Photoelectron decay characteristic of cubic AgCl emulsion sensitized by green-sensitizing dye

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The free photoelectron signals of spectral sensitized AgCl emulsion with different sensitization concentrations are obtained from microwave absorption dielectric spectrum experiment. It is found that when sensitization concentration is small (0.04 mg dye per 40 g AgCl emulsion) or great (4 mg dye per 40 g AgCl emulsion), the decay of free photoelectron of sensitized emulsion is slower or faster than that of pure emulsions; when sensitization concentration is between the above values (0.4 mg dye per 40 g AgCl emulsion), the decay of free photoelectron is the same for sensitized and pure emulsion. The results indicate that the adsorbed green-sensitizing dye on the surface of cubic AgCl microcrystals takes on different actions with different sensitization concentrations.

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Silver halide microcrystals are sensitive only to ultraviolet and blue light. Spectral sensitization is used to render photographic materials sensitive to green, red, and infrared light by putting sensitizing dyes on the surface of the Silver halide microcrystals[1]. But only dye adsorbed to the silver halide surface is effective for spectral sensitization[2]. So knowledge of the adsorption of sensitizing dyes to the microcrystals is important for understanding the mechanism of spectral sensitization[3] and has been studied for a long time[4−8]. However the previous methods such as analytical color fluorescence electron microscopy (ACFEM)[4,5], atomic force microscopy (AFM)[6−8] and high-resolution scanning electron microscopy (HRSEM)[6], etc. mainly invested the adsorption by directly observing the adsorption state, but didn't relate to the change of intrinsic photosensitive process of sensitized emulsion. As well known, the photoelectron is the foundation of latent image formation, the decay process of photoelectron can reflect the intrinsic photosensitive process. So the adsorption of dyes to the silver halide microcrystals can be studied from photoelectron decay characteristic of sensitized emulsion.

Microwave adsorption dielectric spectrum equipment with a high time resolution (1 ns) is used in this experiment. The experiment setup and principle are referred to Ref. [9]. The AgCl emulsion in this work was prepared by a controlled double jet method. Different volumes of methanolic solution of dye were individually added to the emulsion, which were agitated for 20 min on 45 °C, coated on cellulose film base, dried, and subjected to the measurement of free photoelectron signal. The dye used in this paper was green-sensitizing dye, whose structure is shown in Fig. 1.

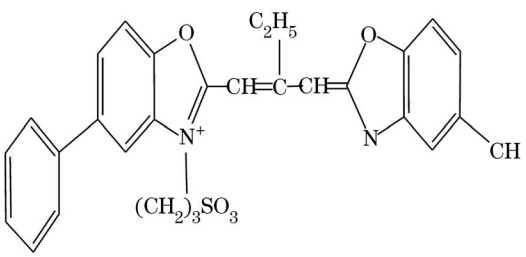

Fig. 1. Dye.

Figure 2 shows the free photoelectron signal of pure cubic AgCl emulsion. Figure 2(a) is the decay curve of free photoelectron, which is normalized. The time during which the photoelectron intensity decays from 100% to 10% is defined as free photoelectron decay time (FDT). Figure 2(b) is the semi-logarithm curve corresponding to Fig. 2(a), which shows that the decay of photoelectron can be divided into two first-order exponential decay sections. Free photoelectron lifetime (FLT) τ for each section can be estimated from the semi-logarithm curve. We define the FLT of each section as the first FLT and the second FLT, individually.

Figure 2(b) shows that the second FLT is smaller than the first FLT. So it can be concluded[10] that there are two kind of intrinsic deep electron traps in the pure

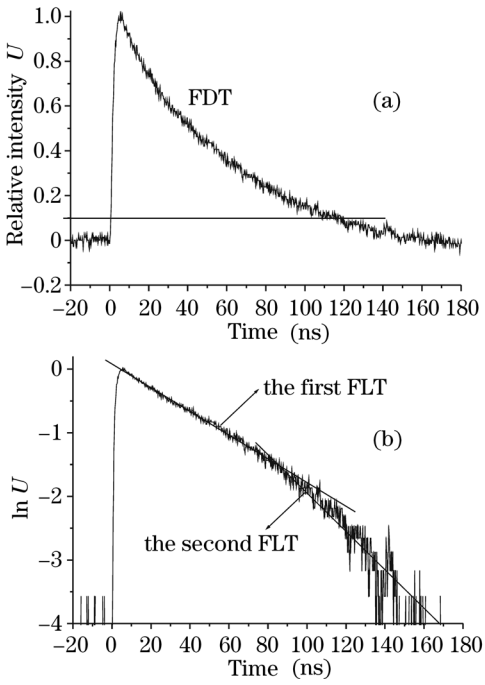

Fig. 2. Free photoelectron signal of pure cubic AgCl emulsion: (a) decay curve of free photoelectron (b) the semi-logarithmic plot of the free photoelectron signal

emulsion, one is the external deep electron traps which are supposed as some big dislocations on the surface and according to the first section of decay, and the other is the internal electron traps which are according to the second section of decay. Photoelectrons firstly are trapped by the external deep electron trap after it is produced, only a few photoelectrons diffuse into the interior of silver halide crystal. So internal photoelectrons relative to internal electron traps are less, the decay of photoelectron in the second decay section is faster.

The free photoelectron signal of spectral sensitized emulsion has the same form to that of pure emulsion. The decay of free photoelectron also can be divided into two first-order exponential decay sections. The changes of FDT and FLTs of AgCl emulsion with sensitization concentration are shown in Fig. 3. It is can be seen that FDT and the first FLT have the same tendency. When sensitization concentration is small (0.04 mg dye per 40 g AgCl emulsion) or great (4 mg dye per 40 g AgCl emulsion), the decay of free photoelectron of sensitized emulsion is slower or faster than that of pure AgCl emulsion; when the sensitization concentration is between the above values (0.4 mg dye per 40 g AgCl emulsion), the FDT and FLT are the same for sensitized and pure emulsion. It also can be seen that when the concentration reaches to a certain level (4 mg dye per 40 g AgCl emulsion), FDT and the first FLT do not change obviously with increasing the sensitization concentration. Be different from FDT and the first FLT, the second FLT only has obvious change when the concentration changes from moderate one (0.4 mg dye/40 g AgCl emulsion) to the big one (4 mg dye/40 g AgCl emulsion) and almost does not change in the other situation. After the change, the decay time in second section becomes very short.

The dye mainly adsorbs on the surface of microcrystals, thus the first FLT exhibits the same tendency with the FDT. The result that small sensitization concentration (0.04 mg dye per 40 g AgCl emulsion) makes FDT and the first FLT become bigger shows that the dye molecules take on a shallow electron trap effect on the whole when the adsorbed dye molecules is few. That is perhaps the result of forming new defects or making the intrinsic deep traps becoming shallower. Although there may be Ag_i^+ brought because of the adsorption of dye[11,12], the effect can be thought very small resulting from few adsorbed dye molecules. With the concentration increasing, the Ag_i^+ becomes more and more. We know that the Ag_i^+ takes on effect of deep electron trap by combining with the photoelectron. So when the concentration is moderate (0.4 mg dye per 40 g AgCl emulsion), the effect of shallow and deep electron trap reach equilibrium. FDT and the first FLT become the same for sensitized and pure emulsion. If the concentration keeps increasing (4 mg dye per 40 g AgCl emulsion), the effect of Ag_i^+ becomes dominant. So here the adsorbed dye molecules take on a deep electron trap effect on the whole. As a result, the FDT and the first FLT become smaller. Normally, the Ag_i^+ is gained from the kinks of the silver halide, where only Ag^+ but no sufficient Cl^- exists[12]. When the sensitization concentration reaches a certain level (4 mg dye per 40 g AgCl emulsion), the Ag^+ on the kinks almost all become Ag_i^+, which induces less Ag_i^+ generated, the FDT and the first FLT of photoelectron do not change obviously.

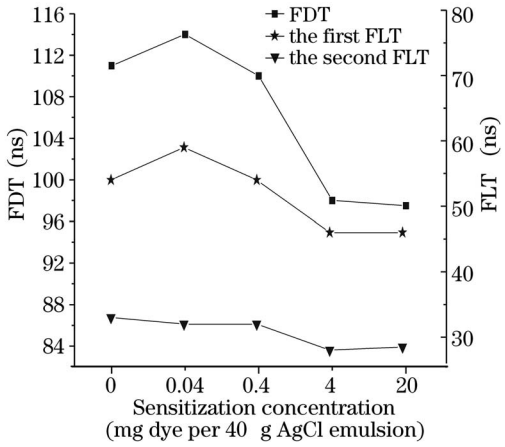

Fig. 3. Changes of FDT and FLTs of cubic AgCl emulsion with sensitization concentration (sensitization temperature: 45°C; sensitization time: 20 min).

The decay of second section is mainly determined by internal traps, so the second FLT is not influenced obviously within the certain range of sensitization concentration. But when the concentration achieves a certain degree (4 mg dye/40 g AgCl emulsion), the Ag_i^+ is so many that the photoelectrons nearly all decay on the surface, the second FLT is thus smaller resulting from the few photoelectrons reaching to the internal of silver halide grains.

In conclusion, when the sensitization concentration is different, the photoelectron decay characteristic of cubic AgCl emulsion sensitized by green-sensitizing dye is not the same. So it is can be concluded that the adsorbed green-sensitizing dye on the surface of cubic AgCl microcrystals takes on different actions with different sensitization concentrations. When the sensitization concentration is small (0.04 mg dye per 40 g AgCl emulsion), the adsorbed green-sensitizing dye takes on a shallow electron trap effect on the whole; when the concentration is great (4 mg dye/40 g AgCl emulsion), the adsorbed dye takes on a deep electron trap effect on the whole, which induce the photoelectrons nearly all decay on the surface; when the concentration is moderate (0.4 mg dye per 40 g AgCl emulsion), the above effects reach a equilibrium.

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