The Interaction between Photographic Gelatins and Chemical Sensitizers*

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The interaction between two kinds of photographic gelatin and chemical sensitizers was studied by X-ray Photoelectron Spectroscopy. After the gelatin samples were immersed into the chloroauric acid solution for 5 min, methionine and methionine sulfoxide in gelatins were oxidized to methionine sulfone, reducing most parts of Au^{3+} to Au which was coordinated by gelatin macromolecule. According to the ratio of Au^{3+} to Au in gelatins, it is shown that the reducing power of Rousselot gelatin is stronger than that of Baotou gelatin. When sodium thiosulfate was added to gelatins, methionine sulfoxide was reduced to methionine. Sodium thiosulfate, which is a reductant stronger than both methionine and methionine sulfone, could coexist steadily with methionine and methionine sulfone in the gelatin. Two kinds of photographic gelatins added with sodium thiosulfate could reduce Au^{3+} to colloid gold. In this redox reaction, the main reductant is sodium thiosulfate, but not methionine in the gelatin. The addition of sodium thiosulfate enhanced the reducing power of the photographic gelatin.

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Introduction

Chemical sensitization is an important procedure in the preparation of the photographic emulsion. Chemical sensitization can increase the emulsion sensitivity significantly, as compared with that after physical ripening, by increasing the efficiency of trapping photoelectrons and photoholes. There are three principal categories of chemical sensitization:
(1) sulfur sensitization,
(2) gold sensitization, and
(3) reduction sensitization.

Sodium thiosulfate and $HAuCl_4$ are most commonly used for sulfur sensitization and gold sensitization, respectively. Studies on the sensitization mechanism and the chemical nature of the sensitive center have been reported widely.[1–3] Recently, the effect of the composition and structure of the photographic gelatin macromolecule—an essential material in the photographic emulsion—has been securing more attention from photographic scientists.[4] The properties of a photographic emulsion depend to a great extent on the composition of the inert gelatin. If an oxidized gelatin with less methionine is used, better photographic properties can been obtained for T-grain emulsions. Dickinson[5] studied the effect of non-gelatin protein containing cystinol and cysteine on the sulfur plus gold sensitization. The photographic gelatin plays important roles in all steps of the imaging process and its main property—the reducing power, surely influences the chemical sensitization. With the development of the technology for the preparation of inert gelatin, the reducing power of gelatin is mainly contributed by methionine and methionine sulfoxide.[6] Xun[7] measured the contents of methionine, methionine sulfoxide and methionine sulfone in various photographic gelatin samples with an amino-acid analyser.

In this article the interaction between two typical kinds of photographic gelatin and sodium thiosulfate, $HAuCl_4$, and sodium thiosulfate + $HAuCl_4$ were studied by X-ray photoelectron spectroscopy, respectively.

Experimental

The Preparation of Photographic Gelatin Samples

Two kinds of photographic gelatin, Rousselot gelatin N51811 (France) and Baotou gelatin 600# (Baotou, China) were used. The gelatins of each kind were soaked in water at room temperature for 30 min, then were heated to 50°C and dissolved. Sodium thiosulfate

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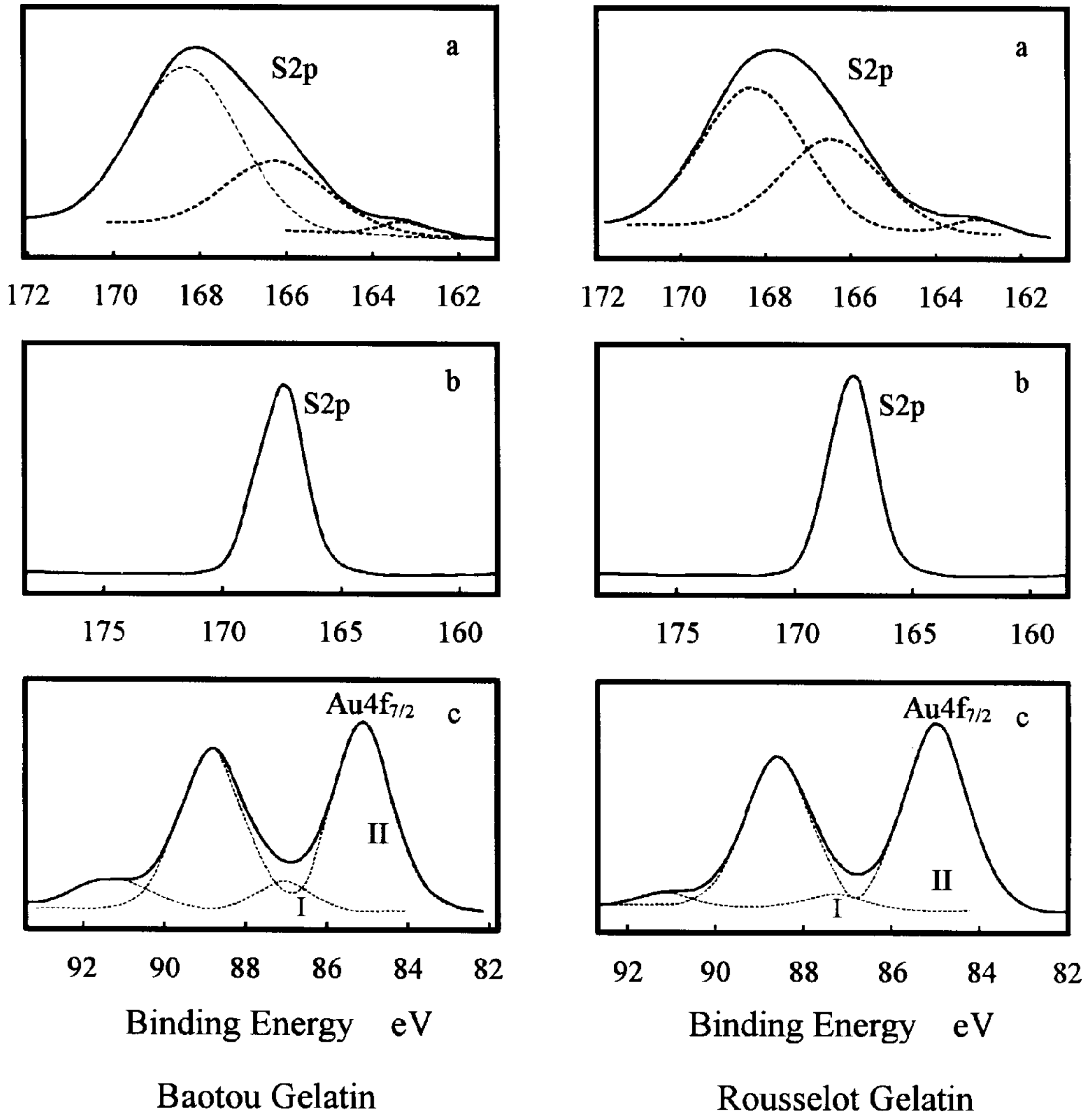


Figure 1. X-ray photoelectron spectra of S2p and Au4f of photographic gelatins before and after reacting with $AuCl_3$. (a) XPS of S2p before reaction, (b) XPS of S2p after 5 min reaction, (c) XPS of Au4f after 5 min reaction; solid line: experimental spectra, dotted line: deconvoluted spectra

($Na_2S_2O_3$, 14.8 g/g gelatin) was then added. The gelatin solutions, with and without sodium thiosulfate, were coated on the film bases, was the polyester film made in Lucky Film Co. (Baoding, Hebei, China). When dried thin film samples of gelatins were obtained.

All dried film samples were immersed into the $HAuCl_4$ aqueous solution (4.86×10^{-3} mol/L) for 5 min, then were dried rapidly by blowing cold air and their XPS spectra were measured immediately. All reagents used in this study were analytic grade reagents made in Shanghai Reagent Factory (Shanghai, China).

The Measurement of XPS Spectra

ESCA analysis was carried out with a multi-function X-ray photoelectron spectrometer, Model ESCA-LAB MK II(VG Co. England). The pressure in the ultrahigh vacuum chamber of the spectrometer was lower than 5×10^{-7} Pa. Mg Kα radiation with photon energy hν = 1253.6 eV was used as a radiation source. The power of the X-ray target was 320 W and the pass energy in the analyzer was 30 eV. Carbon deposited on the sample surface that exhibits the sharp peak of C1s at 284.5 eV was used as the standard of binding energy. The characteristic peaks of $S2p_{3/2}$ and $Au4f_{7/2}$ were used in the analysis of sulfur and gold, respectively. The deconvolution and synthesis of XPS spectra and the integration of the areas under the spectral curves were done with the aid of the computer attached to the spectrometer. The relative contents of each state were calculated from the areas under the peaks of the corresponding spectral curves after deconvolution.

Results and Discussion

The Chemical State of Sulfur In Undoped Gelatin Samples

The XPS spectra of sulfur in undoped gelatins (B-0 and R-0) are shown in Fig. 1a, where the solid curves represent the experimental spectra and the dotted curves represent the computer deconvoluted spectra of various states. From Fig. 1a it is obvious that the ex-

TABLE I. Binding Energy of $Au4f_{7/2}$ After the Interaction Between $AuCl_3$ and Undoped Photographic Gelatin

Gelatin sample	Binding energy $Au4f_{7/2}$ eV	Relative content %
Baotou gelatin	85.1	75.66
	87.1	24.34
Rousselot gelatin	85.1	78.94
	87.2	21.06

TABLE II. Binding Energy of $S2p_{3/2}$ in Sodium Thiosulfate

Standard sample	Binding energy $S2p_{3/2}$ eV	Relative content %
$Na_2S^*SO_3$	161.9	46.03
sodium thiosulfate		
$Na_2SS^*O_3$	167.9	53.97

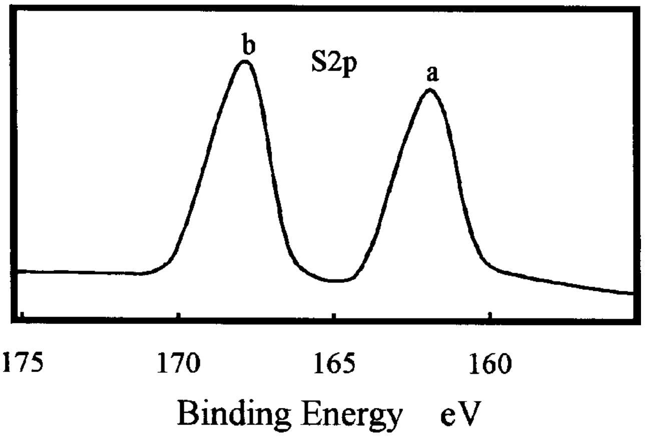
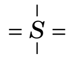


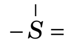
Figure 2. X-ray photoelectron spectrum of S2p in sodium thiosulfate standard sample. a: ligand sulfur atom, b: central sulfur atom

perimental spectra show wide, non-Gaussian asymmetric envelope signals, indicating that the sulfur in undoped gelatins is in various states. The XPS spectra were deconvoluted by the computer. The deconvoluted spectra indicate that in both gelatins there are three chemical states of sulfur. In comparison with the XPS spectra of the standard samples of methionine sulfone, methionine sulfoxide and methionine,[8] it can be seen that the three peaks in the deconvoluted spectra correspond to the following structures: the peak with binding energy 168.2 ± 0.1 eV is contributed by the group



$$=\overset{|}{\underset{|}{S}}=$$

in methionine sulfone; the peak with binding energy 166.2 ± 0.0 eV is contributed by the group



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in methionine sulfoxide, and the peak with binding energy 163.2 ± 0.1 eV is contributed by the group $-S-$ in methionine.

Interaction Between Undoped Gelatin and $AuCl_3$

The spectra of sulfur and gold after the interaction between the two undoped gelatins and gold are shown in Fig. 1b and 1c, respectively. Figure 1b indicates that the shapes of the spectral curves are typically Gaussian symmetric, and sulfur is in a single chemical state of methionine sulfone whose binding energy is 168.2 eV. The wider envelope signal shown in Fig. 1c was deconvoluted by the computer and two spectra were obtained indicating that two chemical states of gold, I and II, coexisted. When compared with XPS data base[9] it is seen that state I corresponds to Au^{3+}, while state II corresponds to Au^0. The binding energy values of gold of both states and their relative contents are listed in Table I.

Because the preparative technology of inert gelatin has been improved and perfected, the reducing power of the photographic gelatin is mainly due to the reducibility of some sulfur-containing amino-acid groups in the gelatin macromolecule which are principally methionine and methionine sulfoxide. Figures 1b and 1c indicate that both methionine and methionine sulfoxide in the two kinds of undoped gelatin were oxidized to methionine sulfone by Au^{3+} and most Au^{3+} absorbed in soaked gelatins were reduced to Au^0. If the reduced Au were in a metallic state, its binding energy should be 84.0 eV.[9] Table I shows that its binding energy is 85.1 eV. The chemical shift to higher value about 1.1 eV indicates that gold in the photographic gelatin is in a complex state, and its density of the outmost shell electron cloud is lower than that of metallic Au.

The difference in the contents of methionine, methionine sulfoxide and methionine sulfone in various gelatins will certainly result in difference of their reducing power.[10] In this study this difference may be represented by the difference in relative contents of Au^{3+} and Au in the two gelatins. From Table I it can be seen that the ratio of Au^{3+} to Au for Rousselot gelatin is 0.28 and that for Baotou gelatin is 0.38, indicating that the reducing power of Rousselot gelatin is stronger than that of Baotou gelatin.

Chemical State of Sulfur in the Photographic Gelatin After Doping Sodium Thiosulfate

The configuration of $S_2O_3^{2-}$ is a tetrahedral one, resulting from replacing an oxygen atom by a sulfur atom in SO_4^{2-}. Therefore, there are two oxidation states of sulfur in the sodium thiosulfate molecule, i.e., central sulfur atom and ligand sulfur atom. In order to study the effect of doping sodium thiosulfate on photographic gelatin, the XPS spectrum of sulfur of the standard sodium thiosulfate sample was measured, shown in Fig. 2.

In Fig. 2 the XPS spectrum of sulfur contains two independent peaks. Their binding energy values and relative contents are reported in Table II. The binding energy value reflects the density of the outermost shell electron cloud. The lower the binding energy is, the higher the density of the electron cloud in the outermost shell, and hence the stronger the reducing power. The moderate reducing power of sodium thiosulfate is attained by the ligand sulfur atom whose binding energy is 161.9 eV.

The XPS spectra of sulfur in the two gelatins doped with sodium thiosulfate are shown in Fig. 3a, respectively, and their binding energy values and relative contents of each component corresponding to each peak are listed in Table III. From Fig. 3a it is found that although there are still three chemical states for sulfur in both gelatins after doping with sodium thiosulfate, their binding energy values and relative contents change considerably

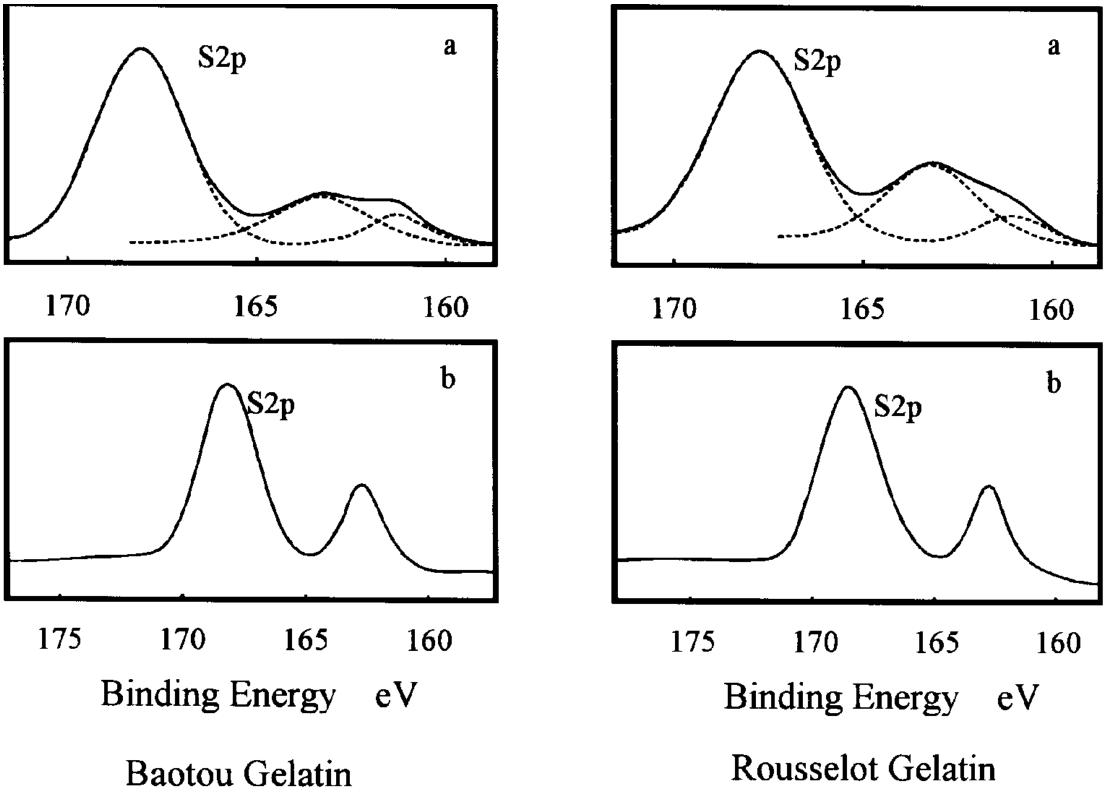

Figure 3. X-ray photoelectron spectra of S2p of photographic gelatin added with sodium thiosulfate before and after reacting with $AuCl_3$. (a) before reaction, (b) after 5 min reaction; solid line: experimental spectra, dotted line: deconvoluted spectra

TABLE III. Binding Energy of $S2p_{3/2}$ in Undoped and Doped Photographic Gelatins

	Gelatin sample	Binding energy S2p eV	Relative content %
Baotou Gelatin	B – 0	168.3	68.23
		166.2	29.03
		163.2	2.74
	$B+Na_2S_2O_3$	168.2	59.82
		163.3	20.37
		161.3	19.81
	$B+Na_2S_2O_3+AuCl_3$	168.3	79.89
		163.1	20.11
Rousselot Gelatin	R– 0	168.1	57.64
		166.2	40.09
		163.3	2.27
	$R+Na_2S_2O_3$	168.2	62.98
		163.2	26.33
		161.1	10.69
	$R+Na_2S_2O_3+AuCl_3$	168.4	74.02
		163.2	25.98

compared to before doping. The peak with binding energy 166.2 eV corresponding to methionine sulfoxide in undoped gelatin disappears, and a new peak with binding energy 161.2 ± 0.1 eV appears (shown in Fig. 3a and Table III). According to the XPS spectrum of the standard sodium thiosulfate sample (shown in Fig. 2 and Table II), it can be known that this peak is associated with the ligand sulfur atom in sodium thiosulfate.

Wood[11] reported that the natural sensitizer in the photographic gelatin was a thiosulfate salt or a compound with very similar properties, and the thiosulfate salt was formed by the degradation of sulfur-containing amino acid during the processing of collagen. From Figs. 1a, 3a and Table III, the following conclusions can be obtained. (1) The two kinds of gelatin used in this study do not contain any thiosulfate salt, because in preparing inert gelatin the impurity substances have been removed as many as possible. (2) The reducing power of sodium thiosulfate added is stronger than that of methionine, methionine sulfoxide and methionine sulfone in the photographic gelatin, so that all methionine sulfoxide is reduced to methionine by added sodium thiosulfate. (3) After the interaction between the gelatin and sodium thiosulfate the remainder sodium thiosulfate can steadily coexist with methionine and methionine sulfone.

Because the amount of sodium thiosulfate added is higher than the content of sulfur-containing amino-acid in gelatin,[12,13] the peak in Fig. 3a with binding energy 168.2 eV can be considered to be contributed by SO_4^{2-} and methionine sulfone. SO_4^{2-} is the oxidation product of $S_2O_3^{2-}$. The central sulfur atom forms conjugated double bonds O = S = O, with two oxygen atoms. This structure is very similar to that in methionine sulfone. The peak with binding energy 163.2 eV is contributed by methionine.

Interaction Between the Photographic Gelatin Doped with Sodium Thiosulfate and $AuCl_3$

Tani[13] indicated that methionine in gelatin was not only a natural peptizing agent for silver halide, but also a main reductant for Au^{3+}. After sodium thiosulfate is added into the gelatin, it may appear, at first, that the reducing power were contributed by two kinds of sulfur-containing groups, $S_2O_3^{2-}$ which is added and the – *S* – group that originally exists in methionine. However, the XPS spectra after the interaction between the gelatin doped with sodium thiosulfate and $AuCl_3$ indicate the following facts.

From Fig. 3b, and Tables II and III it can be seen that the peaks corresponding to $S_2O_3^{2-}$ disappear, while the relative content of methionine remains almost constant and the relative content of SO_4^{2-} increases. The results indicate that it is the $S_2O_3^{2-}$ group that reduces Au^{3+}.

Figure 4 shows that for the two kinds of gelatin doped with sodium thiosulfate after 5 min interaction with $AuCl_3$, all Au^{3+} is reduced to Au, whose binding energy is 84.0 eV,[9] and Au is in a colloid state because of the high concentration of gelatin.[14,15] The interactions between both undoped and doped gelatins with $AuCl_3$ take place at the same condition, so that it can be concluded that the reducing power of the doped gelatin is stronger than that of undoped gelatin.

Conclusions

1. Both of the two kinds of photographic gelatin undoped with sodium thiosulfate can partly reduce Au^{3+} absorbed in soaked gelatin to Au, which is in a colloid state in the gelatin. At the same time the sulfur-containing amino-acid—methionine and methionine sulfoxide are completely oxidized into methionine sulfone.
2. After the addition of sodium thiosulfate, methionine sulfoxide in gelatin is entirely reduced into methionine; $S_2O_3^{2-}$ can coexist with methionine and methionine sulfone in the gelatin system. The reducing power of the foreign sodium thiosulfate is stronger than that of methionine and methionine sulfoxide.
3. After the addition of sodium thiosulfate, Au^{3+} adsorbed in both of the two kinds of gelatin can be completely reduced to colloid Au. In this situation the main reductant is $S_2O_3^{2-}$, and not methionine of gelatin. ◆

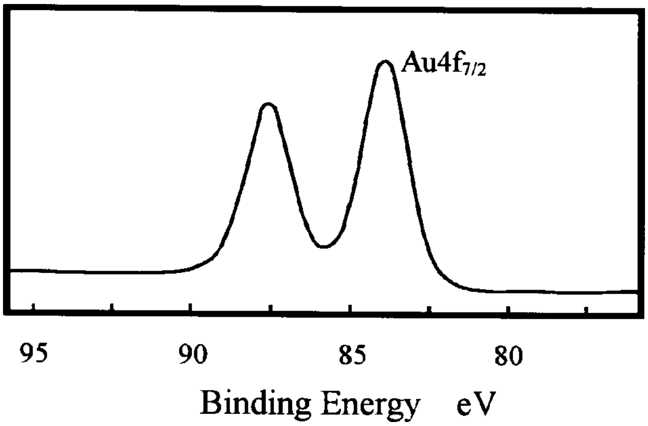

Figure 4. X-ray photoelectron spectra of Au4f of photographic gelatin added with sodium thiosulfate after reacting with $AuCl_3$ for 5 min

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