

NEXAFS Spectroscopic Study of Organic Photographic Dyes and their Adsorbed States on AgCl and AgBr

Tohru Araki[†], Eisuke Ito[†], Kazuyoshi Oichi[†], Ryuichi Mitsumoto[†],
 Masaki Sei[†], Hiroshi Oji[†], Yasushi Yamamoto[†], Yukio Ouchi[†],
 Kazuhiko Seki[†], Yasutaka Takata[§], Kunishige Edamatsu^{*}, Toshihiko Yokoyama[□],
 Toshiaki Ohta[□], Yoshinori Kitajima[#], Satoko Watanabe[¶],
 Katsuhiko Yamashita[¶], and Tadaaki Tani[¶]

[†] Department of Chemistry, Faculty of Science, Nagoya University, , Japan,
[#] Photon Factory, National Laboratory for High Energy Physics, Ibaraki, Japan,
[§] Institute for Molecular Science, Myodaiji, Okazaki, Japan
 Photon Factory, Institute of Materials Structure Science, High Energy Accelerator
 Research Organization, Tsukuba, Ibaraki, Japan
^{*} Department of Materials Science, Faculty of Science, Hiroshima University, Japan,
 Department of Chemistry, Faculty of Science, The University of Tokyo, Japan
 Ashigara Research Laboratories, [¶] Fuji Photo Film Company Ltd., Kanagawa Japan

Abstract

The near-edge X-ray absorption fine structure (NEXAFS) spectra were studied at the S K-edge using synchrotron radiation for various sulfur-containing organic photographic materials in the solid state and in the adsorbed states on AgCl and AgBr grains. The features in the spectra of neat solids were assigned by mutual comparison and the polarization dependence. The spectra of merocyanine dyes including thiocarbonyl group were drastically affected by the adsorption on AgCl and AgBr, with significant suppression of the peak corresponding to the excitation of S 1s electron into the π^* orbital at the S=C bond. This change is interpreted as indicative that these compounds are adsorbed at the S atom in the thiocarbonyl group with rearrangement of the chemical bonds leading to a contribution from the zwitterionic form with $S^-C=N^+$ structure. By taking account of the area occupied by a molecule estimated from the measurements of adsorption isotherm, a rather detailed picture emerged about the adsorbed state of this kind of dyes. In contrast, the spectra of merocyanine and cyanine dyes containing sulfur in the five-membered aromatic ring showed little change by the adsorption on AgCl, indicating that S atom is not the absorption site or the interaction between the molecule and AgCl is weak.

Introduction

In silver halide photography, many organic materials are added to the photographic emulsions to complement the performance of silver halide grains¹. A typical example is spectral sensitization in which dyes adsorbed on silver halide grains enable not only to extend the sensitivity of silver halide to the whole visible region, but also to perform the reduction of the spectral sensitivity into three principal colors.^{1,2}

For understanding and improving the function of these materials, the elucidation of their adsorption geometry on silver halides and the resultant interfacial electronic structure are important. These states are also interesting from the basic viewpoint of the interaction between organic and ionic materials. Techniques such as X-ray photoelectron spectroscopy (XPS) and infrared absorption spectroscopy have been applied to the study of these systems³, but only incomplete understanding could be accomplished.

Recently, near edge X-ray absorption fine structure (NEXAFS) spectroscopy is rapidly growing into a new branch of X-ray absorption spectroscopy with various applications in chemistry⁴. In this spectroscopy, core electrons in a molecule are excited into various vacant orbitals by the absorption of soft X-ray radiation. Since the energies of the initial core orbitals are well separated among elements, one can selectively obtain element-specific information by examining the absorption edge of respective element. The core-electron excitation is subject to strict

selection rules, and the spectra of oriented samples show significant dependence on the polarization of the incident light. This is a useful guideline for reliable peak assignments. Further, the high sensitivity achieved by employing appropriate mode of measurement⁴ enables the study of adsorbed states and ultra thin films of organic materials on solid surfaces. Thus there have been several applications of NEXAFS to the study of the solid and adsorbed states of organic photographic materials⁵⁻⁹ by using synchrotron radiation, which is an excellent polarized light source.

Among the elements found in organic photographic materials, sulfur is one of the most interesting. It has high affinity to silver ions in silver halides, and often forms a part of π -conjugated system in the molecule. Smith *et al.*^{5,6} reported an extensive work on the S and Cl K-edge NEXAFS for the bulk solids of organic photographic materials and related compounds. We have also reported NEXAFS measurements of sulfur-containing organic photographic materials in bulk solid at the S, N, and O K-edges⁷, with special interest in the tautomerism in the thioamide group.

One of the most important aspects of these materials is the information about their submonomolecular layer adsorbed state on silver halides. We have already discussed briefly how the spectra of some dyes containing thiocarbonyl group were drastically changed by the adsorption on AgCl, indicating their strong interaction with AgCl at this site^{8,9}. On the other hand, Smith *et al.*⁶ reported preliminary observations on their adsorbed state on AgBr sheets, and claimed that the spectra of the adsorbed dyes show little indication of strong interaction between the adsorbed molecules and silver halide. In this paper, we report NEXAFS studies of dyes in the bulk and the adsorbed states on AgCl grains at the S K-edge, using well-characterized specimens. The comparison of the spectra of these states clearly demonstrates the existence of strong interaction with silver halide for dyes containing thiocarbonyl group. For one of these dyes, we also performed experiments on the dye/AgBr interface, and obtained similar results with those for the dye/AgCl interface. From the combination of the NEXAFS studies and the study of adsorption isotherm to silver halides, a rather detailed picture of the adsorbed state of this class of dyes has emerged. The implication of such adsorption geometry on spectral sensitization is also discussed in relation to the interfacial electronic structure obtained by UV photoelectron spectroscopy^{9,10}.

Experimental

Samples

Merocyanine dyes were synthesized in Ashigara Research Laboratories according to the literature cited in ref 11. The purities of these materials exceeded 99%, as assessed by elemental analysis and liquid chromatography. The NEXAFS samples for the bulk solid were prepared by rubbing their powder on Ag sheets or by vacuum evaporation on Cu sheets of 50 to 100nm thicknesses. For the preparation of the NEXAFS specimen of dyes adsorbed on these grains, a methanolic solution of the dye was added

to an aqueous suspension of AgCl powder, which was then agitated at 45°C for 2h. The AgCl powder with dyes adsorbed was separated from the suspension, washed by water, then dried in a draft chamber. As described later, the dye adsorption is of Langmuir-type, leading to saturated adsorption under this condition. As for AgBr specimens in NEXAFS measurements, we prepared AgBr films with thickness of 50nm by vacuum evaporation on Ag sheet. The evaporated AgBr film was immersed in methanolic solution of merocyanine dye and washed by water in a way similar to the case of AgCl powder.

NEXAFS Measurements

NEXAFS spectra were measured on BL-11B and 2A soft X-ray beamlines at the Photon Factory in the National Laboratory for High Energy Physics (KEK-PF) with synchrotron radiation from a bending magnet (11B)^{12,13} or an undulator (2A)¹⁴⁻¹⁶ monochromatized by a double crystal monochromator. The resolution with an InSb(111) (BL-11B) or a Si(111) (BL-2A) crystal in the S K-edge region was about 1.0 and 0.3 eV, respectively. The spectra were measured in the photon energy region of 2460 - 2510 eV, and the photon energy was calibrated by taking the lowest energy peak of K₂SO₄ to be at 2481.7 eV¹⁷.

The spectra were measured in a vacuum chamber evacuated to 10⁻⁶ Pa range. The spectra of the bulk samples were measured in the total electron yield mode (TEY)⁴. The amount of emitted photoelectrons was measured as the drain current from the sample. It was amplified by a picoammeter, converted to a train of pulses by a VF converter, and counted by a counter. The incident photon intensity was measured as the drain current from a nickel or copper mesh inserted in the light path. The obtained photoemission yield as a function of photon energy is known to be a good replica of the absorption spectrum⁴.

In the case of the adsorbed states, the amount of the adsorbed dye molecules per surface area is small, and only one or a few S atom(s) are contained in a large organic molecule. For overcoming this difficulty, we employed fluorescence yield detection⁴ using a UHV-compatible gas proportional counter¹³, combined with the use of AgCl powder samples. Since many dye molecules on the large area of powder surfaces could be probed by virtue of the large penetrating depth of incident and fluorescence photons, we could obtain spectra with rather good signal to background ratio. On the other hand, we could not get spectra of good quality for AgBr powder samples, since the energy resolution of the proportional counter was not sufficiently high to distinguish between the weak S K-fluorescence from the dye and the strong Br L-fluorescence from AgBr powder.

To reduce the ratio of Br L-fluorescence to S K-fluorescence we reduced the total amount of AgBr in the specimen by using dye adsorbed on very thin evaporated film of AgBr (50 nm thick) instead of AgBr powder of thousands nm size. With these samples, we could obtain spectra of reasonable quality.

One difficulty in the high energy spectroscopy of Ag halides is the radiation damage of the sample, as observed in previous XPS experiments³. This effect was not so severe in

experiments using synchrotron radiation from a bending magnet (BL-11B), but we observed some damage when we employed intense radiation from the undulator (BL-2A). This effect could be reduced to almost negligible level by cooling the sample below 120K with liquid nitrogen.

Results and Discussion

In Figure 1 we show the spectra of two typical S containing merocyanine dyes in the solid and the adsorbed states on AgCl powder.

At first we examine the spectra of the solid state. In the case of Dye1, which has a thiocarbonyl S(C=S), the peaks at 2470-71 eV and 2473-74 eV are assigned to the transitions from S 1s to $\pi^*(S=C)$ and $\sigma^*(S-C)$ orbitals, respectively, by the comparison with the results of extensive studies of thioamides⁷. The assignments of the higher energy features than the π^* and $\sigma^*(S-C)$ resonance peaks in the spectrum of Figure 1 are not clear at present¹⁹. In the case of dye 2, which has only a thia type S, the lowest energy peak at 2473-74 eV should contain the transition from the S1s orbital to the σ^* orbital localized on the S-C bond ($\sigma^*(S-C)$). Also we expect that it may contain the contribution from the excitation to the π^* orbital in the aromatic five-membered ring including the S atom. The lowest energy peak in the spectrum of thiophene, in which the sulfur atom is also included in an aromatic ring, actually consists of two excitations to $\sigma^*(S-C)$ and π^* orbitals^{20, 21}. These assignments for the excitations of thia and thio type S atoms also agree with those reported by Smith *et al.*^{5,6} for similar dyes and dye intermediates from extensive polarization measurements and the measurements of Ag salts.

Spectra of Adsorbed Dyes on Silver Halides.

After establishing the correspondence between the local environments of S atoms and the peaks in the spectra, we now examine the adsorbed states, with attention to the relation between the adsorption behavior of dyes and their chemical structure. To begin with we note that there have been several experimental findings suggesting that dyes containing a thiocarbonyl type S are adsorbed to silver halides at this S atom. Firstly, dyes containing C=S double bond have high adsorptivity, which implies that the C=S part has a strong interaction with a silver halide²⁴. Secondly, the adsorption of these dyes decreases the ionic conductivity of cubic AgBr grains in photographic emulsion. This can be interpreted as that the dye is adsorbed to the surface Ag⁺ sites, preventing the formation of interstitial Ag⁺ ions responsible for ionic conduction^{23,24}. These are, however, indirect evidence, and more direct information is desired. Trials by X-ray photoelectron spectroscopy (XPS), or ESCA, have suggested the change of the spectra in the S 2s and 2p region, but severe radiation damage and charging prevented definite conclusion³.

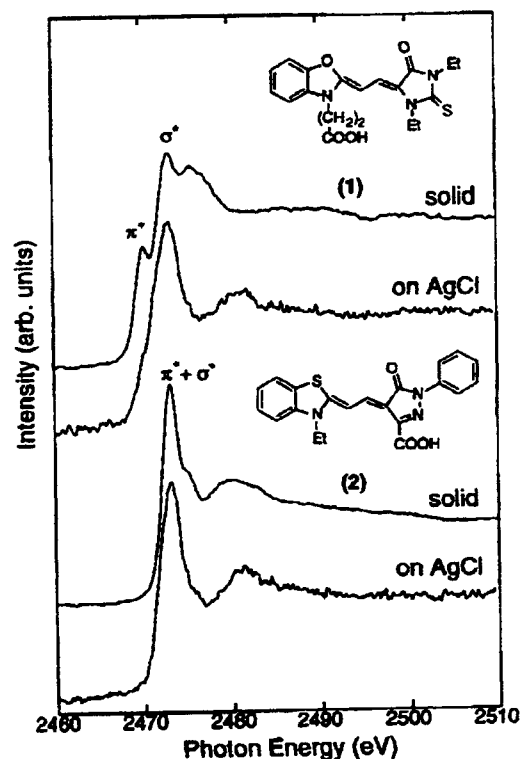


Figure 1 The S K-edge NEXAFS spectra of dyes 1 and 2 in the solid state and in the adsorbed state on AgCl powder.

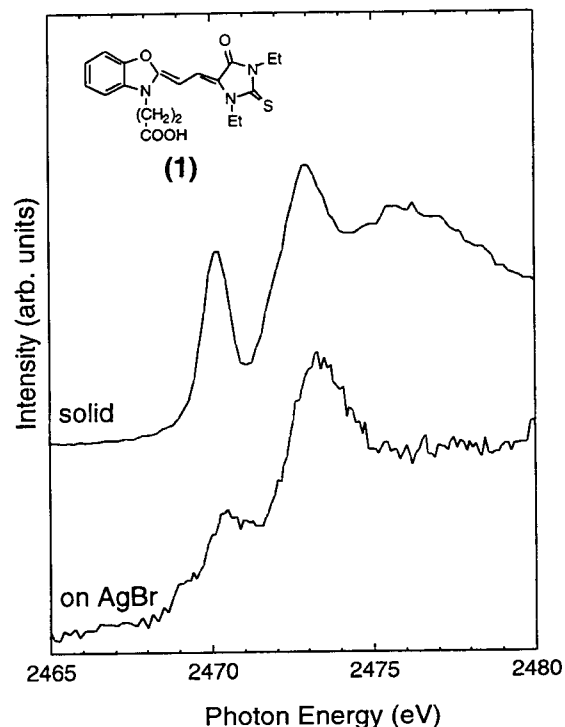


Figure 2. The S K-edge NEXAFS spectra of dye 1 in the solid state and in the adsorbed state on evaporated AgBr film.

(i) Adsorbed States on AgCl

In Figure 3, the NEXAFS spectra of two simple merocyanine dyes 1 and 2 adsorbed on AgCl are shown for comparison with the spectra of bulk solids. For dye 2, which contains a thia type S, the spectra show almost no change on adsorption, suggesting that either the S atom is not the adsorption site or the interaction between the S atom and AgCl is weak. On the other hand, for dye 1, which contains a thiocarbonyl type S, we see a drastic change of the NEXAFS spectrum from that of solid dye, with much decreased intensity of the $\pi^*(S=C)$ resonance peak. This clearly demonstrates that the thiocarbonyl part is the adsorption site, leading to significant change of the chemical bonding around the S atom.

(ii) Adsorbed State on AgBr

In Figure 2, the NEXAFS spectrum of the thiocarbonyl type merocyanine dye 1 adsorbed on AgBr evaporated film is shown in comparison with the spectrum of the bulk solid. The spectra show similar change by adsorption to that of 1 on AgCl powder, with reduction of the intensity of the $\pi^*(S=C)$ resonance peak. The feature at about 2470eV is better resolved in these spectra than those in Figure 1 in AgCl, due to the difference in the energy resolution of the beam-lines used. Still we suppose that the behavior of this dye is essentially similar for the adsorption on AgCl and AgBr.

Adsorption Geometry and Chemical Bonding of Thiocarbonyl Dyes.

As explained above, the NEXAFS spectra of the dyes with thiocarbonyl group point to the adsorption to AgCl and AgBr at the S atom in this group, with a large change of chemical bonding. With auxiliary information from the adsorption isotherm measurements, we can deduce more details about the adsorption geometry and chemical bonding.

The measured area/adsorbed molecule on AgCl and AgBr grains was 77.6 \AA^2 and 61.4 \AA^2 , respectively. The similar area/molecule for AgCl and AgBr suggests a similar way of adsorption on the two silver halides.

By approximating the shape of the dye with a rectangular body, we can suppose probable dye orientations on the grain surface to be flat-on, edge-on, and end-on²⁵, and estimate the area/molecule for these orientations to be 157, 72, and 44 \AA^2 , respectively. Thus the observed value of area/molecule is close to that expected for the edge-on geometry. By combining the information from NEXAFS and adsorption isotherm experiments, the adsorption geometry in Figure 3 can be deduced.

In the NEXAFS spectra of this type of dyes in Figures 1 and 2 we see the reduction of the intensity of the $\pi^*(C=S)$ resonance peak. This is indicative that the double bond nature of the CS bond is slightly modified to that of a single bond, corresponding to the partial occupation of the π^* orbital by the intramolecular polarization of the electron cloud. Such a change can be reasonably explained when we assume the adsorption at the C=S site onto the Ag^+ ion of silver halides. This will induce the rearrangement of the chemical bond of the S=C-N structure into a zwitterionic S^- -C=N⁺ structure.

Thus the actual chemical bonding in the adsorbed dye will be as the one depicted in Figure 3, which is between these two extreme structures.

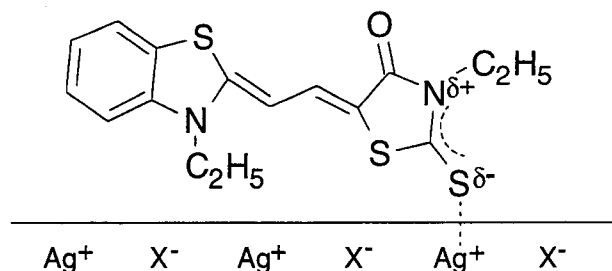


Figure 3. Estimated adsorption geometry and chemical bonding of dye 4 adsorbed on silver halide. X⁻ denotes the halide ion (Cl⁻ or Br⁻).

From the polarized chemical bonding in Figure 3, we expect the formation of a dipole layer at the surface of silver halides adsorbed with thiocarbonyl dyes, with the positive charge at the vacuum side. This will lead to the lowering of the vacuum level of silver halides by dye adsorption. Actually, our study of the electronic structure of thiocarbonyl dye/AgCl and dye/AgBr interfaces by UV photoelectron spectroscopy (UPS)^{9,10} revealed a large lowering of the vacuum level of the order of 1 eV. At least some part of this lowering may be due to the oriented dipole formed by the polarized dye molecules, besides the possible contribution from the transfer of electrons from the dye molecules to silver halides and the surface reconstruction of Ag halides by adsorption.

Conclusion

In this work, we have shown that NEXAFS spectroscopy at the S K-edge can be effective in the study of the adsorption of S-containing organic photographic dyes on silver halides. In particular, carefully prepared samples of submonomolecular layer of merocyanine dyes with thiocarbonyl group showed drastic changes in NEXAFS spectra upon adsorption to AgCl and AgBr. The analysis of the change, together with other information, offered rather detailed picture about the adsorption geometry and chemical bonding of the adsorbed state. In contrast, dyes containing sulfur in the aromatic five-membered ring showed little change of the NEXAFS spectra on adsorption on AgCl, indicating that the sulfur atom is not the adsorption site or the interaction of the dye with AgCl is not so strong.

Such an assignment of the adsorption site may be also possible by XPS, but NEXAFS has advantages over XPS in that (i) NEXAFS provides direct information such as the detection of unsaturated bond by π^* resonance, (ii) NEXAFS is free from the difficulty of energy calibration due to sample charging in XPS, and (iii) radiation damage can be smaller than in conventional XPS experiments, possibly because of the weaker photon flux in NEXAFS or the absence of sample heating by X-ray tubes close to the specimen. The last consideration is important to radiation-sensitive materials such as photographic systems.

Thus the present study has clearly demonstrated the usefulness of NEXAFS for the study of the adsorbed states of large functional organic molecules adsorbed on inorganic solid surfaces.

Moreover, direct determination of molecular orientation of dyes might become possible by measuring the polarization dependence of the NEXAFS spectra at these edges, if we can prepare dye samples adsorbed on well defined flat surfaces (e.g. (100) or (111) surfaces) of AgX single crystal. Although the preparation of such surfaces is rather difficult, we are now making effort in this direction.

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