Formation of micro crystals of 3,4,9,10-pelyrenetetracarboxylic dianhydride by synchrotron radiation

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Preparation of functional organic materials by photo chemical processes such as laser ablation, photo chemical vapor deposition and surface modification with various kinds of light sources attracts a great deal of attention[1,2]. Polyperinaphthalenic organic semiconductor (PPNOS) which is promising as an energy storage and conversion material, for example, has been tried to prepare by laser ablation. One of the authors succeeded to prepare PPNOS nanoparticles by laser ablation of mixture target of 3,4,9,10-perylenetetracarboxylic dianhydride (PTCDA) with cobalt powder using third harmonic of Nd:YAG laser (355nm) through effective elimination reaction of anhydride groups of PTCDA[3]. Selection of light source, wavelength, fluence, and pulse width is important to design photo chemical reactions to prepare functional organic materials. However, sufficient research has not been made yet. Soft X ray is one of them. In this study, disk-shaped pellets of PTCDA and/or mixture of PTCDA with cobalt powder were irradiated with synchrotron radiation beam with soft X ray to induced surface modification of the pellets.

Synchrotron radiation on the beam line No. 14 (BL-14) at the SR Center of Ritsumeikan University was employed for the surface modification. Reddish PTCDA and/or mixture target of PTCDA with cobalt powder at 1:4 in molar ratio were formed to be disk shaped pellets. The molecular structure of PTCDA is shown in Fig. 1. The surface of each pellet was irradiated with the synchrotron radiation beam in a vacuum chamber evacuated under 10^{-8} Torr at a photon flux of $3x10^{13}$ photons s^{-1} mA^{-1} mm^{-2} with a cylindrical mirror for 500 and 1000 sec. The surface morphology and the molecular structure were investigated by scanning electron microscopy (SEM) and micro Raman spectroscopy.

Color of the surface of PTCDA and PTCDA/Co pellets turned to black from red after SR beam irradiation for 500 sec. Figure 3 (a) and (b) show the surface morphologies of the PTCDA/Co pellet before and after SR irradiation, respectively. Although ablation did not occur on the exterior, the region irradiated with SR became remarkably rough compared with

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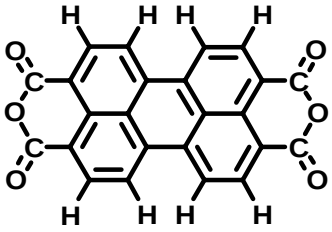

Fig. 1. Molecular structure of PTCDA.

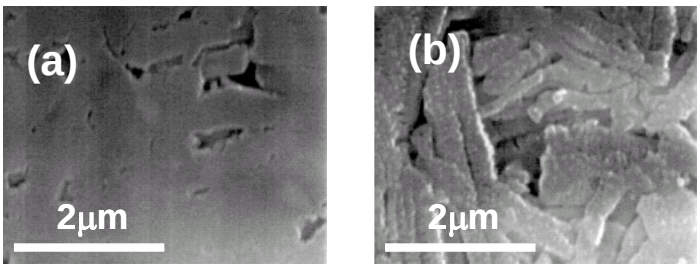

Fig. 2. Surface SEM images of PTCDA/Co pellets (a) before and (b) after synchrotron radiation.

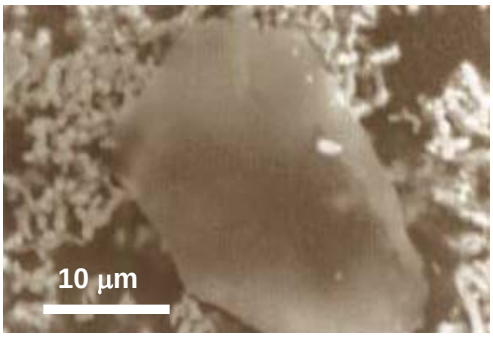

Fig. 3. A micro crystal with a cylindrical form observed on the irradiated surface of PTCDA/Co

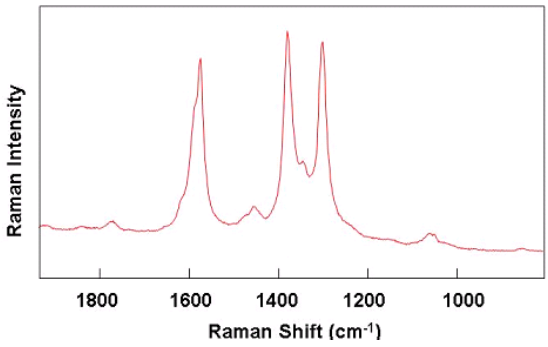

Fig. 4. The Raman spectrum of the micro crystal.

that before irradiation.

Micro Raman spectroscopy was carried out for the surface of PTCDA and PTCDA/Co after SR irradiation for 500 sec. The Raman spectrum for PTCDA indicated that of characteristic amorphous carbon with broad bands around 1360 and 1600 cm^{-1}. On the other hand, the spectrum for PTCDA/Co showed sharp peaks at 1290, 1360 and 1600 cm^{-1}, which were characteristics of PTCDA, suggesting that cobalt powder acted as a protector for preventing perylene structure of PTCDA from damaging by direct absorption of SR beams.

Various micro crystals with a variety of forms were observed all over the place irradiated with SR beams. A crystal with a cylindrical form is shown in Fig. 3, as an example. Such crystals were observed only on the irradiated surface of PTCDA/Co. Figure 4 indicates the Raman spectrum of the crystal. These peaks are corresponded with those of PTCDA, meaning crystallization of PTCDA by synchrotron radiation. The mechanism of the formation of PTCDA microcrystal is now under investigating.

References

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