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Chemical States of Silver Species in an Organic Charge Transfer Salt at Different Stages during UV-VIS Illumination

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Introduction

It is indispensable for miniaturization of various electronic products to develop nanodevices based on conducting organic compounds. A direct fabrication of circuits and nanodevices on a chip will be possible if we can control the electrical conduction at arbitrary limited parts of organic solids by illumination.

We have recently found that an organic charge transfer salt, Ag(DM)$_2$ (DM = 2,5-dimethyl-dicyanoquinone-diimine), is a prospective candidate for the above-mentioned control [1]. The electrical conductivity occurs solely through the DM radical anion species in this material. However, it is suggested that we should control the formal charge on DM$^{\delta-}$ by UV-VIS illumination due to the photo-induced oxidation reactivity of Ag^{+}. In order to clarify the mechanism of the photo-induced change in conducting behavior observed in Ag(DM)$_2$, we measured a series of Ag L-edge XAFS of the sample at different stages during UV-VIS illumination.

Experimental

XAFS was measured on the pressed pellet samples around LI (3829 eV), LII (3548 eV) and LIII (3374 eV) edges at room temperature (RT) using total electron yield method. The single crystals of Ag(DM)$_2$ were well ground to fine powder and illuminated using Hg/Xe-lamp with intermittent stirring until the whole powder (dark blue) turned brown. On the other hand, a bundle of single crystals of Ag(DM)$_2$ turned black by much stronger illumination. Along with silver foil (99.95%, Alfa Aesar), we measured XAFS of the pristine, the brown, and the black samples to determine the chemical states of silver species in each solid state. Measurements were repeated to confirm that the result was not affected by X-ray irradiation during the measurement. We observed identical XAFS spectra after the several repetitions.

Results and Discussion

Comparison of the obtained spectra (**Fig. 1**) unambiguously indicates that the silver species contained in the “black” samples is bulk silver, and that silver in the “brown” sample closely resembles bulk silver. Along with the results of infrared spectra, elemental analyses and XPS, the XAFS results are consistently explained supposing that the illumination progressively induced an electron transfer (redox reaction) between the Ag(I) ions and the DM radical-anion species. From our previous work [1], continuous illumination of the sample finally deposited a silver solid on its surface. Therefore the photo-induced electron-transfer deprive the Ag ion of the crystal lattice of Ag(DM)$_2$, and the free Ag ions spontaneously gathered to become bulk silver via “brown” and “black” states. X-ray powder diffraction revealed that the averaged diameter of the silver prticles in the “black” sample is ~9 nm, while the “brown” sample is amorphous [2]. Therefore, it is found from XAFS that the “brown” and the “black” samples both contain bulk silver and that the difference among them lies in the average diameter of the Ag particles. Also we have found an illumination stage, where the original crystal lattice remains yet the conduction behavior differs from the pristine crystals. A preliminary XAFS of the sample in this state did not reveal a clear difference in spectra from the pristine sample. Based on the XANES, XPS, elemental analysis, IR, XRD, SEM, DSC and other data, this state cannot be explained as a mixture of the pristine and the brown states. Evidently, this state should be further studied in more detail.

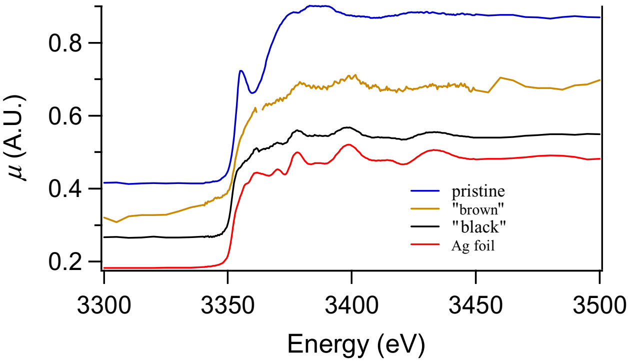

Fig. 1. Ag L-edge XAFS spectra for pristine, “brown”, and “black” states of Ag(DM)$_2$ during UV-VIS illumination with that of authentic Ag foil as a reference.

References

[1] T. Naito et al., Adv. Mater. 16, 1786 (2004).
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