

Site-selective ionic dissociation of surface-oriented ester compounds using self-assembled monolayers by core-electron excitations

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Introduction

Core-electron excitations have quite unique nature differently from valence excitations because of special localization of core electrons. So, ion desorption induced by core excitations also reveals characteristic phenomena, in particular site-selective ionic dissociation is one of noteworthy characteristics. In this study, from the viewpoint of the site-selective ion desorption in core-excited PMMA ($-\text{[CH}_2\text{-(CH}_2\text{)CCOOCH}_3\text{]}_n\text{-}$), ion desorption of a series of ester terminated self-assembled monolayers (SAMs) was demonstrated.

Experimental

Experiments were carried out at the beamline BL7A, whose details were described elsewhere [1,2]. SAMs were prepared by immersing Au substrate into 1.0 mM ethanol solutions of MHDA ($\text{HS(CH}_2\text{)}_{15}\text{COOCH}_3$), MHDA- d_3 ($\text{HS(CH}_2\text{)}_{15}\text{COO-CD}_3$) and EHDA ($\text{HS(CH}_2\text{)}_{15}\text{COOC}_2\text{H}_5$).

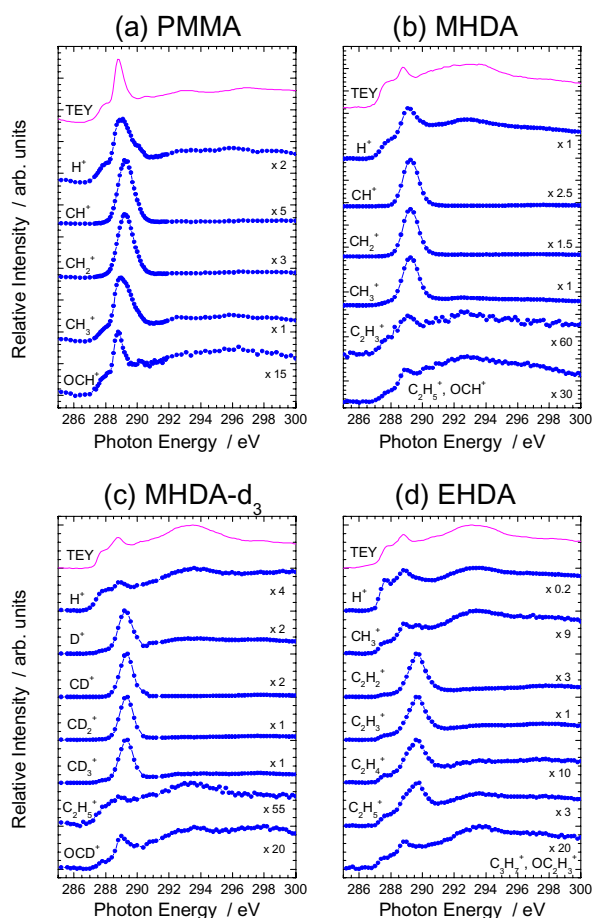


Fig. 1 PIY spectra of (a) PMMA, (b) MHDA, (c) MHDA- d_3 and (d) EHDA SAMs in the C K-edge region.

Results and Discussion

The total electron yield (TEY) and partial ion yield (PIY) spectra obtained in the C K-edge core excitation are indicated in Fig. 1. Site-selective dissociation can be clearly seen in the spectra of CH_n^+ (CD_n^+) and C_2H_m^+ series at the $\sigma^*(\text{O-CH}_3/\text{C}_2\text{H}_5)$ excitations. In comparison between PMMA and MHDA(- d_3), enhancements of the site-selectivity are seen especially in the CH_3^+ desorption. The observed variations in the PIY spectra are due to the variations of the ratio between the direct desorption (site-selective) and indirect desorption (non-selective) due to x-ray induced electron stimulated desorption (XESD), and the enhancement of the site-selectivity in MHDA indicates the suppression of the XESD component in the desorbing ions by utilizing a SAM as a monolayer. Relative reduction of the selectivity of C_2H_m^+ ions in EHDA compared to CH_n^+ in MHDA is due to suppression of the ion desorption caused by neutralization in desorbing. Fig. 2 depicts representative PIY spectra in the O K-edge, which also indicates the site-selective desorption in two excitations and the improvement of selectivity in MHDA.

References

- [1] K. Tanaka et al., Rev. Sci. Instrum. 66, 1474 (1995).
[2] S. Wada et al., Surf. Sci. 528, 242 (2003).

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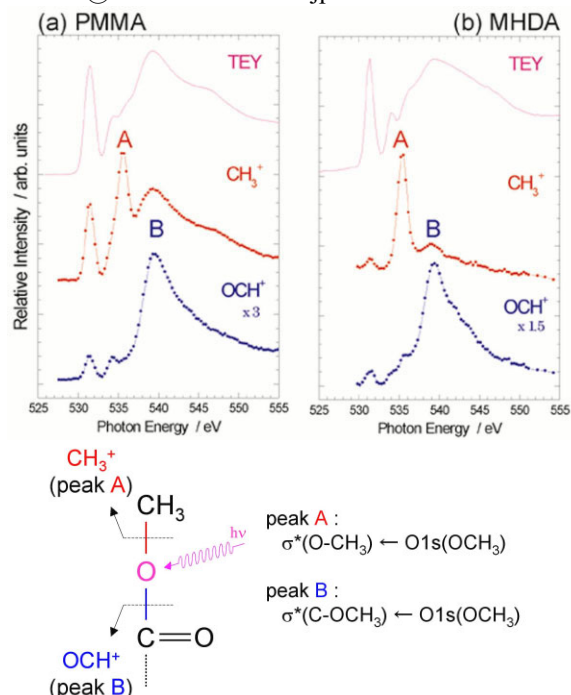


Fig. 2 Typical PIY spectra of (a) PMMA and (b) MHDA SAM in the O K-edge region.