45.2: XPS Characterization of Photo-alignment Using Adsorbed Dichroic Materials

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Abstract

Successful photo-alignment using adsorbed dichroic dyes can be obtained by properly matching the properties of substrates and adsorbed materials. Our results suggest that photo-induced anisotropic desorption produces photo-alignment in such systems. We used various characterization techniques to study the photo-alignment process. Polarized UV-vis spectrometry reveals the anisotropy of the alignment layer before and after exposure to linearly polarized UV light (LPUV). X-ray photoelectron spectroscopy (XPS) shows chemical changes at the surface and interfaces of the substrate materials, adsorbed materials, and liquid crystal. Angle resolved XPS provides information on the distribution of the adsorbed dichroic materials on the substrate surface. The information on the interaction between liquid crystals and alignment layer is crucial to understanding the alignment effect on a molecular level.

1. Introduction

Photo-alignment of liquid crystals has become the most promising substitute for conventional rubbing. Exposure to polarized light generates an anisotropic alignment layer. Numerous alignment materials and methods were used in the past decade to search for the optimum alignment effect. Although many mechanisms have been proposed to explain the effect of the alignment layer on liquid crystals, interactions between these two parts have not been fully understood on the molecular level.

2. Results and Discussion

In photo-alignment of liquid crystals using adsorbed dichroic materials, the alignment layer is constructed as follows: Low molecular weight dichroic materials, including dichroic dyes, are adsorbed onto a non-photosensitive substrate followed by exposure to linear polarized UV light (LPUV). The resulting surface serves as the alignment layer for the liquid crystal. Successful alignment results can be obtained by controlling the materials and the formation of the alignment layers. Typical examples of the adsorbed and substrate materials used and their photo-alignment effects are shown in Table 1. Various characterization techniques reveal the mechanism for this type of photo-alignment. Polarized UV-vis spectroscopy provides information on the anisotropy of the alignment layer. X-ray photoelectron spectroscopy (XPS), particularly angle resolved XPS, is used to study adsorbed dichroic materials. XPS spectra were acquired for Brilliant Yellow (BY), Polyvinylalcohol (PVA), and both LPUV irradiated and non-irradiated samples of BY adsorbed on PVA.
Polarized UV-vis spectroscopy reveals changes in the distribution of the adsorbed dichroic materials on the substrate surface before and after irradiation, as shown in Table 2. Compounds that have polar groups on both ends, such as 4,4'-dihydroxy azobenzene and 4,4'-biphenol, exhibit similar behavior under LPUV exposure. As shown in figure 1, the \( \lambda_{\text{max}} \) of 4,4'-dihydroxy azobenzene changes from 270nm in hexane solution to 400nm on PVA. This red shift results from the strong intermolecular interaction between the adsorbed dichroic materials and the substrate.

![Figure 1](image1.png)

**Figure 1.** The UV-vis spectra of 4,4'-dihydroxyazobenzene in hexane (solid line) and on PVA (broken line). The red shift of \( \lambda_{\text{max}} \) from 270nm to 400nm is due to intermolecular interaction between adsorbed dichroic material and substrate PVA.

Our results indicate that the azo group in 4,4'-dihydroxy azobenzene does not contribute to the alignment process and the cis/trans isomerization usually associated with azo compounds is not necessarily involved in this photo-alignment process. Photo-induced anisotropic desorption is proposed as the mechanism for this type of photo-alignment.

The interaction between the anisotropic alignment layer and liquid crystals after filling the cell is influenced by the distribution of dichroic molecules at the interface. Surface-sensitive characterization techniques are needed to closely examine the changes occurring at the surface and interfaces before and after irradiation. XPS provides extensive structural and chemical information about sample surfaces. Elements on a sample surface can be identified by their specific binding energy values according to the chemical environments they are in. In our system, any changes in the composition or chemical states of the alignment layer before and after LPUV exposure can be captured by XPS.

![Figure 2](image2.png)

**Figure 2.** Spectra deconvolution using pure BY and PVA as templates.

![Figure 3](image3.png)

**Figure 3.** High-resolution C 1s spectra of BY adsorbed on PVA. Left Column: non-irradiated sample; right column: LPUV irradiated sample. TOA from first to last row: 90°, 60°, 45°, 30°, 15°, respectively.

Angle resolved XPS provides information on concentration gradient as a function of depth. When the take-off angle is 90°, which indicates that the X-ray beam is vertical to the sample surface, the sampled depth is at the maximum of ~ 10nm. The detected signal becomes more surface specific at shallower angles.
Figure 2 shows the high-resolution C 1s spectra at 90° TOA. The spectra of pure BY and PVA, shown in part (a) and (b) respectively, are used as templates for spectra deconvolution. Part (c) is the spectrum of BY adsorbed on PVA before LPWV irradiation. It is made of PVA, BY and an extra peak at 286.7 eV. This peak represents the intermolecular interaction component (IMI) between BY and PVA. It is most likely to be the hydrogen bonding between the polar end groups of BY and the hydroxyl groups on PVA.

The change of the ratio BY/PVA with TOA is shown in figure 4. These values are calculated using the C 1s peak area assigned to each component. A general trend appears for both LPWV irradiated and non-irradiated samples. When the take off angle becomes smaller, the signal consists of more information from surface species. BY/PVA ratio increases with decreasing TOA, which indicates BY is mostly on the surface of PVA. This is consistent with the fact that the dichroic materials are spin-coated onto PVA in our system. The value of BY/PVA is smaller for irradiated sample than the non-irradiated samples, which indicates that there is less BY on PVA surface after LPWV irradiation.

The distribution of ratio of the intermolecular interaction component versus BY (IMI/BY) with takeoff angle is shown in figure 5. The ratio is decreasing with decreasing TOA, which indicates that intermolecular interaction occurs at the interface between adsorbed BY and PVA. At shallower takeoff angle, the signal consists of more information from BY and less information from the IMI component. The illustration of the structure of the Brilliant Yellow-PVA system is shown in figure 6.

XPS characterization on the interactions between liquid crystals and alignment layer is currently under investigation and will be reported in the future.

3. Conclusion
X-ray Photoelectron spectroscopy (XPS) is used to study photoalignment of adsorbed dichroic materials. Angle resolved XPS provides depth profile of the alignment layer. XPS characterization of adsorbed dichroic dye Brilliant Yellow on Polyvinylalcohol indicates that strong intermolecular interaction occurs between adsorbed BY and PVA. It also shows that LPWV irradiation results in photo-induced desorption of BY, which is in consistency with previous study results.

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5. References


