

Enhanced yield of photoinduced electrons in doped silver halide crystals

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The conventional photographic process^{1–3} involves several steps: the photogeneration of electron–hole pairs in crystals of a silver halide; the reduction of silver cations to atoms by some fraction of these electrons; the subsequent build up of atoms to give clusters (the ‘latent image’); and the complete reduction by a developer of crystallites having more than a critical number of silver atoms per cluster. The effective quantum yield, Φ_{eff} , of photoinduced electron–hole pairs produced per photon absorbed is less than the theoretical limit ($\Phi_{\text{theory}} = 1$), because of the fast recombination of some fraction of the pairs^{1–6}. Here we describe an approach for enhancing the yield of useful photogenerated electrons, in which the silver halide is doped with formate ions, HCO_2^- . The dopant ions act as hole scavengers, thus enhancing the escape of electrons from pair recombination. Moreover, the resulting CO_2^- radical can itself transfer an electron to another silver cation, so raising the theoretical yield to two silver atoms per photon absorbed. This photoinduced bielectronic transfer mechanism is strictly proportional to the light quanta absorbed—the dopant ions do not induce spontaneous reduction of silver cations in the dark—and appears to be close to the theoretical limit of efficiency. The efficiency is constant at all illumination levels and applies to both dye-sensitized and unsensitized crystals. We suggest that this approach is a promising route for improving the performance of photographic emulsions⁷.

According to the classical model of photography^{1–3}, at least some of the initially photogenerated electrons reduce silver cations to atoms. A cation near one of these atoms is then reduced by another electron, and so on; the result is a cluster of silver atoms. Some other (initially photogenerated) electrons are lost by direct recombination with holes, with (at low temperatures) the emission of light. Before being irreversibly trapped, holes are also able to oxidize the newly formed silver atoms, so counterbalancing somewhat the former reduction. The ensemble of photoinduced clusters constitutes the latent image. A critical number n_c of silver atoms per cluster must be formed to induce (in a second step) the complete reduction of the crystallite by a developer.

Different strategies^{1–5} are used to produce—at a given flux of light and crystal cross-section—the required n_c with the shortest exposure, and thus to enhance the sensitivity of the emulsion containing the silver halide crystals. One quite efficient approach is to reduce the fraction of electron–hole pairs that recombine by enhancing transient electron trapping in specific surface sites (sulphide or/and gold centres). Classical developers then require only $n_c = 3$ atoms per crystallite⁸. The initial number n_i of photons absorbed to reach this threshold (quantum sensitivity) is generally from 10 to 30 per crystal⁶, the difference ($n_i - n_c$) being lost by recombination. Thus the effective quantum yield $\Phi_{\text{eff}} = n_c/n_i$ is in the range 0.30–0.10. Values of $n_i = 6–8$ ($\Phi_{\text{eff}} = 0.50–0.37$) have been reported at optimized S–Au sensitization of octahedral crystallites, after correction for fogging level^{6,7}, but these figures are much lower than $\Phi_{\text{theory}} = 1$.

Another possible method of enhancing emulsion sensitivity involves scavenging the holes by adding an electron donor (reduction sensitizer) before exposure^{4–6}. Ideally, pre-reduction of these emulsions yields a dimer (Ag_2) per crystal. It is supposed to scavenge

holes, and to yield the equivalent of two electrons for silver cluster formation (one electron escaping from the recombination with the hole scavenged by Ag_2 , the second coming from Ag_2^+)^{4–6}. Therefore a third atom only has to be provided by light to reach n_c . Indeed, the value of n_i is found now to be 2–3 photons per crystal⁶ (in that case, $\Phi_{\text{eff}} = n_c - 2/n_i = 0.50–0.33$). However, the limit of 2 pre-reduced atoms per crystal is easily exceeded in practice, and as much as 50% of the crystal population may be developable, irrespective of the number of photons absorbed (the fogging effect).

Here we report the effect of doping the silver halide crystals with the bielectronic donor ion formate (HCO_2^-), which by itself is not a direct reduction sensitizer (the redox potential $E^\circ(\text{CO}_2^-/\text{HCO}_2^-) = 1.07 \text{ V}_{\text{NHE}}$ at pH 7 in water) and is unable to reduce silver cations in the dark, so avoiding the risk of fogging. In contrast, the formate ion can scavenge photo-produced holes, and moreover, the radical product of such scavenging (CO_2^-) is a strong electron donor able to inject a supplementary electron into the conduction band to form—from a silver ion associated with an atom (Ag^+) or a cluster (Ag_n^+)—a supplementary silver atom: $E^\circ(\text{CO}_2/\text{CO}_2^-) = -1.9 \text{ V}_{\text{NHE}}$ in water⁹. Such behaviour of bielectronic donors is known in the interaction of radiation and of light with aqueous solutions (molecular hydrogen, formate, alcohols)^{9–12}, and the photoelectrochemistry that occurs at the interface of solutions and semiconductors^{13,14}. We prepared doped emulsions as described in Fig. 1 legend: both these and the reference emulsions were coated on a flat support, exposed to light at a wavelength λ_{exp} of

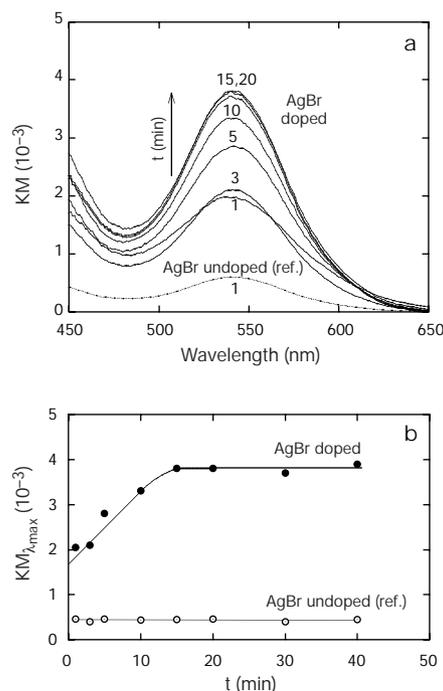


Figure 1 Effect of formate dopant on photoproducted silver clusters. **a**, Evolution with time of the absorbance spectra with 2 s illumination of formate-doped ($10^{-6} \text{ mol HCOO}^-/\text{mol Ag}^+$) AgBr cubic grains (solid lines) and undoped AgBr cubic grains (dotted line), both sensitized by S–Au. The absorbance is derived from the Kubelka–Munk¹⁵ factor $\text{KM} = (1 - R)^2/2R$, where R is the diffuse reflectance. **b**, Time dependence of the absorption maximum for the undoped (open circles) and formate-doped (filled circles) emulsions. Formate doping of emulsions was performed during the precipitation of AgBr. Core cubic grains of AgBr (0.37 μm diameter), suspended in an aqueous gelatin solution, were first prepared using a controlled double jet of AgNO_3 and KBr solutions³. Then triple-jet precipitation was used to coat these grains with dopant HCO_2Ag as a 25-nm-thick shell, so that the total grain diameter was 0.42 μm . The overall relative molar concentration $\text{HCOO}^-/\text{Ag}^+$ was $10^{-7}–10^{-5}$. The emulsions, consisting of colloidal suspensions of AgBr microcrystals stabilized by gelatin, were then subjected to digestion for S–Au chemical sensitization and coated onto a flat support (1.5 g Ag^+ per m^2).

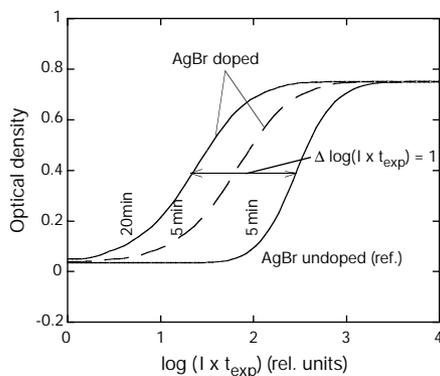


Figure 2 Sensitivity of undoped and formate-doped (10^{-6} mol HCOO^- /mol Ag^+) AgBr emulsions. Both emulsions were sensitized with S+Au. Development by M-AA-1 (aminophenol and ascorbic acid) for 8 minutes (ref. 8) was delayed by the indicated times, after a constant exposure time $t_{\text{exp}} = 10^{-2}$ s, at variable intensity I (in relative units).

410 nm, and studied by diffuse reflectance¹⁵, fluorometry, and sensitometry (absorbance measurement after photographic development).

In Fig. 1 we show the typical evolution with time of spectra which were obtained after exposure of doped and reference emulsions, and which we assigned to photoproducted silver clusters^{5,16}. The intensity at long times increases linearly with the dopant concentration until a plateau is reached at a ratio of 10^{-6} mol formate per mol Ag^+ . When in the dark, the formate-doped emulsion is completely stable. When illuminated (Fig. 1), its absorbance immediately after the exposure is five times that of the undoped emulsion; after 15 minutes, its absorbance is still twice that just after the exposure (10 times the reference absorbance).

In the presence of formate, the relative increase of absorbance with respect to the undoped emulsion within the exposure is assigned to hole scavenging by HCOO_2^- , which is faster than the electron-hole recombination or the trapping of unrecombined holes. Thus, more electrons escape from the pair recombination and are available to reduce silver cations to silver atoms; moreover, fewer silver atoms are oxidized by the holes.

Fluorescence at 77 K (due to electron-hole recombination) is detected in undoped emulsions exposed to light (fluorescence occurs at 560 nm if $\lambda_{\text{exp}} = 410$ nm; data not shown): this emission is completely quenched in formate-doped emulsions, confirming complete hole-scavenging by HCOO_2^- , at least for a concentration beyond 10^{-6} mol HCOO^- per mol Ag^+ .

In the range of minutes after the end of exposure of formate-doped emulsion, the number of silver atoms slowly increases until they have doubled (Fig. 1). In fact, the delayed supplementary formation of silver atoms arises from the second electron transfer to Ag^+ ions from the CO_2^- radical formed by hole scavenging during the exposure. The reaction is very slow, probably because the CO_2^- radical is trapped in the crystal matrix and because the direct reduction of free mobile silver ions would require a more negative redox potential^{17,18}. So we assign the slow supplementary silver atom formation to the reduction of Ag_2^+ or Ag_n^+ , possibly by electron hopping from CO_2^- into the conduction band. The maximum at 545 nm in these diffuse reflectance data with a rather long exposure is assigned to large clusters¹⁶. The absorbance is proportional both to the nominal concentration of atoms formed and to the extinction coefficient per atom. So the slow increase may arise from the formation of additional clusters, or from the growth of a few large clusters per crystal formed during the exposure and enriched by the new atoms. The first hypothesis is more probable if we consider the mechanism of the slow extra electron production in hydrogen-sensitized emulsions¹⁹.

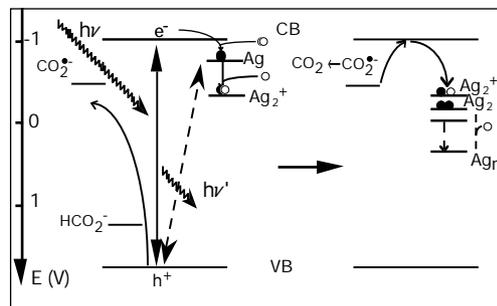


Figure 3 Diagram of the double action of formate in doped silver halides. The scale of energy levels refers to the normal hydrogen electrode potential (for AgBr, CB is -1.04 and VB at 1.6 V_{NHE}). Here CB indicates conduction band, and VB, valence band. The formate level is above the VB and HCOO^- scavenges the photo-hole. The energy level of the CO_2^- radical formed is such that an electron is transferred to charged silver dimers, yielding a second atom per photon absorbed. The energy levels of HCOO^- and CO_2^- in an AgBr matrix are shifted relative to those in solutions, due to the lack of solvation and to the matrix effect.

Quantitatively, as the absorbance at the plateau is just twice that immediately after the exposure, each CO_2^- radical formed by scavenging of a hole produces one supplementary silver atom in one of the clusters. Thus the overall mechanism implies extremely fast hole scavenging; this photoinduced bielectronic transfer is strictly proportional to the number of photons absorbed, down to the shortest exposure times that we studied.

The sensitivity of doped and undoped emulsions have been compared; this was done by measuring their absorbance after an exposure time t_{exp} of 10^{-2} s with a light source of variable intensity I and photographic development, which allows the investigation of effects caused by the absorption of only a few light quanta (Fig. 2). When the development is delayed by 20 minutes after exposure, the number of photons required to induce development of half the grain population is 10 times less in doped than in undoped emulsions ($\Delta \log(I \times t_{\text{exp}}) = 1$). This enhancement in the sensitometric curves corresponds to the absorbance data and provides the same evidence of the double role of formate dopant as a hole scavenger and as a delayed secondary reduction source. We note that the sigmoid response curves of doped AgBr emulsions are systematically less steep than in undoped emulsions. Calculations by Silberstein²⁰ with small values of n_c predicted such a change in the curve shape; it arises from the Poisson statistics of the distribution throughout the crystal population of the photon number required for development⁶. It is remarkable that though the doping highly enhances the sensitivity, fogging remains at the same insignificant level.

We now consider absolute quantum yields, measured as in refs 6 and 8. We find that $n_i = 20 \pm 3$ photons per crystal must be absorbed in the undoped emulsions to make half of the grains developable ($\Phi_{\text{eff}} = n_c/n_i = 0.15 \pm 0.03$), in agreement with other data⁶. For formate-doped emulsions, we obtain 2 ± 0.3 photons per crystal. The resulting value $\Phi_{\text{eff}} = n_c/n_i = 1.5 \pm 0.3$ is exceptionally high, and approaches the theoretical limit of $\Phi_{\text{theor}} = 2$ suggested by the mechanism shown in Fig. 3 and confirmed by low-temperature fluorescence data. We note that as photon absorption is a quantum phenomenon, values of the threshold $n_c \geq 3$ cannot be reached by less than the integer number $n_i = 2$ photons per crystal (producing 4 silver atoms).

As most emulsions for practical use are also sensitized by dye molecules, in order to broaden their spectral absorption in the green and the red, our study was extended to the effect of formate-doping on dye-sensitized crystals. In such a system, light produces an excited state of the chromophore adsorbed at the AgBr surface; this excited state is known to inject an electron into the crystal conduction band. We therefore need to check whether a hole can

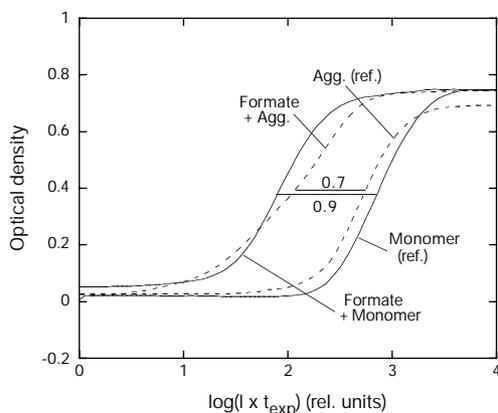


Figure 4 Effect of formate doping on the sensitivity of AgBr emulsions sensitized with carbocyanine dye. After the precipitation and doping (10^{-6} mol $\text{HCOO}^-/\text{mol Ag}^+$) by formate as in Fig. 2, the AgBr crystals were sensitized by the dye (3-(2-(3-(5-chloro-3-(3-sodium-sulpho-propyl)-benzoxazol-2-yl)-2-ethyl-allylidene)-5-chloro-benzoxazolium-3-yl)-propane-1-sulphonic acid betaine) in the monomeric form ($\lambda_{\text{max}} = 480$ and 500 nm, surface coverage = 0.2) and excited at $\lambda_{\text{exp}} \geq 477$ nm, or in the J-aggregate form (additional λ_{max} at 552 nm, surface coverage = 0.8) and excited at $\lambda_{\text{exp}} \geq 519$ nm. Development by M-AA-1 is delayed for 20 min, after $t_{\text{exp}} = 10^{-2}$ s.

also be transferred from the highest occupied molecular orbital (HOMO) of the dye to the Fermi level of the dopant formate, so blocking electron-hole recombination³. Our results from emulsions sensitized by a carbocyanine thought to fulfill the above criterion indicate that the sensitivity is indeed increased (Fig. 4), compared to emulsions without formate supposed to absorb the same quantity of photons. Depending on the surface coverage by dye molecules, these are in the form of either monomers or J-aggregates, which are two-dimensional arrays of edged-on adsorbed dye molecules with a large slip angle. The difference is about $\Delta \log(I \times t_{\text{exp}}) = 0.9$ for emulsions sensitized by dye monomers ($\lambda_{\text{max}} = 480$ and 500 nm), excited at $\lambda_{\text{exp}} \geq 477$ nm; for emulsions sensitized by J-aggregates (additional λ_{max} at 552 nm), excited at $\lambda_{\text{exp}} \geq 519$ nm, we obtain $\Delta \log(I \times t_{\text{exp}}) = 0.7$. This enables us to assess the effect of aggregates only without coexisting monomers. The sensitivity enhancement that is systematically observed in the presence of formate ion therefore attests to efficient hole transfer to the dopant formate from the HOMO level of the dye, in both the monomer and the J-aggregate forms. This mechanism is comparable with the scavenging of the intrinsic hole created by direct AgBr excitation, and results in a marked inhibition of recombination. □

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Periodic mesoporous organosilicas with organic groups inside the channel walls

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Surfactant-mediated synthesis methods have attracted much interest for the production of inorganic mesoporous materials, which can, on removal of the surfactant template, incorporate polymeric, organic, inorganic and organometallic ‘guests’ in their pores^{1,2}. These materials—initially made of silica^{3–5}, but now also available in the form of other oxides^{6–9}, sulphides^{10,11}, phosphates¹² and metals¹³—could find application in fields ranging from catalysis, adsorption and sensing technology to nanoelectronics. The extension of surfactant-mediated synthesis to produce inorganic-organic hybrid material (that is, materials that contain organic groups as an integral part of their framework structure) promises access to an even wider range of application possibilities. Such hybrid materials have been produced in the form of amorphous silicates (xerogels) that indeed display unique properties different to those of the individual components^{14–20}, but their random networks with broad pore-size distributions severely limit the shape and size selectivity of these materials. Mesoporous hybrid materials with periodic frameworks have been synthesized, but the organic groups are all terminally bonded to the pore surface, rather than incorporated into the pore walls^{21–26}. Here we describe a periodic mesoporous organosilica containing bridge-bonded ethene groups directly integrated into the silica framework. We are able to solvent-extract and ion-exchange the surfactant templates to create a stable and periodic mesoporous ethenesilica with high surface area and ethene groups that are readily accessible for chemical reaction. Recent syntheses of similar periodic mesoporous organosilicas^{27,28} and the ability to incorporate a variety of bridging organic and organometallic species raise the prospect of being able to fuse organic synthesis and inorganic materials chemistry to generate new materials with interesting chemical, mechanical electronic, optical and magnetic properties.

In a typical synthesis, a mixture of bis(triethoxysilyl)ethene (BTE) and tetraethylorthosilicate (TEOS) was added to a solution of cetyltrimethylammonium bromide (CTABr), NH_4OH and H_2O . Samples were prepared containing BTE:TEOS in mole fractions of 1:0 (BTE100), 0.75:0.25 (BTE75), 0.50:0.50 (BTE50), 0.25:0.75