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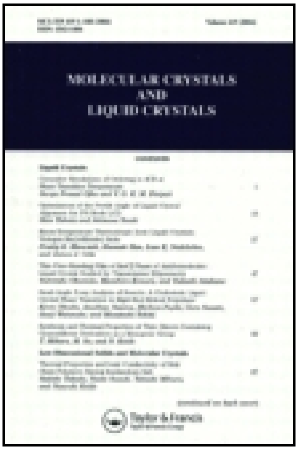

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Electron Spectroscopic Imaging of Organic Fine Crystals

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ELECTRON SPECTROSCOPIC IMAGING OF ORGANIC FINE CRYSTALS

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Abstract Morphologies and crystal structures of organic fine crystals were characterized by electron spectroscopic imaging (ESI) technique combined with electron energy loss spectroscopy (EELS).

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INTRODUCTION

Organic fine crystals with a size of several tens nm to μm have a potential to exhibit a quantum effect in optical properties. The preparation method is very simple to inject the solutions of organic compounds into stirred water as a poor solvent kept at room temperature.[1] The reprecipitation method has been applied to several functional compounds such as merocyanines, perylene, *pseudo*-isocyanine, and polydiacetylene.[1-3]

It is difficult to observe directly such a fine particle by a transmission electron microscope (TEM). Most of organics should be broken by high energy incident electrons. In addition with such radiation damage, the contrast of sample should be low because the microcrystals had same thickness as the supporting plastic films, formbar or vacuum-deposited carbon film with a thickness of 5 - 10 nm, which consist of carbon.

Some of incident electrons in TEM were lost the energy by the interaction with atomic potentials in substances. The inelastically scattered electrons through the thin specimen have an information of thickness and the characteristic features in electron energy loss spectra (EELS).[4] It is effective to visualize very thin samples by using energy-lost electrons.[5]

This paper presents structural characterizations of organic fine crystals by

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electron spectroscopic imaging (ESI) technique.

EXPERIMENTAL

Nickel phthalocyananine (Ni-Pc) and fullerene (C60) were dissolved into the solutions of H_2SO_4 and hexane, respectively. They were injected into a distilled water to form fine crystals dispersed in the water. In the case of Ni-Pc, iodine was added into the solution to make a charge transfer complex of Ni-Pc and iodine (Ni-Pc(I)).[6,7] Fine crystals in distilled water were dropped onto the mesh and then dried.

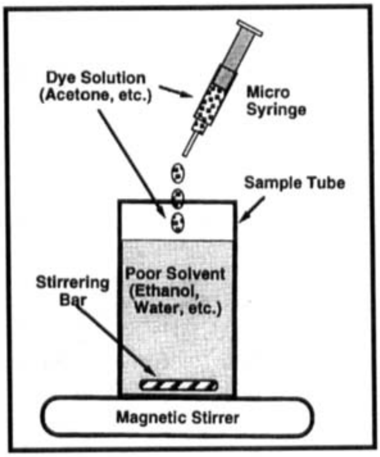

FIGURE 1.Reprecipitation method

The supporting films without any carbon were prepared as follows. The vapor of osmium tetraoxide (OsO_4) was glow-discharged in a voltage of 0.7 kV in D.C. by using NL-OP80-NS, Nippon Laser and Electronics Lab. The plasma-polymerized osmium film exhibits electronic conductivity to prevent from the charge-up of organic sample in TEM observation.[8] Thin films formed on KCl (001) plane were stripped off from the substrate on the water surface and then transferred onto Cumesh. The TEMs used here were Zeiss CEM-902 equipped with Casting-Henry type energy filter[4] and a conventional TEM, JEOL-2000FX.

RESULTS AND DISCUSSION

Typical TEM images and electron diffraction patterns are shown in Fig. 2, which are fine crystals of Ni-Pc (a) and (b) and Ni-Pc(I) (c) and (d), respectively. While, fine crystals of Ni-Pc are light and formless shapes, whose spacing between phthalocyanine rings is 0.375 nm, Ni-Pc(I) exhibits sharp crystal habit, needle crystals, whose spacing is 0.345 nm. The lattice spacings coincide with those of single crystals.[6,7]

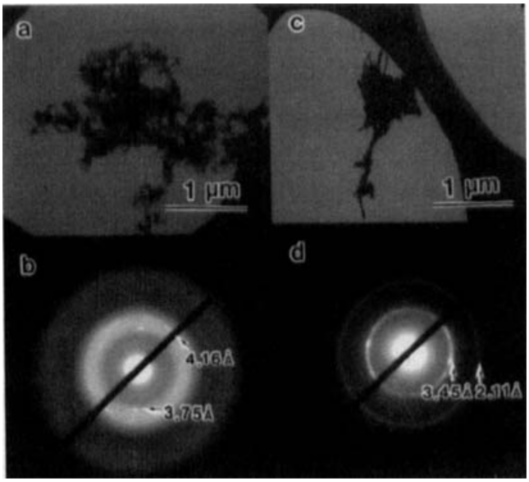

FIGURE 2. Transmission electron micrographs and electron diffraction patterns of nickel phthalocyanine (Ni-Pc) (a and b), and iodine doped Ni-Pc (Ni-Pc(I)) (c and d), respectively.

The electron energy loss spectra (EELS) from such fine crystals represent surely the existence of elements of nickel and iodine in addition to carbon, nitrogen and oxygen as main components, as shown in Fig. 3. Each element has identical core-loss peak in EELS; 285 eV for carbon K-edge, 397 eV for nitrogen K-edge, 532 eV for oxygen K-edge, 634 eV for iodine $M_{4,5}$-edge and 850 eV for nickel $L_{2,3}$ edge.[4]

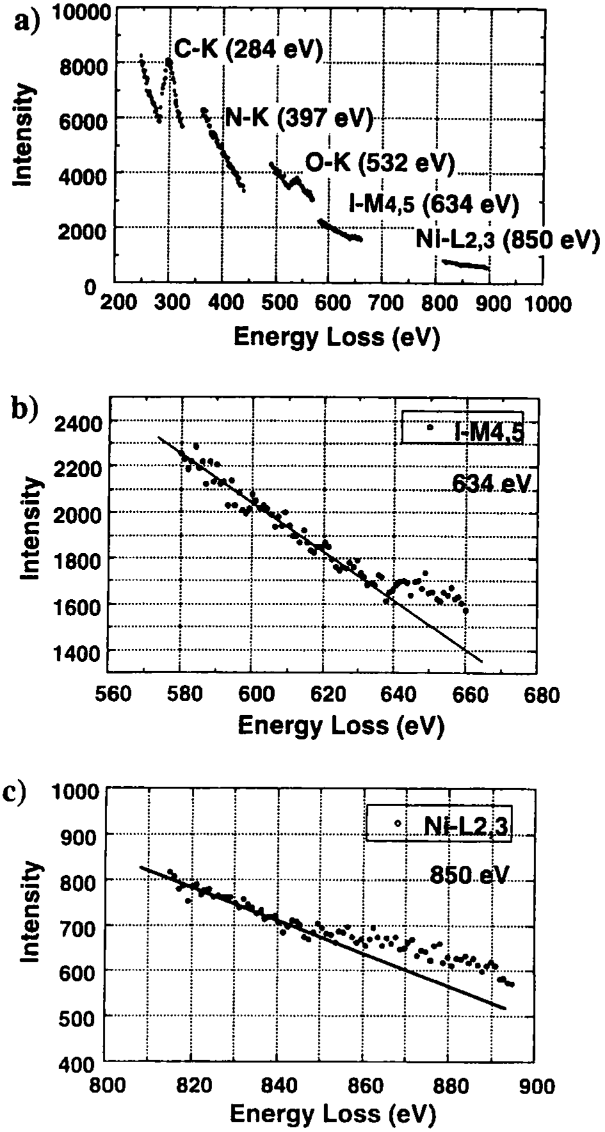

FIGURE 3. Electron energy loss spectra of micro-crystals of iodine doped nickel phthalocyanine (Ni-Pc(I)); (a) Whole spectra, (b) I-M edge and (c) Ni-L edge.

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In the case of such fine crystals, it is expected that they would have no crystal boundaries but being single crystal. To confirm it, high resolution observation was done in the fine crystals of fullerene (C60). It has less radiation damage than other organic materials.[5] Figure 4 shows the lattice images with a distance of 0.8 nm in a fine crystal of C60. The fringes were extended from one edge to another. It should prove that the fine crystals consist of single domain.

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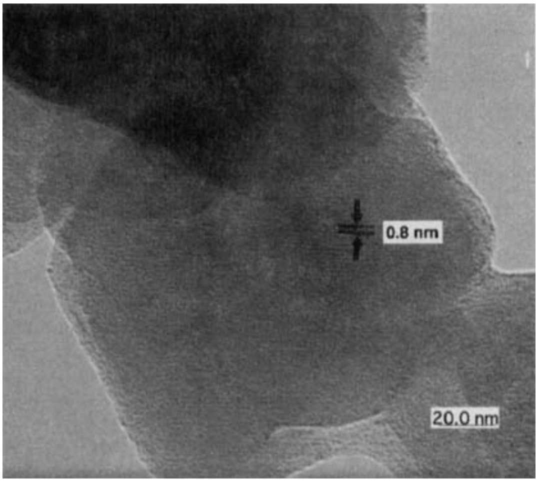

FIGURE 4. High resolution transmission electron micrograph of a fine crystal of fullerene (C60). Hexagonal plate-like crystal represents the lattice fringes with a distance of 0.8 nm, which corresponding to the diameter of C60 ball.

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