# Preparation of $C_{60}$ Microcrystals Using High-Temperature and High-Pressure Liquid Crystallization Method

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Using reprecipitation technique from high temperature and high pressure liquid, $C_{60}$ microcrystals with size of about 40 nm and narrow size distribution could be fabricated in the dispersion liquid. And it was found that the optical properties of $C_{60}$ microcrystals were also dependent on crystal size in a similar manner as the other π-conjugated organic microcrystals.

A series of carbon molecules such as $C_{60}$ has received considerable attention on their characteristic structure and properties.[1–4] In their crystalline states, many interesting physical properties have been clarified. However, their crystal size effects, which are expected to appear in the crystals at a nanometer size, have been little studied. Although Mochizuki et al. reported the optical absorption spectra of $C_{60}$ microcrystals and the size effect,[3] uncertainty on crystal size remained. In order to evaluate the property of $C_{60}$ microcrystals without their aggregation, the fabrication technique of microcrystal dispersion in free-standing state has to be established. Regarding to this point, G. A. Andrivsky et al. proposed a production method of dispersed $C_{60}$ colloidal solution.[4] They stated that the size of $C_{60}$ aggregates was less than 200 nm because the colloidal solution could be filtered through a filter with 0.22 μm-size pores. However, the definition and distribution of their microcrystal size were not clear.

On the other hand, we have succeeded in obtaining some organic microcrystals by the reprecipitation method.[5] A characteristic of this technique is that the microcrystals in the dispersion state are prepared. In the case of $C_{60}$, when its carbon disulfide solution was injected into ethanol, the microcrystals with size around 270 nm were fabricated.[6,7] However, the usual reprecipitation method using other solvents could not apply to making microcrystals of $C_{60}$ owing to the low solubility. As a result, even including the past studies, it was hard to obtain $C_{60}$ microcrystals with size ranging from 10 nm to 200 nm in the free-standing state and to estimate the crystal size.

In this letter, we report preparation of $C_{60}$ microcrystals with mono-dispersed size less than 200 nm using reprecipitation technique from high-temperature and high-pressure liquid (HTPL), because HTPL was expected to show high solubility with $C_{60}$. This technique is called to be HTPL crystallization method.

The purity of $C_{60}$ used, which was purchased from Term USA, was 99.98%. The experimental set up and procedure were all the same as those of supercritical fluid crystallization method which was written in the previous paper in detail.[8,9] In short, hot acetone under high pressure is passed through the cell containing $C_{60}$ powder. When $C_{60}$ starts to be solved by increasing the temperature, $C_{60}$ acetone solution can flow from the cell. Cooling water is injected to the HTPL solution. Then, $C_{60}$ microcrystals were fabricated by reprecipitation. The temperature varied and pressure were 380–420 K and 5.0 MPa, respectively. The flow rates of HTPL and cooling solvent were 5 and 10 mL/min, respectively. The size and shape of the microcrystals were observed using a Hitachi S-900 scanning electron microscope (SEM). The size and its distribution of microcrystals dispersed in water were also evaluated by the dynamic light scattering (DLS) technique using Otsuka Electronics DLS-7000. Transmission electron microscopy (TEM) observation was also carried out with a Carl Zeiss EM902 equipped with a Casting–Henry energy filter operated at 80 kV.

When the temperature of HTPL acetone was set to be higher than 380 K, the color of resultant liquid changed into brown. It was same as that of $C_{60}$-microcrystal dispersion obtained by the conventional reprecipitation method. This coloring means that $C_{60}$ microcrystals in acetone–water dispersion were successfully fabricated. The temperature, at which $C_{60}$ microcrystals started to be produced, was much lower than the supercritical temperature of acetone (508 K). The dispersion was very stable for a long time over one month. After $C_{60}$ was treated with HTPL in the above experiments, the obtained $C_{60}$ microcrystals were neither decomposed nor dimerized, because the mass spectrum showed only the monomer peak.

Figure 1 shows a SEM photograph of $C_{60}$ microcrystals prepared using HTPL at 420 K. The average crystal size was around 40 nm. Change in experimental conditions such as temperature of acetone did not affect to the microcrystal size. The crystallinity

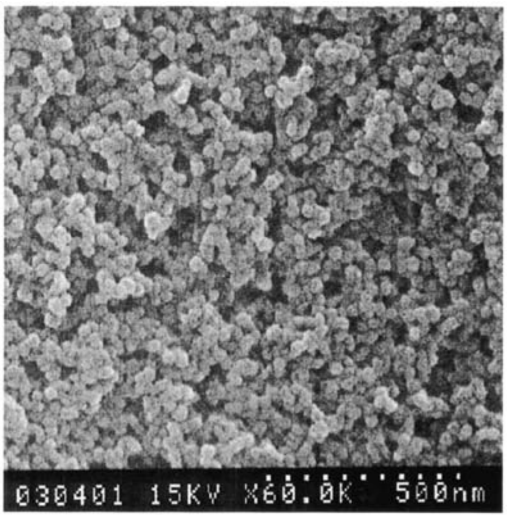


**Figure 1.** SEM photograph of $C_{60}$ microcrystals prepared using high-temperature and high-pressure liquid crystallization method

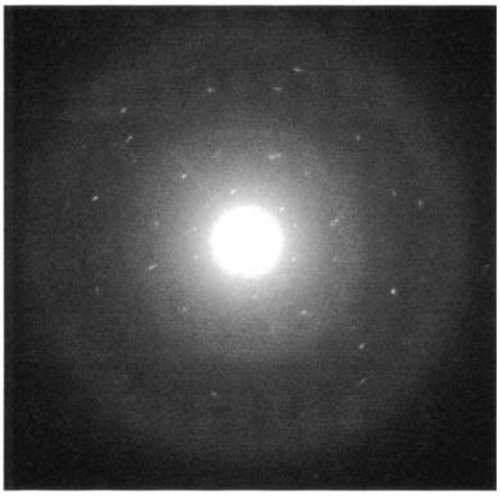

**Figure 2.** Electron diffraction pattrens of $C_{60}$ microcrystals prepared in this study

of the $C_{60}$ microcrystals was recognized by electron diffraction patterns of TEM observation, as shown in Figure 2.

Figure 3 indicates the size distribution of $C_{60}$ microcrystals in the liquid dispersion obtained by DLS measurement. More than 90% of $C_{60}$ microcrystals have crystal size between 40 nm and 55 nm. Averaged size was around 45 nm, which almost agreed with the size estimated by SEM observation.

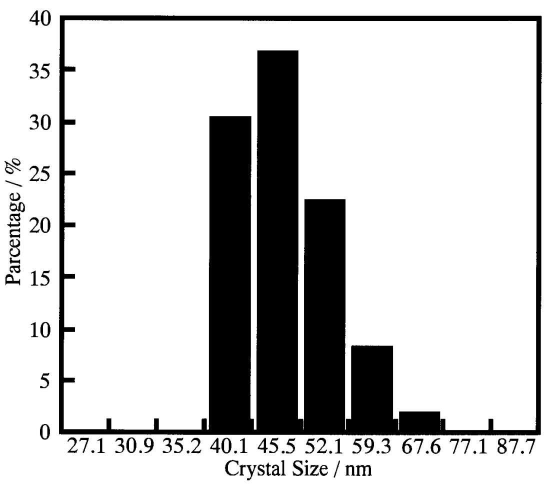


**Figure 3.** Size distribution of $C_{60}$ microcrystals in the liquid dispersion obtained by DLS measurement

The optical absorption spectrum at room temperature of $C_{60}$-microcrystal dispersion obtained using HTPL crystallization method is shown in Figure 4. The most noticeable peak at 340 nm and the accompanying shoulder peaks around 450 nm and 620 nm were characteristic of the absorption spectrum of $C_{60}$ crystals. In the case of $C_{60}$ microcrystals with size of about 270 nm, the absorption peak position was at 350 nm.[10] That is, the optical properties of $C_{60}$ microcrystals were found to be dependent upon crystal size. Mochizuki et al. also described that the peak around 350 nm shifts to the higher-energy side with decreasing $C_{60}$ crystal size. This tendency was in good agreement with the result of our experiment. The similar optical phenomena were also observed in microcrystals of other

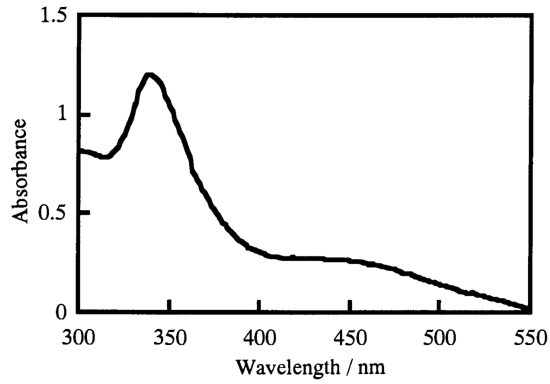


**Figure 4.** Optical absorption spectrum at room temperature of $C_{60}$ microcrystal dispersion obtained using high-temperature and high-pressure liquid crystallization method

organic compounds such as polydiacetylenes, perylene and so on.[11,12] The reason for this peculiar phenomenon is not clear yet, and therefore, systematic investigation on optical properties using a variety of sizes of mono-dispersed microcrystals is necessary.

In conclusion, HTPL crystallization method can be proposed to use for preparing microcrystals of organic compounds with poor solubility for solvents under ordinary conditions as a development of conventional reprecipitation method. Using this method, $C_{60}$ microcrystals with size of about 40 nm and narrow size distribution could be fabricated in the dispersion liquid. The optical property of $C_{60}$ microcrystals was dependent on their size, and its tendency was almost the same as that of other organic microcrystals.

**References and Notes**


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