Review of Latent Image Formation Mechanisms in Silver Halides

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Abstract

Based on the theoretical concepts of Guerney-Mott, Hamilton proposed a four-photon mechanism for the photochemical formation of Ag_4 latent image centers. Subsequently, by including the hole-trapping mechanism by of Ag_2 reduction centers, a two-photon mechanism was developed. Several authors evaluated certain photographic experiments as one-photon processes. No mechanisms were given to explain those results. Others claimed that one-photon processes in silver halide systems would result in fog-centers. From the concepts of the previous mechanisms, a photon mechanism is proposed that does not result in fog. This one-photon process is based on the presence of both electron and hole-trapping Ag_2 centers on the same crystal before exposure. Both photoelectron and photohole, which are formed by light absorption, participate in this mechanism. The needed electron-hole energy separation is estimated to about 1.4eV and is thus well above the thermal energy at room temperature (about 0.03eV). Published experimental evidence for one-photon processes in silver halide systems will be reviewed.

Introduction

The ultimate efficiency of silver halide photographic systems is determined by the mechanism by which latent image is formed. Thus, it is essential to review the proposed mechanisms and to explore if the ultimate efficiency, one-photon processes, can be achieved.

First Step: Exposure

Photographic processes rely on the absorption of photons (hv) by the active material and the formation of photoelectrons, e^- and their counterparts photoholes h^+ as proposed by Guerney and Mott.[1]

$$hv \rightarrow e^- + h^+ \qquad (1)$$
$$hv = light$$

Photoelectrons and holes may be formed by intrinsic exposure, or by sensitizing dyes through spectral sensitization. The efficiency for the formation of photoelectrons and holes by sensitizing dyes is determined by the redox potentials of the sensitizing dyes, the silver halide substrate, chemical sensitization, and doping.[2]

In the photographic process, photoelectrons combine with silver ions to form small clusters of silver atoms that act as catalysts for the reduction of the silver halide crystals. These microclusters are referred to as latent image.

The Guerney Mott model did not detail the following steps towards latent image formation, nor was the minimum size of the latent image determined.

The Four-Photon Mechanism

Based on the theoretical concepts of Guerney-Mott,[1] Hamilton proposed a four-photon mechanism for the photochemical formation of Ag_4 latent image centers.[3]

The mechanism is based on the concept that at highest efficiency four absorbed photons will create four photoelectrons. These react stepwise with four silver ions to form Ag_4 latent image centers.

$$e^- + Ag_i^+ \rightarrow Ag_1 \text{ unstable}$$

$$e^- + Ag_i^+ + Ag_1 \rightarrow Ag_2 \text{ stable (Sublatent Image)}$$

$$e^- + Ag_i^+ + Ag_2 \rightarrow Ag_3 \text{ unstable}$$

$$e^- + Ag_i^+ + Ag_3 \rightarrow Ag_4 \text{ stable (Latent Image)}$$

$$4\,e^- + 4\,Ag_i^+ \rightarrow Ag_4 \text{ stable}$$

Ag_2 is a stable, but generally non-developable sublatent image center (referred to in this paper as Ag_2(E) centers).

Ag_4 is the developable latent image center.

Ag_i^+ is a silver ion that is free to react with the electron to become reduced to a silver atom or silver cluster, e.g., an interstitial silver ion.

Including the primary photon process leads to the following equation:

$$4hv + 4\,Ag_i^+ \rightarrow Ag_4 + 4\,h^+$$

Holes formed in the exposure step must be removed to avoid loss processes by electron/hole recombination.

Since in the proposed mechanism photoholes do not participate in the latent image formation, their removal for the reduction of recombination is a primary requirement.

It is also apparent that the progression from Ag_1 to Ag_4 depends on the stability of the intermediate silver atom and clusters and the kinetic rates of the different reaction steps. This will express itself in the reciprocity properties of the photographic material.

The Two-Photon Mechanism

The two-photon mechanism including the Lowe hole mechanism was reviewed by R.Hailstone et al.[4]

Lowe proposed that photoholes could be converted to electrons when they reacted with chemically preformed Ag_2 centers referred to as reduction or "R" centers (denoted in this paper as Ag_2(H)). This mechanism leads to the removal of a photohole, and thus reduces recombination. At the same time dissociation of the remaining silver atom provides an electron that might participate in the Hamilton latent image process, thus reducing the number of photons necessary to provide photoelectrons.

In the two-photon mechanism, two photons form two photoelectrons and two photoholes:

$$2hv \rightarrow 2\,e^- + 2\,h^+$$

Electron Mechanism:

Following the Guerney-Mott and Hamilton mechanisms, the two photoelectrons combine with interstitial silver ions to form Ag_2 sublatent image centers.

$$2\,e^- + 2\,Ag_i^{\,+} \rightarrow Ag_2 \text{ (Sublatent Image)}$$

If the sublatent image centers trap electrons to form latent images, they act as Ag_2(E) centers.

Hole Mechanism (Lowe)

Two hole-trapping Ag_2 (H) centers are required to trap the two photoholes formed in the initial step.

$$2\,h^+ + 2\,Ag2\,(H) \rightarrow 4\,Ag_i^{\,+} + 2\,e^-$$

If these secondary electrons react with an electron trapping sublatent Ag_2 center (Ag_2 (E)) and add two silver ions, Ag_4 latent image centers are formed.

Over-all Process:

$$2\,e^- + Ag_2 + 2\,Ag_i^{\,+} \rightarrow Ag_4 \text{ Latent Image}$$

Summary of Two-Photon Mechanism.

$$2hv + 2\,Ag_2 \rightarrow Ag_4$$

Both Ag_2 centers used in this process are hole trapping centers (Ag_2 (H)).

The One-Photon Mechanism

Frequently, no difference is made between one-photon and one-electron detection mechanisms. For instant, electronic imaging systems do not distinguish between electrons that were formed by thermal or optical processes. To enhance the detection of optically generated electrons and to suppress the thermal electron, high sensitive electronic detection devices, e.g. photo-multipliers, are cooled to cryogenic temperatures.

Based on the equation of one-electron with one-photon processes for the silver halide systems, Tani concluded that "the formation of a latent image center by one absorbed photon in an emulsion grain means the disappearance of the threshold of latent image formation, and probably results in the deterioration of keeping stability of the emulsion. Therefore, it is considered that the formation of latent image by two absorbed photons in an emulsion grain gives the ultimate limit of practical quantum sensitivity".[5]

The need for a two-photon mechanism for latent image formation is echoed by Mitchell who states that "the absorption of two effective photons allows an $AuAg_4$+ development center to be formed at a surface sensitivity center".[6] Apparently, one-photon processes were not considered viable mechanisms.

A review of the four- and two-photon processes suggests a one-photon process that is not a one-electron event but depends on both the photoelectron and photoholes. This one-photon process thus needs light exposure to provide both the electron and the hole and is not triggered by thermal electron or hole events.

As in the other mechanisms, the proposed one-photon photographic process begins with the absorption of a photon and the formation of a photoelectron and a photohole.

It is proposed that by controlled reduction sensitization and crystal manipulation electron trapping Ag_2 (E) centers can be formed which are equivalent to sublatent image centers. Electron trapping by reduction sensitization centers was observed by Collier[7] and Tani.[8] Christianson gave a general review of reduction sensitization.[9]

In the one-photon mechanism, the photoelectron from exposure adds to an electron trapping Ag_2 (E) center.

$$e^- + Ag_2\,(E) \rightarrow Ag_2^{\,-}$$

In a following ionic step, this center is stabilized by the addition of an interstitial silver ion.

$$Ag_2^{\,-} + Ag_i^{\,+} \rightarrow Ag_3 \text{ Latent Image Precursor}$$

The resulting Ag_3 center is the same latent image precursor as proposed in the Hamilton mechanism discussed above. The Ag_3 center can be stabilized by the addition of an interstitial silver ion to form another latent image precursor, $Ag_4^{\,+}$:

$$Ag_3 + Ag_i^{\,+} \rightarrow Ag_4^{\,+} \text{ Latent Image Precursor}$$

The missing electron to form an Ag_4 latent image can now be provided by the electron formed in the Lowe-Process.

$$h^+ + Ag_2(H) \rightarrow e^- + 2\,Ag^+$$

Latent image is then formed by reaction with the latent image precursors:

Ag_3:

$$Ag_3 + e^- \rightarrow Ag_3^-$$

$$Ag_3^- + Ag_i^+ \rightarrow Ag_4 \textit{ Latent Image}$$

$$Ag_4^+$$

$$Ag_4^+ + e^- \rightarrow Ag_4 \textit{ Latent Image}$$

Summary of One-Photon Mechanism.

$$hv + 2\,Ag_2 \rightarrow Ag_4$$

Of these Ag_2 centers, one acts as an electron trap, $Ag_2(E)$, and the other as a hole trap, $Ag_2(H)$. This is in contrast to the two-photon mechanism where both Ag_2 centers are hole trapping centers ($Ag_2(H)$).

The energy requirements for this one-photon process can be estimated from spectral sensitization studies, using the redox-potential of the dyes to determine the effective energy thresholds for spectral sensitization and for hole-trapping by reduction centers. The threshold for the electron processes was determined to about –1.0 (V vs. Ag/AgCl).[2]

For the one-photon mechanisms, photoholes must be provided with energies that can provide the Lowe-mechanism of oxidizing Ag_2 (H) centers. In the redox energy scheme, these dyes must have an oxidation potential more positive than +0.4V.[10]

The minimum energy requirement is the sum of these two energy levels, about 1.4 eV. This energy can not be provided by thermal electrons (about 0.03eV) but must be provided by absorption of photons.

Effective sensitization techniques need to be developed that lead to electron trapping Ag_2 (E) centers akin to sublatent image Ag_2 centers.

The One-Photon Mechanism including Gold Centers

The following reactions can be postulated if non-fogging stable AgAu-centers can be chemically pre-formed.[5] The mechanism for electron trapping Au_2 centers follows the same pattern and will not be discussed explicitly.

$$e^- + AuAg \rightarrow AuAg^- \quad \textit{Latent Image Precursor}$$

$$AuAg^- + Ag_i^+ \rightarrow AuAg_2 \quad \textit{Latent Image? Precursor?}$$

$$AuAg_2 + Ag_i^+ \rightarrow Au\,Ag_3^+ \quad \textit{Latent Image? Precursor?}$$

The $AuAg_2$ center has been proposed to be a stable latent image center. This would provide an alternative one-photon mechanism. However, it is not known if a stable AuAg-center can be pre-formed by chemical sensitization. In analogy to above, the $AuAg_2$ center may be further stabilized by the addition of an interstitial silver ion to form $AuAg_3^+$.

Summary for One-Photon $AuAg_3$—Latent Image Formation

As stated before, the one-photon mechanism relies on the formation of a secondary electron by the Lowe mechanism:

$$h^+ + Ag_2(H) \rightarrow e^- + Ag^+$$

Reaction of the secondary electron with the latent image precursor leads to the desired latent images.

$AuAg_2$ (formed from AuAg plus the photoelectron)

$$AuAg_2 + e^- \rightarrow Au\,Ag_2^-$$

$$AuAg_2^- + Ag_i^+ \rightarrow AuAg_3 \quad \textit{Latent Image}$$

$AuAg_3^+$

$$Au\,Ag_3^+ + e^- \rightarrow AuAg_3 \quad \textit{Latent Image}$$

Summary of One-Photon $AuAg_3$ Latent Image Formation:

$$hv + AuAg + Ag_2(H) \rightarrow AuAg_3$$

Here the AuAg center acts as an electron trap and Ag_2 (H) as a hole trap.

Experimental Evidence for One-Photon Processes in Silver Halides

Surprisingly, experimental evidence for one-photon processes in silver halide systems has been available for a significant length of time. However, this evidence was not considered viable since no latent image forming processes based on one-photon mechanisms were known.

Evidence for number-of-photon mechanisms are generally based on a model developed by Silberstein and others.[3]

In the present context, the work by Spencer et al. is significant.[11] They determined that for reduction sensitized cubic and octahedral emulsions curves were obtained that could be fitted to 1-, 2-, 3-, and 4-photon curves depending on the exposure conditions. Spencer et al. concluded that one could not specify a critical size for latent image centers by determining the shape of the Silberstein curve. Mechanisms for the different curves were not discussed. As shown above, mechanisms for the two and higher photon curves were available, but the one-photon curve could not be explained.

Babcock and James[12] and Hailstone et al.[13,14] showed one-Photon latent image formation in photographic experiments for sulfur plus gold and hydrogen hypersensitized emulsions. However, these results were not discussed or were considered unreliable because no mechanism was available to explain them.

Kawasaki reported experiments where the Silberstein curve shape evaluation suggests one-photon latent image formation; however, no detailed mechanism was proposed.[15]

Conclusion

Mechanisms for the formation of latent image in silver halides were reviewed. Starting from two and four-photon mechanisms a one-photon mechanism was derived that is not initiated by thermal processes. In addition, one-photon processes including gold sensitization were reviewed. Published experimental evidence supports the proposed latent image mechanisms.

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