites S (sulfide or/and gold centers). Classical developers then require for development only $n_{\mathrm{c}} = 3$ atoms per crystal or an initial number of photons $n_{\mathrm{i}} = n_{\mathrm{c}}(1 - R) = 10$ to 30 photons per crystal. Thus, apart from the absorption properties and the area of the crystal, the photosensitivity of a film depends directly on the quantum yield of the cluster formation.

A recent approach to enhance the sensitivity was to specifically scavenge the holes, faster than their possible recombination with the electrons or the atoms, with the help of a dopant [33]. In addition to a small size and an ionic character to allow its inclusion in the AgBr crystal, the dopant should obey other strict criteria concerning the redox potential. This should be that of an electron donor, in order to let the dopant scavenge the holes (Fig. 4(b)), but it should be very weak to avoid a possible spontaneous reduction (in the dark) of free Ag^+ and the production of fogging. To avoid also a possible hole-like behaviour of the dopant oxidized form, it is necessary to use as the dopant a bielectronic donor with a very negative second redox potential, so blocking any reversible oxidation. The anion formate HCO_2^- fulfills all the conditions. The redox potentials of this two-electron donor are in water $E°(\mathrm{CO}_2^-/\mathrm{HCO}_2^-) = 1.07\ V_{\mathrm{NHE}}$ and $E°(\mathrm{CO}_2/\mathrm{CO}_2^-) = -1.9\ V_{\mathrm{NHE}}$ [34].

When the dopant is included in AgBr at the relative concentration of 10^{-6} mol HCO_2^- per mol Ag^+, the emulsion is completely stable in the dark. When illuminated, its absorbance immediately at the end of a

2 s exposure is five times that of the undoped emulsion. Then it increases slowly up to a plateau and after 15 minutes the absorbance is twice that just after the exposure (Fig. 5). The first step is assigned to the fast hole scavenging by formate during the exposure (Fig. 4(b)). In the second step, each formyl radical CO_2^- resulting from the hole scavenging transfers slowly an additional electron to a silver cation, so doubling the gain (Fig. 4(c)). This photoinduced bielectronic transfer is strictly proportional to the number of photons absorbed down to the shortest exposure times.



(a) (b)

Figure 5. Absorbance of AgBr crystals at increasing times after light exposure (measured by Diffuse Reflectance Spectroscopy. The Kubelka–Munk factor is proportional to the absorbance) [33]. (a) Optical absorption spectra. (b) Kinetics of the absorbance increase at the maximum.

Figure 5. *Absorbance de cristaux de* AgBr *à temps croissants après exposition lumineuse* (*mesurée par Spectoscopie de Réflexion Diffuse. Le facteur de Kubelka–Munk est proportionnel à l'absorbance*) [33]. (a) *Spectres d'absorption optique.* (b) *Cinétique de croissance de l'absorbance au maximum.*

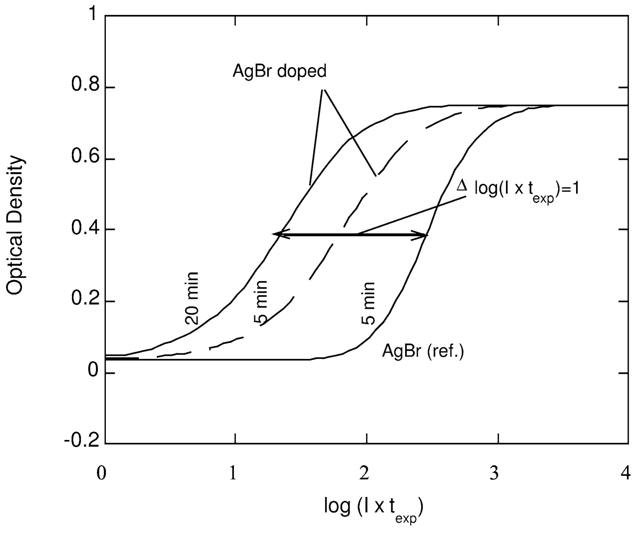


Figure 6. Sensitometry curves for formate doped emulsions developed after 5 or 20 minutes [33]. The same absorbance is observed for a number of photons absorbed 5 or 10 times less, respectively, than in the undoped emulsion.

Figure 6. *Courbes sensitométriques pour des émulsions dopées par le formiate et développées aussitôt ou après* 20 *minutes* [33]. *La même absorbance est observée pour un nombre de photons absorbés respectivement* 5 *ou* 10 *fois moindre que dans l'emulsion non dopée.*

Sensitometric tests at variable light intensity I under conditions of photography ($t_{\text{exp}} = 10^{-2}$ s, development with aminophenol and ascorbic acid) confirm the absorbance data (Fig. 6). The number of photons required to induce development of the same grain population fraction is 5 times less (immediate development) or 10 times less (development delayed by 20 minutes after exposure) in doped than in undoped emulsions. As the quantum yield is about $\Phi_{\text{eff}} = 0.2$ atom/photon in the undoped emulsion, this means that the yield is close to the theoretical limit $\Phi_{\text{eff}} = 1$ atom/photon in immediately developed doped emulsion, or that electrons escape totally to recombination ($R = 0$). When development is delayed, the yield is doubled, $\Phi_{\text{eff}} = 2$ atom/photon, due to the additional reduction produced by the formyl radical. An important sensitivity enhancement is similarly observed for dye-sensitized crystals [33].

These formate doping studies not only provide a better understanding of the mechanism of the latent image formation, but also offer a promising route for improving the performance of all kinds of silver emulsions, for black-and-white and color photography, radiography, holography, etc.

6. Conclusion

Since photography was invented, the importance of its applications constantly grew and stimulated fundamental research in optics, photophysics and photochemistry. In counterpart, new methods have been used to better understand the underlying mechanisms and numerous improvements were suggested to increase the efficiency of the photographic process. Cluster science is now also contributing to the explanation of phenomena in photography at atomic scale and to the improvement of sensitivity, up to the complete suppression of electron loss due to recombination.

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[1] The effect is equivalent to a photoejection of an electron from a Br^- site. However, the result is not a fixed Br radical but a vacancy migrating very fast from Br^- site to site.

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