

Effect of ultraviolet–ozone anode surface treatment on small-molecule organic solar cells

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The treatment of indium tin oxide (ITO) anodes with ultraviolet (UV)–ozone has been reported to play an important role in improving the initial device performance and durability against illumination stress in small-molecule organic solar cells (OSCs). The OSCs subjected to UV–ozone treatment showed only an 8% decrease in power conversion efficiency (η_p) after 100 repetitions of a 3-s-duration illumination and a subsequent 12 s under darkness. The OSCs with no UV–ozone exposure, however, exhibited a decrease of approximately 65% in η_p [1]. The mechanism for the improvement of the durability is not well understood. In this short report, the effect of UV–ozone treatment on the molecular orientation of copper phthalocyanine (CuPc) is investigated by near-edge X-ray absorption fine structure (NEXAFS) spectroscopy, where CuPc is widely used as an excellent donor layer material.

Figure 1 shows the cross-sectional view of a sample comprising a 2-nm-thick CuPc layer on ITO. The ITO surface was subjected to a 10-min UV–ozone treatment with an intensity of 13.5 mW/cm². CuPc was then evaporated onto the ITO substrate at a rate of 0.5 Å/s under a pressure of approximately 1.0×10^{-3} Pa. NEXAFS measurements were then performed at the BL-8 beamline of the SR Center at Ritsumeikan University. Attention was focused on the π^* peak intensity related to the N 1s $\rightarrow\pi^*$ transition at approximately 398 eV of photon energy. Three incident angles (θ) of the synchrotron radiation, 30°, 150°, and 90°, were adopted to assess the tilt angle (α) of the CuPc molecular plane. Two cases with and without 100 mW/cm² and AM1.5G illumination stress of 300-s duration through ITO were examined.

Figure 2 shows the nitrogen K-edge NEXAFS spectra of 2-nm-thick CuPc on the 10-min UV–ozone treated ITO with and without the 300-s-duration light illumination. Using the intensity ratio $R(\pi^*) = I(\theta = 90^\circ) / I(\theta = 30^\circ \text{ or } 150^\circ)$, we estimated the average tilt angle, α [2]. The intensity ratio $R(\pi^*)$ for the illuminated condition is larger than that for the dark condition. The angle α for the illuminated condition is 71°, whereas for the dark condition is 66°. These results indicate that the CuPc molecular orientation is changed into a more standing-

up configuration after light illumination in the near-surface region on ITO. However, the NEXAFS measurement for the 20-nm-thick CuPc sample shows that the angle α is almost constant at 65° irrespective of whether the UV–ozone treatment or the illumination was conducted.

Separate X-ray diffraction analysis shows that the light illumination and UV–ozone treatment cause the crystal disorder of CuPc films. Additional NEXAFS and atomic force microscopy measurements demonstrate that the crystal disorder during the illumination is concentrated in the near-surface region on ITO. An X-ray photoelectron study shows that the UV–ozone treatment substantially reduces the amount of carbon contaminants and increases the proportion of clean surface with polar atomic components on the ITO surface. The attraction between the ITO and the CuPc film would prevent further CuPc crystal disorder and void formation at the ITO/CuPc interface, thereby achieving durability against illumination.

In summary, NEXAFS spectroscopy demonstrates that the illumination stress changes the molecular orientation of CuPc film in the near-surface region on UV–ozone-treated ITO.

References

- [1] F. E. Farina, W. S. B. Azmi, K. Harafuji, *Thin Solid Films* vol. 623, 72 (2017).
 [2] J. Stöhr, “NEXAFS Spectroscopy”, Second Printing, Springer, Berlin, 2003, chap.9.

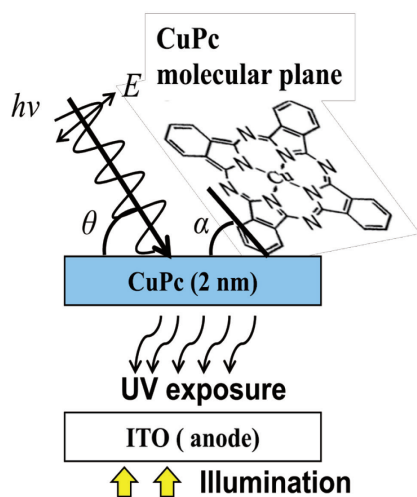


Fig. 1 Schematic of the sample for NEXAFS.

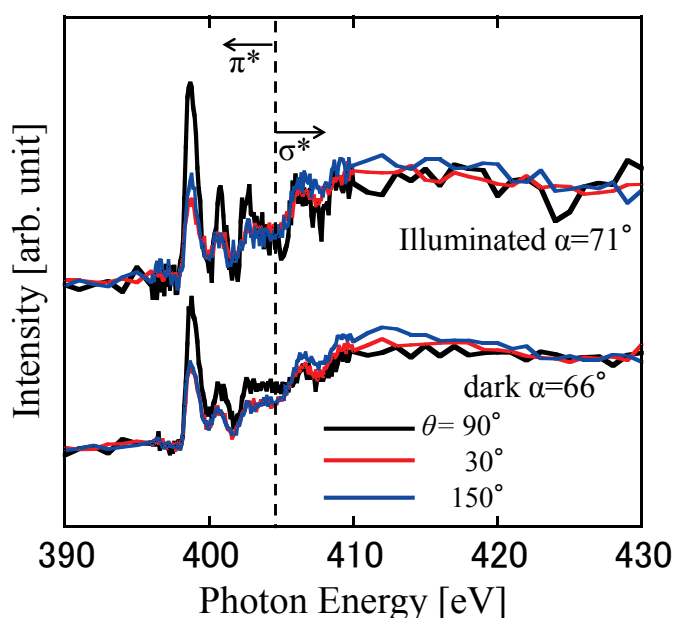


Fig. 2 N K-edge NEXAFS spectra of a 2-nm-thick CuPc film on UV–ozone-treated ITO.