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Additional dye options for spectral sensitization of photo processes in silver stearate—silver bromide system

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Abstract. The paper discusses spectral sensitized photo processes in silver bromide caused by dyes adsorbed on the surface of silver stearate via the lightguide mechanism and a direct hit of the luminescent light from dye molecules localized near the microcrystal of silver bromide to the microcrystal of silver bromide. The paper submits an estimation of the contribution of dye molecules localized on the surface of silver stearate to overall spectral sensitization. These calculations demonstrate that the contribution of dye molecules adsorbed on the particle of silver stearate to spectral sensitization of silver stearate—silver bromide structure is comparable to the contribution of dye molecules placed on the microcrystal of silver bromide. Dye molecules localized on the particle of silver stearate allow to raise the efficiency of spectral sensitization by 40 to 60 percent.

Keywords: spectral sensitization, thermally developable photographic materials, silver stearate–silver bromide structure, lightguide mechanism, luminescence of adsorbed dyes, computer calculations.

Introduction

Organic dyes are effective in spectral sensitization of photophysical and photochemical processes in different semiconductors (AgHal, ZnO, TiO_2 and other) both in visible and infrared ranges (Akimov et al. 1980; Goryaev 2015; 2016; 2018; 2019; James 1977). Spectral sensitization is the most effective control method of the sensitivity degree and the sensitivity spectrum for classic silver halide photo materials (James 1977). The photoelectrochemical cells based on TiO_2 particles with adsorbed sensitizing dyes are an alternative to silicon solar cells (Gratzel 2003). The photothermographic materials based on silver halide and silver salts of fatty acids (in particular, silver stearate) are used widely in the recording of optical images (Goryaev 1991; Morgan 1993; Sahyun 1998). When preparing such photosensitive composition, silver bromide is synthesized on the surface of silver stearate (Goryaev et al. 1992; Goryaev 1994a). The addition of organic sensitizing dyes to the compositions provides spectral sensitization of these photo materials in visible and infrared range (Goryaev et al. 1992; Goryaev, Shapiro 1997). The optimal concentration of sensitizing dyes for photothermographic materials is about one hundred times more than the optimal concentration of these dyes for classic silver halide photo materials (Goryaev et al. 1992). Dye molecules precipitate both on the surface of silver stearate and on the surface of silver bromide when this dye is adsorbed into photothermographic compositions. The paper explores spectral sensitized photo processes in silver bromide caused by dyes adsorbed on the surface of silver stearate.

The paper also submits an estimation of the contribution of dye molecules localized on silver stearate surface to the overall spectral sensitization.

Results and discussion

The scanning electron microscopy of photo thermo structures has indicated that cube microcrystals of silver bromide of around 0.1 μm form on the surface of silver stearate at the optimal concentration of silver bromide to silver stearate of 10 mol% (Goryaev 1994a; Goryaev, Smirnov 2020a). The particles of silver stearate are oblong prisms about 1 μm in length and the height of 3 to 5 times smaller than the length. In this case, the relation of silver stearate surface area to silver bromide surface area is 30 to 50. As a first approximation, the quantity of dye molecules localized on the surface of silver stearate is also 30 to 50 times bigger than the quantity of dye molecules placed on the microcrystal of silver bromide. This fact explains the difference of optimal concentrations of dyes for classic silver halide materials and photothermographic materials.

The transfer of energy from dye molecules localized on the surface of silver stearate into the microcrystal of silver bromide via an inductive resonant mechanism (Ermolaev et al. 1996) cannot be significant at this particle sizes because critical radius of such transfer is 6 to 8 nm (Akimov et al. 1980). Besides, the electrons from the excited dye molecules cannot pass through the silver stearate layer because silver stearate is a typical dielectric. Dye molecules adsorbed on non-light sensitive silver stearate radiate with luminescence quantum yield of a few dozen percent (Goryaev, Smirnov 2020a; 2020b). Silver stearate is a transparent dielectric in the visible range which makes it possible for dye luminescent light to hit into the microcrystal of silver bromide through the silver stearate particle. The absorption and luminescence spectra of the dyes adsorbed on silver stearate strongly overlap. This fact stipulates the effective absorption of the luminescent light by dye molecules localized on the microcrystal of silver bromide. Consequently, spectral sensitization effectiveness of photo processes in silver halide increases according to the classic theories of spectral sensitization process (Akimov et al. 1980).

The lightguide mechanism in silver stearate—polyvinylbutyral system (polyvinylbutyral is a binder component in photothermographic materials), the strong overlapping of dye luminescence and absorption spectra, the significant quantum luminescence yield of different dyes adsorbed on the surface of silver stearate are indicative of the significant contribution of dye molecules placed on the particle of silver stearate in spectral sensitization of photothermographic materials.

In complex photothermographic structures the silver stearate—silver bromide system locates in the binder component—polyvinylbutyral. The total internal reflection on the optical interface of silver stearate—polyvinylbutyral is provided by the lightguide mechanism of spectral sensitization (Goryaev 1994b; 1998). The refractive index of polyvinylbutyral is 1.485 (Kabanov 1974). In turn, the refractive index of silver stearate is 1.515 (Goryaev, Smirnov 2012). As a result, the luminescent light in silver stearate realizes total internal reflection at angles of incidence of about 78.5°. This value allows to conclude that the lightguide mechanism of spectral sensitization in photothermographic materials is effective enough.

The contribution of dye molecules adsorbed on the particle of silver stearate to spectral sensitization was calculated according the model shown in Figure 1*a*. The silver stearate particle sizes are 1000 × 500 × 500 nm. The silver bromide microcrystal sizes are 100 × 100 × 100 nm. The dye molecule size is 5 nm. The distance between dye molecules is 5 nm. The refractive index of silver stearate is 1.515. The relative quantity calculation of the luminescent light passing from the molecules localized on the surfaces of silver stearate into the microcrystal of silver bromide was calculated by own software. The relative quantity of the luminescent light passing into silver halide via the lightguide mechanism is 0.0042.

However, the quantity of dye molecules placed on the particle of silver stearate is 30 to 50 times more than the quantity of dye molecules placed on the microcrystal of silver bromide. Consequently, 0.0042 is to be multiplied by 40. In this case, the contribution of dye molecules localized on the particle of silver stearate via the lightguide mechanism relative to the contribution of the dye molecules placed on the microcrystal of silver bromide is 0.17.

The investigations of silver stearate with adsorbed dye Rhodamine 6G by dielectric spectroscopy and differential scanning calorimetry showed a significant influence of dye adsorption on the properties of silver stearate (Castro et al. 2017a; 2017b; Smirnov et al. 2017). For example, the adsorption of Rhodamine 6G leads to an extreme increase of permittivity. This is probably due to the emergence of supplementary dipole–dipole interactions at the adsorption of silver stearate by Rhodamine 6G. The significant increase of permittivity enhances spectral sensitization via the lightguide mechanism.

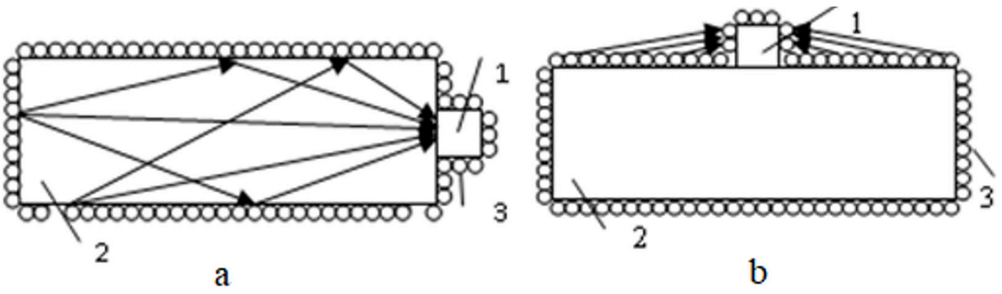

Fig. 1. The visual illustration of spectral sensitization by dyes adsorbed on the surface of silver stearate:
a—the lightguide mechanism, b—the direct hit of the luminescent light.
1 — silver halide, 2 — silver stearate, 3 — molecules of sensitizing dye

However, the lightguide mechanism does not make allowance for the potential influence of dye molecules localized on the surface of silver stearate particle containing the microcrystal of silver halide on spectral sensitization (Fig. 1*b*). The luminescent light emitted by these dye molecules may potentially hit into the lateral surfaces of the silver bromide microcrystal. The input data (the particle sizes etc.) for the calculation of this model are similar to the data used to calculate the lightguide mechanism model. In this case, the relative quantity of the luminescent light passing into the microcrystal of silver halide is 0.052. Then, we calculated the ratio of the quantity of dye molecules localized on the microcrystal of silver halide lateral face and the quantity of dye molecules localized on the surface of the silver stearate particle. Optimally, this relation is calculated as the ratio of surfaces area of the silver halide and silver stearate particles, i.e. $\frac{S^{//}}{S^{*}} = \frac{S^{/} - S}{5 \cdot S}$, where $S^{/}$—the area of silver stearate surface where the microcrystal of silver bromide is placed, S—the area of silver bromide microcrystal surface, $S^{//}$—the area of silver stearate surface without the area of silver halide microcrystal surface where the microcrystal of silver bromide is placed (the microcrystal of silver halide localizes on this face of the silver stearate particle). $S^{*} = 5 \cdot S$ (dye molecules localize on five surfaces of the silver halide particle). After the substitution it turned out that the quantity of dye molecules placed on silver stearate plane is 10 times more than the quantity of dye molecules placed on the microcrystal of silver halide. Therefore, the contribution of dye molecules localized on the silver stearate plane relative to dye molecules localized on the silver halide microcrystal is 0.52.

The total contribution estimation of dye molecules placed on the particle of silver stearate in relation to the contribution of dye molecules placed on the microcrystal of silver halide has to take into account relative contributions of the two described mechanisms and the multiplication of the given result by luminescence quantum yield of dye adsorbed on silver stearate. The luminescence quantum yield of Rhodamine 6G adsorbed on silver stearate is 0.55. In this case, the value of the contribution of dye molecules localized on silver stearate is 0.38, i.e., approximately 40 percent in relation to the contribution of dye molecules placed on the microcrystal of silver halide.

It is worth noting that the contribution value of dye molecules placed on the surface of silver stearate depends on the dye type because luminescence quantum yield is conditioned by the sort of dye adsorbed on the particle of silver stearate. If luminescence quantum yield of a dye is about 1.0 then the considered contribution is more than 60% in relation to the contribution of this dye adsorbed on the microcrystal of silver bromide.

Conclusion

The calculations show that the contribution of dye molecules localized on the particle of silver stearate to spectral sensitization of silver stearatesilver bromide structure is comparable to the contribution of dye molecules placed on the microcrystal of silver bromide. The effectiveness of spectral sensitization of photothermographic materials can be increased by 40 to 60 percent by the dye molecules adsorbed on the silver stearate particles. This is conditioned by both the lightguide mechanism and the direct hit of the luminescent light from dye molecules localized near the microcrystal of silver bromide. These calculations have confirmed the results of the investigations of photothermographic materials spectral sensitivity and absorption spectra of adsorbed dyes which showed comparable contributions of dye molecules placed on the particles of silver stearate and dye molecules localized on the microcrystal of silver bromide (Goryaev 1998).

Conflict of interest

Authors declare that they have no conflict of interest.

Author contributions

A. A. Luzkov: The development of the calculation software for the estimation of the contribution of dye molecules localized on the surface of silver stearate to spectral sensitization in photothermographic materials. M. A. Goryaev and A. P. Smirnov: The formulation of the problem and analysis of the calculated results.

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