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# Investigation of photoelectron action in cubic AgCl emulsion doped with formate ions*

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In recent years, the formate ion ($HCO_2^-$) as a kind of hole-to-electron converter has attracted much attention of photographic researchers. The formate ions can trap photo-generated holes, eliminate or reduce the electron loss caused by electron–hole recombination in latent image formation process. Through the hole-to-electron conversion, it can also release an extra electron or electron carrier, improving photosensitivity. In this paper the microwave absorption and dielectric spectrum detection technique is used to detect the time evolution behaviour of free photoelectrons generated by 35ps laser pulses in cubic AgCl emulsions doped with formate ions. The influence of different doping conditions of formate ions on the photoelectron decay kinetics of AgCl is analysed. It is found that when the $HCO_2^-$ content is $10^{-3}$mol/mol Ag and the doping position is 90% the electron decay time and lifetime reach their maxima due to the efficient trap of holes by formate ions.

**Keywords:** hole trap, formate ion, photoelectron, microwave dielectric spectrum detection
**PACC:** 4270G, 8130, 7960

## 1. Introduction

In the past, researchers have exerted much effort to study the behaviour and the process of photoelectrons in hopes of finding out a method of improving the efficiency of latent image formation in silver halide, but paid less attention to the behaviour of photo-generated holes. In recent years, however, they have been attracted by utilizing the photo-holes for the same purpose. By use of a chemical method, holes can be converted into electrons or electron carriers to enhance the efficiency of latent image formation. Formerly, as two commonly used methods iodine ions were injected into AgCl emulsion or silver atom cluster $Ag_2$ was introduced into the AgCl crystals with the help of deoxidize sensitization. But the former would block the development, and the latter would lead to fog centre and compete with exterior latent image for capturing electrons. The two methods above would both lead to the decline in exterior photosensitivity.[1] Using absorbance measurement, Belloni *et al* detected the time evolution spectra and sensitivity of AgBr emulsion. They reported that the $HCO_2^-$ as a kind of hole-trap dopant was able to improve photosensitivity significantly, and proposed the following mechanism for the sensitization by formate ions:[2–4]

$$HCO_2^- + h^+ \rightarrow \bullet CO_2^- + H^+ \quad (1)$$

$$\bullet CO_2^- + Ag_n^+ \rightarrow Ag_n + CO_2, \quad (2)$$

where the formate ion in AgCl emulsion captures the photo-hole, and therefore enhances the escape of electrons from electron-hole recombination, and the resulting $\bullet CO_2^-$ radical in turn transfers an electron to another silver cation. In this way, the quantum yield increases to two silver atoms per photon absorbed. These authors also pointed that the formate ion did not directly reduce sensitizer and could not reduce silver cation in the dark either, so the risk of fogging was avoided. Using Electron spin resonance technique, Guo Hong *et al* gave indirect evidence for the existence of Reaction (1).[5] The work in Refs.[2–5] did not involve the sensitization mechanism of enhancing

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effective photoelectron yield by formate ion from the point of view of photoelectron change with time. In the present work by using the microwave absorption and dielectric spectrum detection technique and employing the formate sodium as a hole-trap dopant, we detect the time evolution behaviour of the photoelectrons in AgCl emulsions. The photoelectron decay action and trap-capture properties of formate ion are discussed. Finally the optimal doping quantity and position of the formate ions in the cubic AgCl emulsion are also determined.

## 2. Experiment

### 2.1. Sample preparation

A double-jet apparatus was used to prepare two series of cubic AgCl emulsions doped with formate sodium.

1) The doping quantity of $HCO_2^-$ was $10^{-4}$mol/mol Ag. The positions in cubic AgCl grains were 20%, 40%, 60%, 80%, 90% and 95%, separately. It is confirmed, that the optimal doping position is 90% (see Result and Discussion below).

2) The doping position was fixed at 90%, the doping quantities of formate ions were $10^{-6}$, $10^{-5}$, $10^{-4}$, $10^{-3}$and $10^{-2}$mol/mol Ag, separately.

The undoped emulsion is marked with 0. All parameters in the emulsifying process were controlled by computer. Electron microscopy was used for the measurement of the cubic grain sizes. The average edge length of cubic grains in the emulsions is 0.4$\mu$m. The doping quantity is expressed as the doping mole fraction of formate ion per mole Ag. The doping position is defined as the ratio of the additional accumulative amount of Ag at the time of doping formate sodium to the total additional amount of Ag at the ending of precipitation. Therefore, the larger the value of the doping position, the closer the dopant is to the surface.

### 2.2. Measurement of the time-resolved spectrum of photoelectrons

The microwave absorption and dielectric spectrum detection equipment [6−10] shown in Fig.1 was used to measure the samples.

Photoelectrons were generated when the Fig.1 sample of AgCl emulsion was exposed to laser pulses. The generation of photoelectrons led to the change of the dielectric function $\varepsilon$ ($\varepsilon = \varepsilon' + \mathrm{i}\varepsilon''$), and to the change of the reflected microwave $U$ as well. The reflected signal $U$ can be calculated by[11]

$$U = U_0 Q_0^2 \beta^2 - \frac{1}{2} U_0 f Q_0 \varepsilon'' + \mathrm{i} U_0 Q_0 \beta - \mathrm{i} \frac{1}{2} U_0 f Q_0 \varepsilon', \quad (3)$$

where $Q_0$ is the quality factor, $f$ is the filling factor and $U_0$ is the input microwave power. Reflected microwave power $U$ is the response signal of the microwave field to the change of the dielectric function. So $U$ is called dielectric spectrum, which reflects the photoelectron action. The signal was recorded with a digital oscilloscope. By analysing the photoelectron signal, we obtained the photoelectron action and its influence on the latent image formation.

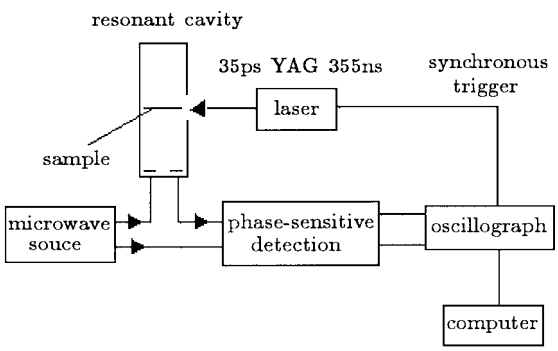



**Fig.1.** Block diagram of the experimental apparatus.

## 3. Result and discussion

Photoelectron decay process reflects the trend of the variation of photoelectron quantity with time, which is the basis of investigating the photoelectron yield. The photoelectron decay process includes the photoelectron trapping by electron trap, the photoelectron-hole recombination, and the electron capture involved in the silver clusters formation, so the free photoelectron decay time and lifetime reveal the decay properties in the formation process of the latent image. The photoelectron decay time (PDT) is defined as the time needed for the photoelectron quantity decaying from 90% to 10%. The photoelectron lifetime (PLT) can be calculated from the half-logarithm curve of the photoelectron delay curve as follows:[12]

$$\tau = -\frac{1}{k} = -\frac{\mathrm{d}t}{\mathrm{d}\left[\ln\left(U/U_0\right)\right]}, \quad (4)$$

where $U_0$ and $U$ are input microwave power and reflected microwave power respectively, and $k$ is the slope of the half-logarithm curve.

### 3.1. Influence of different doping positions of formate ions on the free photoelectron decay action of cubic AgCl emulsions

When the doping quantity of the formate ions is $10^{-4}$mol/mol Ag, the decay time and lifetime of the free photoelectrons of cubic AgCl emulsions doped with formate ions at different doping positions are given in Table 1. Clearly, when the doping position is 20%, the decay time and lifetime decrease, even lower than those of the undoped sample. With the dopant being close to the surface, the decay time and lifetime firstly increase and then decrease. At a doping position of 90%, the decay time and lifetime reach their maxima. Figure 2 shows a comparison between the free photoelectron decay time and lifetime curves for an undoped sample and a sample with a doping position of 90%. From the half-logarithm curve, it is seen that the decay process can be separated into two parts: A and B. With the formula (4) we can obtain $\tau_A(0) = 56$ns, $\tau_A(90\%) = 76$ns, $\tau_B(0) = 27$ns and $\tau_B(90\%) = 33$ns, i.e. $\tau_A(90\%) > \tau_A(0)$ and $\tau_B(90\%) > \tau_B(0)$. These results indicate that the free photoelectron decay of the sample with a doping position of 90% is slower than that of the undoped sample in the whole process. This is due to the fact that the doped formate ions act as hole traps capturing photoholes, thus the escape of electrons from the pairing recombination is promoted and the photoelectron decay time and lifetime are prolonged.

**Table 1.** The decay time and lifetime of free photoelectrons in a cubic AgCl emulsion with $10^{-4}$mol/mol Ag formate ions at different doping positions.

| Doping position (Ag) / % | The decay time of free photoelectrons (PDT)/ns | The lifetime of free photoelectrons (PLT)/ns |
|---|---|---|
| 0 | 108 | 56 |
| 20 | 94 | 51 |
| 40 | 118 | 74 |
| 60 | 112 | 62 |
| 80 | 101 | 52 |
| 90 | 123 | 76 |
| 95 | 109 | 58 |

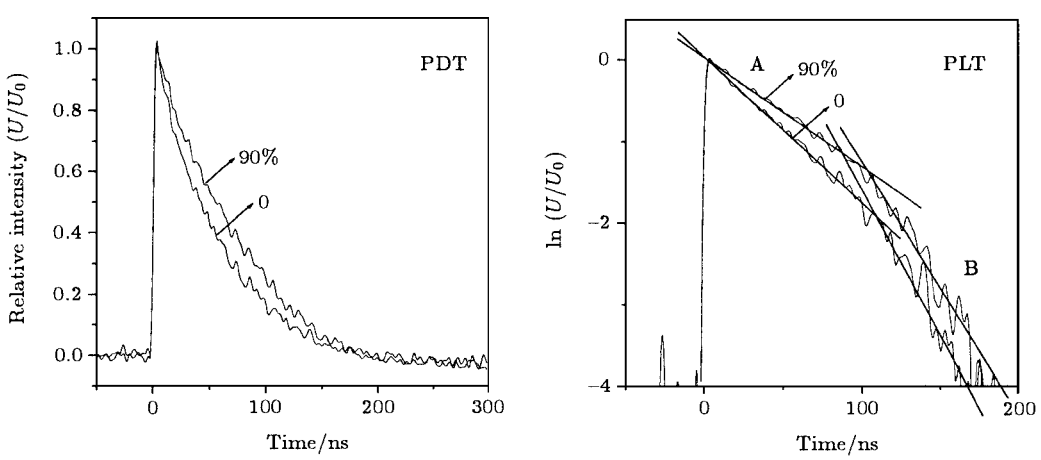



**Fig.2.** Comparison between the photoelectron decay time and lifetime curves for the undoped sample and the sample with a doping position of 90%.

### 3.2. Influence of the doping quantity of formate ions on the free photoelectron decay action of cubic AgCl emulsions

Figure 3 shows the variations of free photoelectron decay time and lifetime with the doping quantity of formate ions doped into cubic AgCl emulsions to a doping position of 90%. It is seen that with the increase of the doping quantity the decay time and lifetime increase, and then reach their maxima at a doping quantity of $10^{-3}$mol/mol Ag.

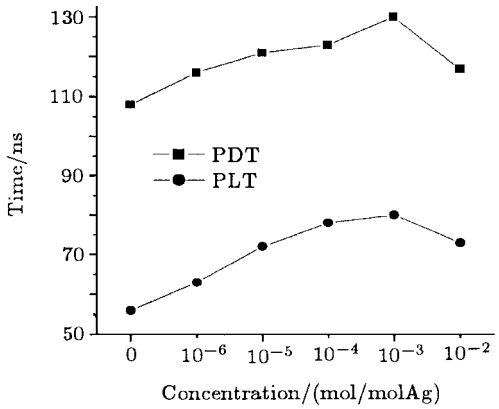



**Fig.3.** Decay time and lifetime of free photoelectrons in AgCl doped with different quantities of formate ions at a doping position of 90%.

Figure 4 gives a comparison between the free photoelectron decay time and lifetime for the undoped sample and the one doped with $10^{-3}$mol/mol Ag. From the half-logarithm curve, we obtain $\tau_A(0) = 56$ns, $\tau_A(10^{-3}) = 78$ns, $\tau_B(0) = 27$ns and $\tau_B(10^{-3}) = 34$ns, i.e. $\tau_A(10^{-3}) > \tau_A(0)$ and $\tau_B(10^{-3}) > \tau_B(0)$. These results indicate that the free photoelectron decay of the sample doped with $10^{-3}$mol/mol Ag is slower than that of the undoped one in the whole process. Therefore, the doped formate ions act as hole traps effectively.

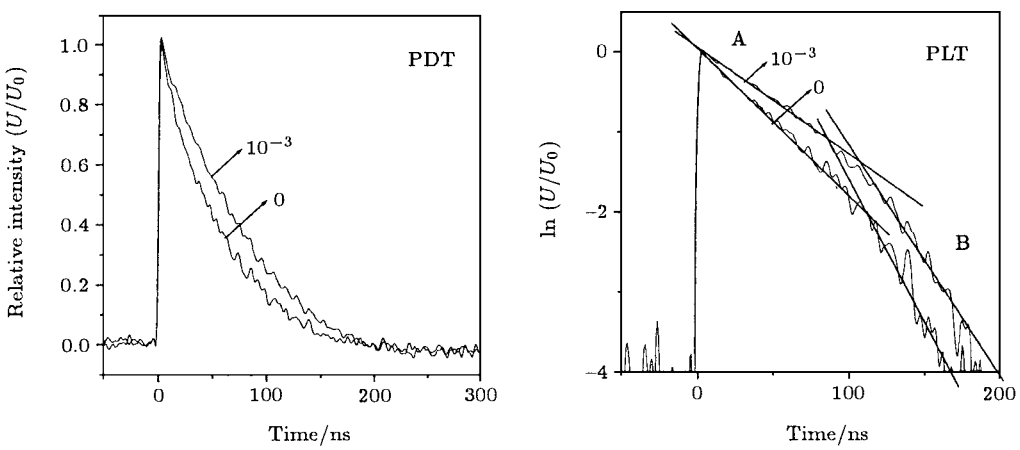



**Fig.4.** Comparison between the free photoelectron decay time and lifetime curves for the undoped sample and the one doped with $10^{-3}$ formate ions.

## 4. Conclusion

The time evolution behaviour of the free photoelectrons in an AgCl emulsion is detected with the microwave absorption and dielectric spectrum detection technique. The influence of doping conditions of formate ions on the photoelectron decay properties of cubic AgCl emulsions is discussed. We conclude that the optimal doping position is 90%, and the optimal doping quantity is $10^{-3}$mol/mol Ag. Further investigation of formate ion as hole-trap dopant is in progress.

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