Irradiation of Perylene Related Compounds with Synchrotron Radiation

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1. Introduction

Synchrotron radiation including soft X-ray excites electrons in the inner shell of various atoms, allowing us to expect inducement of novel chemical reactions through excited states.[1] On the other hand, one can easily imagine that it is difficult to control chemical reactions, particularly organic chemical reaction, by synchrotron radiation because not only direct bond breaking but also excess thermal effects in relaxation processes after excitation lead to some uncontrolled decomposition reactions of organic compounds. However, such decomposition reactions by synchrotron radiation have not been investigated systematically. It is meaningful if we can control some chemical reactions by synchrotron radiation to prepare various functional organic compounds. In this study, disk-shaped pellets of 3,4,9,10-perylenetetracarboxylic dianhydride (PTCDA), and a PTCDA derivative with sodium atoms prepared by hydrolysis reaction were irradiated with synchrotron radiation beams including soft X ray to induce surface modification of the pellets and the possibility of chemical reaction control was investigated.

2. Experimental

Synchrotron radiation on the beam line No. 14 (BL-14) at the SR Center of Ritsumeikan University was employed for the surface modification. The molecular structure of PTCDA is shown in Figure 1 together with schematic representations of BL-14 and synchrotron radiation to a pellet. The beam line emits high-intensity light covering the energy range from soft X ray to vacuum ultraviolet.[2] Reddish PTCDA, and a PTCDA derivative coordinated with sodium atoms prepared by hydrolysis of PTCDA in NaOH solution (PTCDA/Na) were formed to be disk shaped pellets, the thickness and diameter of which were 2 mm and 7 mm, respectively. The surface of each pellet was irradiated with the synchrotron radiation beam in a vacuum chamber evacuated under 10^{-6} Pa at a photon flux of 3×10^{13} photons s^{-1} mA^{-1} mm^{-2} with a cylindrical mirror for 500 and 1000 sec. The beam shape of synchrotron radiation of BL-14 was rectangle (1mm x 50 mm). The surface morphology and the molecular structure were investigated by scanning electron microscopy (SEM) and micro Raman spectroscopy.

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3. Results and Discussion

Colour of the surface of PTCDA pellets turned to black from red after synchrotron radiation beam irradiation for 500 sec. Although ablation did not occur on the exterior, the region irradiated with synchrotron radiation became remarkably rough compared with that before irradiation.

Micro Raman spectroscopy was carried out for the surface of PTCDA after synchrotron radiation for 500 sec. The Raman spectrum with broad bands around 1360 and 1600 cm^{-1} for PTCDA after synchrotron radiation indicated that the surface was turned to be amorphous carbon. Although surface of PTCDA was easily turned to be amorphous carbon by synchrotron radiation, it was found that numerous micro crystals were formed in the inside close to the carbonized surface after synchrotron radiation. Figure 2 shows a SEM image of the micro crystals measured after peeling the carbonized surface off together with a Raman spectrum of these crystals. Various sizes of plate crystals and cylindrical crystals were found. Extremely sharp peaks at 1290, 1360 and 1600 cm^{-1} enabled us to conclude that these were PTCDA crystals. It is reported that the sublimation and decomposition temperatures of PTCDA are 360 and 450ºC, respectively. [3] Excess thermal energies produced in relaxation processes after excitation diffused and the inside of the PTCDA pellet was heated up at less than 450ºC, resulting in formation of micro crystals. Carbonized rigid surface seemed to prevent PTCDA molecules in the inside from sublimation.

Synchrotron radiation of PTCDA/Na was carried out, in which sodium atoms coordinated in every PTCDA molecules. Synchrotron radiation of PTCDA/Na for 500 seconds enabled us to obtain needle crystals at the whole surface without carbonization as shown in Figure 3. It is hard to consider that almost all PTCDA/Na molecules at the surface forms the micro crystals of itself without sublimation or ablation by synchrotron radiation. The molecular structure of the crystal is not clear at the present, but the possibility of formation of polyperinaphthalene can not be denied either, considering from the resembled crystal structure of polyperinaphthalene prepared by vapour polymerization. [4]

4. Conclusion

Disk-shaped pellets of PTCDA, and PCDA/Na were irradiated with synchrotron radiation beams including soft X ray to induced surface modification of the pellets. It was observed that numerous micro crystals were formed in the inside close to the carbonized surface after synchrotron radiation. Micro Raman spectroscopy indicated that the micro crystals were PTCDA. Furthermore, synchrotron radiation of PTCDA/Na for 500 seconds enabled us to obtain needle crystals at the whole surface without carbonization. These results were interesting because it was revealed the possibility of reaction control of organic compounds to form micro crystals of them. Synchrotron radiation of other organic compounds such as phthalocyanine is now carried out to ascertain whether micro crystals are formed or not. The mechanism of crystal growth is also under investigating.

References

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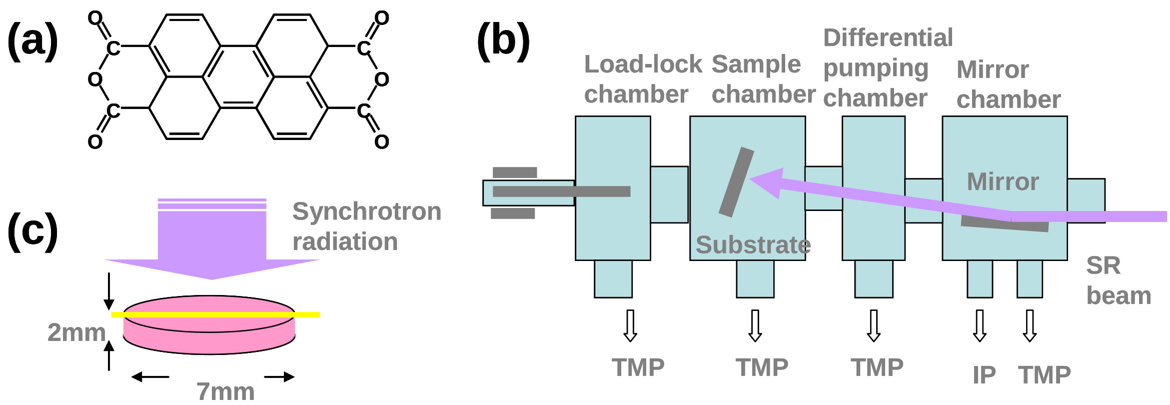

Figure 1. The molecular structure of PTCDA (a) and schematic representations of BL-14 (b) and synchrotron radiation to a pellet (c).

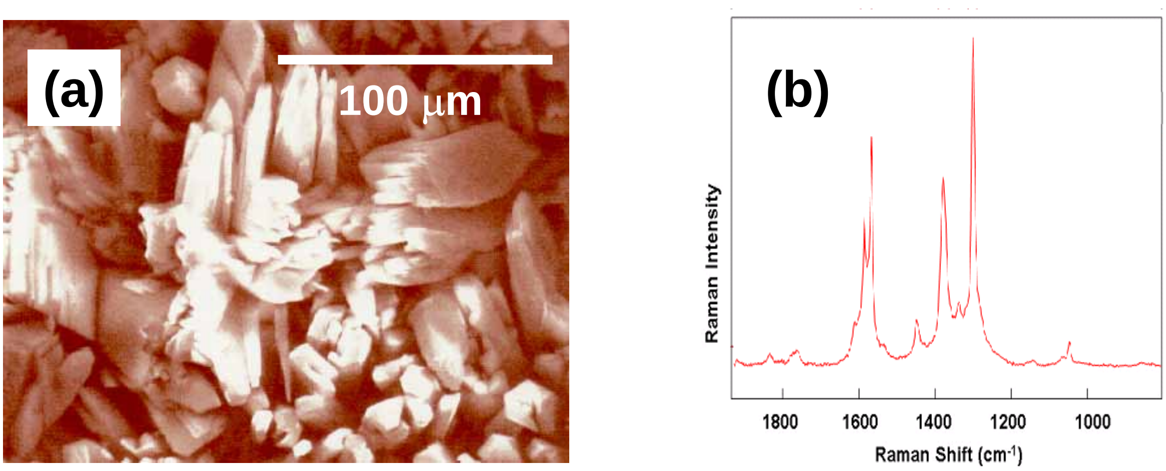

Figure 2. (a) SEM image of the micro crystals and (b) a Raman spectrum of these crystals.

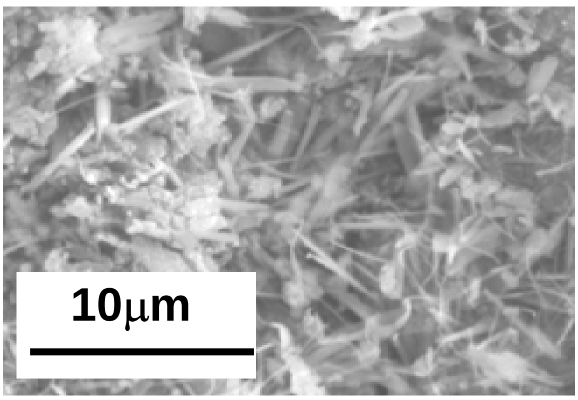

Figure 3. Needle crystals formed at the surface of a PTCDA/Na pellet after synchrotron radiation for 500 sec.