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Chemical States of Ag in $Ag(DMe\text{-}DCNQI)_2$ Photoproducts and a Proposal for Its Photoinduced Conductivity Change Mechanism

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UV–vis light converts $Ag(DM)_2$ (DM = 2,5-dimethyl-*N*,*N′*-dicyanoquionediimine; DMe-DCNQI) to several solids with metallic, semiconducting, or insulating conductivities depending on the irradiation conditions. Ag valence state in each photochemical product was determined by Ag L_3-edge XANES. The XANES result requires the correction of the redox mechanism to explain the photoinduced conductivity change of $Ag(DM)_2$ photoproducts.

Organic electronic devices attract much attention because of their lightness and versatility. A silver salt of 2,5-dimethyl-dicyanoquinonediimine (DM), $Ag(DM)_2$, shows one-dimensional (1D) metallic conduction through the π-electronic band of the DM anion column.[1–3] The salt has a 1/4-filled electronic system. It shows interesting electronic phases: metallic, CDW, and spin Peierls phases.[4] These phases can be transformed reversibly into each other using appropriate temperature and pressure. The salt also shows photoinduced conductivity change; the electric conductivity changes dramatically from metallic to semiconducting or insulating ones only by UV–vis illumination.[5,6] This property is useful to fabricate electronic devices from a single crystal of $Ag(DM)_2$ directly by photolithography. Actually, Yamamoto et al. prepared single crystals of $Ag(DM)_2$ between the electrodes patterned on silicon substrates and made rectifiers with illumination of UV–vis light.[7] Understanding this conductivity change mechanism is very important to tune the illumination conditions to fabricate such devices. As for a conductivity change mechanism, the redox mechanism has been proposed,[8,9] in which solid-state charge transfer occurs between the Ag^+ and DM^- ions under illumination to create neutral Ag^0 and DM^0 species. Accordingly, the number of unpaired electrons on the DM column is reduced, thereby decreasing conductivity. Similar redox mechanisms were proposed to explain the photoinduced metal-to-insulator transitions in AgTCNQ and AgTNAP.[8,9] To establish the mechanism, the chemical state of Ag is a key issue. In this study, we examined chemical states and structures of Ag in the photoproducts of $Ag(DM)_2$ using X-ray diffraction (XRD) and X-ray absorption near edge structure (XANES). The result demonstrated that the phototunable conductivtity change mechanism of $Ag(DM)_2$ could not be explained solely by the simple redox mechanism above. We will propose more detailed mechanism. This will be helpful for further development of devices made of $Ag(DM)_2$. $Ag(DM)_2$ was synthesized using a previously reported method.[1] A 200-W Hg/Xe lamp was used as a UV–vis light (200–1100 nm) source. XRD patterns were measured using an X-ray diffractometer (RINT-Ultra+; Rigaku Corp.) with Cu Kα radiation. The X-ray absorption experiments were performed using the beam line 11B at the Photon Factory of Institute of Material Structure Science (KEK-PF) (PF Proposal No. 2004G062). The Ag L_3-edge XANES spectra were recorded in a total electron yield mode. The X-ray spectra were measured under UHV conditions. In order to have homogeneous sample, we ground samples and they were fixed on conducting carbon tapes. The spectra did not change even after prolonged X-ray irradiation.

We found four photoproducts that were classified by their conductivity as well as their appearances. Table 1 summarizes the properties of the pristine material and the photoproducts. Including the pristine material, we designate them respectively as α (pristine), β, γ, δ, and ε. Among them, β is formed by a weak and short irradiation. The others, γ, δ, and ε are produced with more intense light in this order. α, β, and γ retained the original needle crystalline shape and composition, whereas δ and ε became powdery. The α, β, and γ solids are interesting for device applications.

Figure 1 shows the XRD patterns of α, β, γ, δ, and ε together with Ag foil and neutral DM. In δ and ε, we found peaks in the corresponding to Ag metal, indicating metallic Ag formation. The broad peaks in δ and ε indicate the presence of smaller

Table 1. The properties of $Ag(DM)_2$; α and photo-induced products β, γ, δ, and ε

Product	α (pristine)	β	γ	δ	ε
Color	Black	Black	Brown	Black	Silvery white
Appearance	Needle ($10\,\mu m^{\phi} \times 2\,mm$)	Needle	Needle	Powder	Powder
Stoichiometry [DM/Ag]	2	2	2	1.5	≈ 0
Conductivity	Metallic	Semiconducting	Insulating	Insulating	Metallic

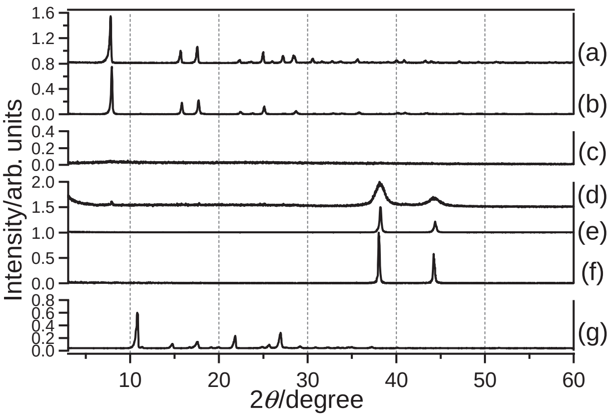

Figure 1. XRD patterns of (a) Ag(DM)$_2$, α, and its photoinduced products (b) β, (c) γ, (d) δ, (e) ε, and (f) Ag foil and (g) neutral DM.

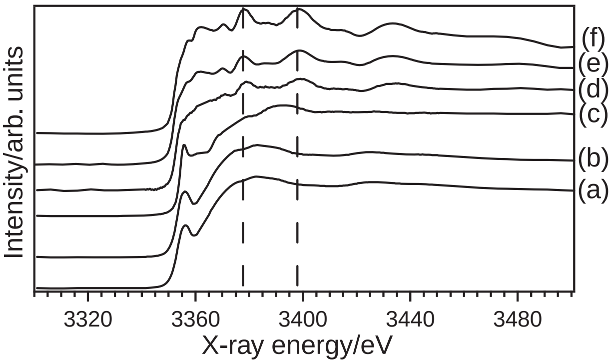

Figure 2. Normalized Ag L$_3$-edge XANES spectra of (a) Ag(DM)$_2$, α, and its photoinduced products (b) β, (c) γ, (d) δ, (e) ε, and (f) Ag foil.

Ag particles; β gives peaks at corresponding positions to that of α indicating that the crystalline structure is mainly retained, whereas γ showed no peaks. Therefore, γ is amorphous.

To identify the chemical states of Ag species, we measured their XANES spectra (Figure 2). Both δ and ε gave similar spectra to that of Ag foil, indicating the formation of Ag metal particles. On the other hand, the β gave a spectrum similar to that of α, indicating that most Ag species in α and β had a similar chemical and geometrical structure. The spectrum of γ differed from that of Ag foil, especially in peak structures at 3378 and 3398 eV depicted by broken lines. In addition, an edge peak appeared at 3355 eV in γ similar to that of α and β although γ was the insulator. The peak are derived form 2p → 4d dipole transition.[10] The 4d vacancy of Ag$^+$ in α is created by the formation of Ag–DM covalent bond. The occurrence of the edge peak in α, β, and γ suggested that the Ag was bound to DM ligand.

There would be metallic Ag particles in γ if the redox mechanisms were adopted in the photoinduced conductivity change of Ag(DM)$_2$. However, the XANES result shows such is not the case. We propose another conductivity change mechanism in this system. We explain the photoinduced conductivity change and classify it into three cases depending on the light intensity.

(**1**) In the weaker light intensity region, a charge transfer between Ag$^+$ and DM$^-$ creates Ag^{0}DM^0 when the light is absorbed. The Ag^0 state is unstable in the complex; therefore, a reverse charge transfer easily occurs form the original state with liberation of extra energy to the lattice. During this recovery process, most of the Ag^0 species revert to the initial structure. However, some part in the original crystal loses its original local structure, which will remain as a defect. Consequently, the 1D stacking column is partially disturbed and the conduction path is disrupted. As a result, semiconducting behavior should appear. This state is considered to be β. Thus, time duration can control the conductivity of Ag(DM)$_2$.

(**2**) Light stronger than a threshold level can destroy the whole three-dimensional network of the original crystal. Consequently, DM conduction column is completely destroyed. Therefore, the structure becomes amorphous. This state corresponds to γ.

(**3**) Even stronger light can simultaneously reduce the several adjacent Ag$^+$ cations in original crystal, and the produced Ag^0 atoms aggregate to stable Ag metal particles accompanied by sublimation or decomposition of DM ligands due to radiation heating. This state corresponds to δ and ε. Thermochemical measurements (DSC and TG-DTA) indicated that heating effects play an indispensable role in this process.

This work has suggested modification of the redox mechanism previously proposed for photoinduced conductivity change of Ag compounds. From our mechanism, the duration time and the light intensity are important factors for the phototunable conductivity. We are now accumulating the more detailed data about the relation of intensity and duration time with conductivities to realize fine tuning of the resistivity of Ag(DM)$_2$ photoproducts to fabricate electric devices.

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