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Photography: enhancing sensitivity by silver-halide crystal doping

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Abstract

The physical chemistry of the silver photography processes, exposure, development and fixing, is briefly summarized. The mechanism of the autocatalytic development by the developer of the clusters produced in silver bromide crystals during the exposure which is controlled by the critical nuclearity of these clusters was understood from pulse radiolysis studies. The effective quantum yield Φ_{eff} of photoinduced silver cluster formation in silver halide microcrystals is usually much lower than the photoionization theoretical limit $\Phi_{\text{theor}} = 1$ electron–hole pair per photon absorbed, owing to a subsequent very fast intra-crystal recombination of a part of the electron–hole pairs. In order to inhibit this recombination and favor the silver reduction by photo-electrons, the AgX crystals were doped with the formate HCO_2^- as a specific hole scavenger. First, the dopant scavenges the photoinduced hole, thus enhancing the electron escape from the pair recombination. Second, the $\text{CO}_2^{\cdot -}$ radical so formed transfers an electron to another silver cation, so that the Φ_{eff} limit may be of 2Ag^0 per photon. This Photoinduced Bielectronic Transfer mechanism is strictly proportional to the light quanta absorbed and induces an exceptional efficiency for enhancing the radio- or photographic sensitivity insofar as it totally suppresses the electron–hole recombination.

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1. Introduction

Photography is a domain where the specificity of very small particles was early suspected, long before the unique properties and the detailed reaction mechanisms of clusters were discovered. This short review describes how the specific cluster properties allow us to understand the physical chemistry mechanisms of photographic processes and to improve their efficiency (Belloni, 2002).

The most important concept on clusters first appeared in early sixties (Kubo, 1962). 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 (Delcourt and Belloni, 1973; Henglein, 1977) or in the vapor phase (Morse, 1986; Schumacher, 1988; Haberland, 1994).

2. Principle of modern silver photography

Fundamentally, the actual basis of photography, black and white or color, (Hamilton, 1977; Moisar and Granzer, 1982; Glafkidès, 1987; Tani, 1995), utilizes the transformation caused by the influence of light reflected from the object in the tiny photosensitive silver halide crystals embedded in a gelatine layer. The crystal constitutes the smallest element of the silver image and its size is about a few tenths of $1\mu\text{m}$. 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. The light effect printed on this layer results in one single cluster per crystal, generally located at the crystal edge, and containing a few atoms only, that is, below the visibility threshold. The ensemble of crystals with clusters of variable atom numbers constitutes the *latent image*. Though it is invisible, reflects the different levels of illumination in the original scene as our eyes perceive it.

The next step of *development* 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 larger than a critical value behave as electron acceptors. If so, the number of atoms of the cluster is increasing autocatalytically by one unit at each transfer from the donor and 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 $n_c = 3 - 5$ atoms/cluster) (Moisar, 1986) and to decrease with the redox potential of the developer (Malinowski, 1980). This was confirmed by experiments on deposition on to the surface of AgBr microcrystals through soft landing of mass-selected silver clusters in the range of a few atoms, produced by the molecular beam method, and then developed under conditions comparable with photography (Fayet et al., 1985). The developability is evaluated by counting in the electron micrograph of the substrate the fraction of crystals effectively reduced (Rosche et al., 1994).

In the last step, the undeveloped crystals are eliminated by dissolution in the *fixing* process. 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. Nuclearity-dependent cluster properties and photographic development

Numerous theoretical models in the past, inspired by phase transition processes (Malinowski, 1980; Moisar and Granzer, 1982; Moisar, 1986) or by ab initio calculations (Hamilton and Baetzold, 1981; Bonacic-Koutecky et al., 1993) have been proposed to explain how the supercritical clusters created by the light act as nuclei to catalyze development. However, they all suffered of weakness in accounting for the observed data (Hamilton, 1980). Also, Trautweiler (1968) early made the speculation that the ionization potential of subcritical sizes should lie below that of the developer. But the experimental and calculated data on bare clusters since then available contradicted this view.

The answer as to how the developer is capable of discriminating supercritical nuclearities among the cluster population of the latent image lies in fact in the

Fig. 1. Nuclearity dependence of the silver cluster redox potential $E^\circ_{\text{NHE}}(\text{Ag}_n^+/\text{Ag}_n)$ in water. Comparison between E°_{NHE} (left ordinate scale) and the ionization potential IP of clusters in the gas phase.

specific *increasing* ionizing potential with the cluster nuclearity for solvated clusters, as suggested by the easy oxidation in solution of radiation-induced atoms and small clusters in contrast with the bulk metals (Delcourt and Belloni, 1973). The increase with nuclearity of the cluster redox potential in solution was demonstrated by a pulse radiolysis study of the development mechanism using electron donors of variable potentials (Mostafavi et al., 1989; Belloni et al., 1991; Khatouri et al., 1993) (Fig. 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 (autocatalytic development on supercritical nuclei, critical nuclearity depending on the developer redox potential, etc.). Therefore the same mechanism which was demonstrated for clusters in solution was proposed for clusters in photography (Mostafavi et al., 1989; Belloni et al., 1991). 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. Another important feature of the Fig. 1 results is that the redox potential in solution and the ionization potential of silver clusters in the vapor (Alameddine et al., 1992; Jackschath et al., 1992) show opposing dependencies on nuclearity. This is explained by the important energy gained in the cation solvation that represents the main part of the difference between IP and IP_{solv} . For $n = 1$, $\Delta E_{\text{solv}}(\text{Ag}^+) = 5.6 \text{ eV}$, as

confirmed by calculations taking into account the solvation and also the ligandation (Remita et al., 1995; Texier et al., 1996), and for larger sizes the difference decreases versus $n^{-1/3}$ according to the Born solvation model (Belloni et al., 1994). Apart the development in photography, most of nucleation and growth mechanisms based on a chemical reduction are likewise controlled by the nuclearity-dependence of the cluster redox potential and by the electron donor potential (Belloni and Mostafavi, 2001).

4. Latent image formation

According to the Gurney–Mott model (Gurney and Mott, 1938), the primary light effect on AgBr is to produce as many electron–hole pairs (e^-h^+) as photons absorbed. One electron reduces a silver cation into an atom, 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 (Fig. 2a). But an important part of electrons are

lost by direct recombination with the parent holes, before they diffuse to the surface where they are irreversibly scavenged by gelatine. 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 direct and indirect recombination, the effective quantum yield is

$$\Phi_{\text{eff}} = \Phi_{\text{theor}}(1 - R) \text{ with } \Phi_{\text{theor}} = 1 \text{ pair/photon.}$$

The yield is enhanced up to $\Phi_{\text{eff}} = 0.10 - 0.30$ (the fraction R is thus 0.90–0.70) by enhancing the electron trapping in specific surface sites (sulfide or/and gold centers) (Hailstone et al., 1987). Classical developers then require for development only $n_c = 3$ atoms per crystal or an initial number of photons $n_i = n_c(1 - R) = 10 - 30$ photons per crystal. Thus, apart 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 inhibit the recombination by specifically scavenging the

Fig. 2. Latent image formation: (a) undoped AgBr crystal; (b) formate doped crystal: hole scavenging step; and (c) formate doped crystal: silver ion reduction by formyl radical.

holes, faster than their possible recombination with the electrons or the atoms, with the help of a dopant (Belloni et al., 1999; Belloni, 2002; Treguer et al., 2002). 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. 2b), 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 behavior 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 of silver atoms. The anion formate HCO_2^- fulfills all the conditions (Allen, 1961; Swallow, 1981). The redox potentials of this two-electron donor are in water $E^\circ(\text{CO}_2^-/\text{HCO}_2^-) = 1.07V_{\text{NHE}}$ and $E^\circ(\text{CO}_2/\text{CO}_2^-) = -1.9V_{\text{NHE}}$ (Schwarz and Dodson, 1989).

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 where the yield is $\Phi_{\text{eff}} = 0.2$ atom/photon absorbed. Then it increases slowly up to a plateau and after 15 min the absorbance is twice that just after the exposure (Fig. 3) (Belloni et al., 1999). The first step is assigned to the fast hole scavenging by formate during the exposure (Fig. 2b). 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. 2c). This photoinduced bielectronic transfer is strictly proportional to the number of photons absorbed down to the shortest exposure times.

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. 4) (Belloni et al., 1999). The number of photons required to induce development of half the grain population is 5 times less (immediate development) or 10 times less (development delayed by 20 min 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. In both cases, all other properties of the emulsion are preserved: the resolution, because the crystal size is unchanged, and the absence of fogging in the dark (Fig. 4, lowest exposures), because formate does not reduce directly the silver ions.

Fig. 3. Absorbance of AgBr crystals at increasing times after light exposure (measured by Diffuse Reflectance Spectroscopy). The Kubelka-Munk factor is proportional to the absorbance: (a) optical absorption spectra; and (b) kinetics of the absorbance increase at the maximum.

Fig. 4. Sensitometry curves for formate doped emulsions developed after 5 or 20 min compared with the undoped emulsion.

An important sensitivity enhancement is similarly observed for dye-sensitized crystals (Belloni et al., 1999).

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

Among the new methods which have been used to better understand the underlying mechanisms at the atomic scale of the photographic processes, the pulse radiolysis allowed us to mimic under wet conditions the development of silver clusters which occurs at the surface of AgBr crystals and to determine the nuclearity-dependence of the redox potential of silver clusters in solution. The sensitivity enhancement recently obtained by formate-doping of the AgBr crystals was also suggested by the classical mechanisms of anti-oxidants well established by radiation chemistry.

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