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A new optical doping method toward molecular electronics

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Abstract

Molecular materials have been recently spotlighted as promising candidates for advanced functional materials. We have developed a novel and simple doping method for a molecular material which utilizes a light-induced solid state reaction. The electrical behavior of a single crystal of a molecular charge-transfer salt of silver(I) ion qualitatively becomes differed after illumination with ultraviolet-visible (UV-VIS) light. The X-ray photoelectron spectroscopy also demonstrated that there was neutral silver species concentrated in the illuminated part of the pressed pellet sample, while only silver (I) ions were detected in the rest part and non-illuminated samples. Raman spectra of the pressed pellet sample showed that the formal charge of the constituent organic π-acceptor molecule, which is responsible for the conductivity of this material, varied in accordance with the time of illumination. Illumination with UV-VIS light upon only half of a thin single crystal of the same material transformed it to junction structure, exhibiting a rectifying character. This doping method has opened a new way for fabrication of devices from molecular solids.

Keywords: Organic conductors based on radical cation and/or anion salts; Metal/semiconductor interfaces; Interface preparation; Transport measurements, conductivity, Hall effect, magnetotransport

1. Introduction

Recently, molecular materials have been discussed as promising candidates for advanced materials [1]. Molecular materials cover a wide range of condensed matters such as crystals, films, polymers, particles, amorphous solids as well as liquid crystals. They are comprised of various kinds of organic molecules, inorganic ions, metal-complexes and radical species, which results in their rich chemistry and enable us to design the new functional materials. Due to their complicated structures originating from the variety of the components, they often have anisotropic electronic structures and thus exhibit unique physical properties. In addition, due to their weak interactions between the constituents, the solid state properties and structures are generally sensitive to external stimulus and thermodynamic conditions such as pressure, temperature, light and magnetic fields, which in turn offers us much choice to control them. On the other hand, it is next to impossible to produce the molecular materials with both of desired structures and favorable properties because of the very diversity of the structures and many possible (meta)stable states. This situation now seriously prevents making them into devices except for a limited number of cases. Carrier doping, if possible, is one of the effective ways to utilize molecular materials without controlling their crystal and electronic structures both at the same time. Known general methods of doping, however, are not always effective or applicable to molecular materials. Those of single crystals are not in particular, because they often seriously lower the crystal qualities or change the structures. What is more, the existing mild methods of doping are inefficient in controlling the dopant contents as well as doped parts in the resultant materials, which is essential in making them devices. Thus, when we note the unique properties of molecular materials, lack of suitable doping methods often seriously hinders the application of them to some practical devices. In order to develop a general and simple doping method for molecular materials, we have been considering the utilization of photo-induced redox reaction occurring between electroactive molecule and light sensitive species [2]. As is well known for photography based on the chemistry of silver halides, photo-induced redox reactivity of silver(I) ions exerts high spatial resolution and selectivity to wavelengths of incident light. If we can irradiate and make such a reaction occur in a selected part

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of a molecular material, we will be able to directly control the number of carriers at the irradiated part. As a first step we have studied the effect of irradiation on the molecular charge-transfer complex Ag(DMe-DCNQI)$_2$, where the conduction π–electrons on the DCNQI stacking columns are directly bonded to the photosensitive Ag$^+$ ions through coordination bonds (DMe-DCNQI = 2,5-dimethyl-dicyanoquinonedi- imine; hereafter abbreviated as DM).

2. Experimental

Materials were prepared following reported procedures [3]. All physical measurements were carried out on freshly prepared samples. The same sample was used before and after illumination for comparison. The UV-VIS light (200 -1100 nm) was focussed onto the specimen using a UV-VIS FIBER LIGHT SOURCE L7893 equipped with a 5 W-tungsten halogen lamp and a 30 W-D$_2$ lamp, and with optical fiber of 800 μm in core diameter (numerical aperture; 0.22) of 1m-length (HAMAMATSU PHOTONICS K. K.). The electrical resistivity measurements were carried out using a standard 4-probe method with gold wires (25 mm in diameter) and gold paste (No.8560, Tokuriki Chemical Research Co., Ltd.) as electrical contacts. A part of the crystal surface (around the middle of a black fine needle typically ~ 10 mm long, ~ 0.1 mm wide and ~ 0.02 mm thick) was continuously illuminated with UV-VIS light from the light source at RT. Subsequently, the physical measurements were carried out for the crystal using conventional procedures in the dark. After the measurements, the illumination was recommenced on the same part of the crystal and further effects were investigated. Parallel measurements of the pristine samples were also conducted for checking out any artefacts. As for the measurements of the temperature-dependent resistivity, fine crystals and additional optical fiber (400 μm in core diameter of 3m-length, Fiberguide Industries) attached at the end of the former fiber were used. The incident beam was adjusted to be perpendicular to the specimen surface using a goniometer head. The end of the fiber was placed as close to the surface as possible (< 150 μm). The output of the incident beam at the end of the fiber was typically 0.1-0.2 μW cm^{-2} nm^{-1} at 300-550 nm, 0.2-1 μW cm^{-2} nm^{-1} at 200-300 & 550-1100 nm. The typical value of the fluctuation of the output during continuous illumination was 0.004 % and the drift was 0.3 %h^{-1}. Irradiation effects were examined at room temperature as well as at 77 K, and no significant variation was observed. As for the fabrication of junction structure, very thin single crystals were illuminated from both sides using two identical optical fibers mentioned above. In order to examine the relation between rectifying behavior and duration of illumination, irradiation was continued for 4-21 days in each run. The XPS (JEOL JPS 9200 spectrometer, Mg K_α 15 kV-10 mA) and Raman (JASCO RMP-210S) spectra were measured on pressed pellets (5mmϕ) made from the single crystals. In the Raman spectra measurements alternate irradiation and spectra measurement were repeated on the same part (center) of the pellet. As for the XPS, magnetic objective lens was used to obtain spatially highly resolved spectra. The typical field of view was 200 μm. By scanning along a diameter, a series of spectra were taken at every 100 μm on the pressed pellet sample, whose center was illuminated with UV-VIS light from the optical fiber for 4 days.

3. Results and Discussion

3.1. Illumination effects on electrical behavior

The resistivity of a pristine sample was confirmed to be consistent with the previous reports [4-10] (Fig. 1): it gradually decreased with decreasing temperature, thus exhibiting typical metal behavior. More exactly, the resistivity decreases slightly down to 150-200 K and then slightly increased down to ~ 100 K as if it were a semiconductor. Such a "narrowly metallic" behavior is indicative of fluctuation generally observed in one-dimensional molecular conductors. Below ~100 K the resistivity suddenly and rapidly increased, which means that a phase transition, i.e. a metal-to-insulator (MI) transition occurs in this material at this temperature. Such a transition is known to be also inherent in one-dimensional metals. On the other hand, the resistivity at room temperature (RT) increases in accordance with the duration of illumination. This is consistent with the simple picture mentioned above that photochemical reduction of Ag$^+$ to Ag(0) agrees with the oxidation of DM$^-$ to DM(0), leading to decrease in the number of unpaired electrons in the DM columns.

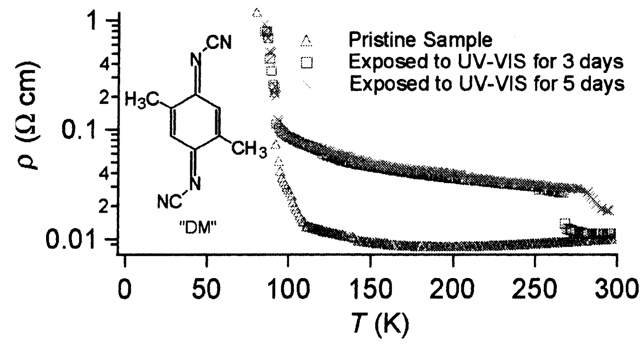

Fig. 1. UV-VIS illumination effects on the electrical behaviour of the single crystal of Ag(DM)$_2$; temperature-dependence of the resistivity with chemical formula of DM.

Direct observations of the Ag(0) and DM(0) species are presented below. The temperature range of the metallic behavior (RT – ~100 K) rapidly narrowed with illumination. However, the metallic behavior around RT and the MI transition at ~ 100 K were both retained. Additionally the resistivity showed a small and sudden increase at ~267 K (squares)/ ~285 K (crosses), respectively, followed by a