

## Synthesis of C<sub>60</sub> Polymer by Free Electron Laser Irradiation with Hole-Doping Effect

Shingo Ando, Ryo Nokariya, Reou Koyaizu, Nobuyuki Iwata, and Hiroshi Yamamoto  
College of Science & Technology, Nihon University, 7-24-1 Narashinodai, Funabashi-shi, Chiba, 274-8501, Japan.  
Tel & Fax: 81-047-469-5457, e-mail: 2005\_ando@yamamoya.ecs.cst.nihon-u.ac.jp

A free electron laser (FEL) with wavelength of 450nm and 345nm and YAG laser with wavelength of 532nm were irradiated to surfaces of moderately compressed pure C<sub>60</sub> and a mixture of C<sub>60</sub> and I<sub>2</sub> in vacuum. After laser irradiation the Raman peak of Ag(2)-derived vibration mode of C<sub>60</sub> sifted to the lower energy side. By 450nm FEL irradiation the Raman shift of a mixture C<sub>60</sub>+I<sub>2</sub> was as large as *ca.* 8cm<sup>-1</sup> and was definitely larger than that of pure C<sub>60</sub>. By 450nm FEL irradiation the decreased in (111) lattice spacing of C<sub>60</sub> in the mixture sample was by *ca.* 8x10<sup>-3</sup> nm. The obtained results strongly suggest that 3-dimensional polymerization of C<sub>60</sub> was effectively induced by laser irradiation and/or addition of iodine.

Key words: C<sub>60</sub>, polymerization, free electron laser ( FEL ), Raman spectrum, Ag(2)-mode, hole doping

### 1. INTRODUCTION

Since the polymerization of C<sub>60</sub> films was successfully done first by a phototransformation [1], many studies have been carried out for fullerene polymerization processes using such as electron-beam irradiation [2], high-pressure [3], plasma-induced excitation [4], and so on. By adequate chemical or physical excitations a carbon double bond in a hexagon of a C<sub>60</sub> cage breaks and transforms into an inter-molecular four-fond ring with a neighbor molecule. As the result two C<sub>60</sub> molecules are combined and changed into a dimer or some higher order of polymers. This is the fundamental process for fullerene polymerization.

The polymerized fullerite structures based on a "2+2 cycloaddition" bonding [1] have been observed experimentally and theoretically [5-7]. It was known about the polymer structure that one-dimensional (1D) chains are in an orthorhombic phase and two-dimensional (2D) planes include a tetragonal and a rhombohedral phase. Only a few experiments [3] have been reported about the possibility of a three-dimensional (3D) polymerized phase. The 3D fullerene polymers are expected, however, to become extremely hard, with lower density and less brittleness than diamond.

The conventional polymerization proceed by high compression at the order of GPa or heating up to higher than a thousands degrees [3]. But these polymerization processes are unsuitable to supply sufficiently large 3D polymers for applications. Furthermore the C<sub>60</sub> cages are partially collapsed under extremely high-pressure conditions and the processes are not well-controlled.

The purpose of this work is to develop a novel photon-assisted process for synthesis of 3D C<sub>60</sub> polymers by Free Electron Laser (FEL) or YAG laser irradiation under moderately high pressure. The absorption spectrum of C<sub>60</sub> revealed large absorption peaks in 221nm, 271nm and 347nm, or small absorption peaks in neighborhood 400-500nm [8]. Then the wavelength of laser irradiated was changed in the range

350-600nm. Especially we studied FEL with wavelength of 450nm and 345nm, and also YAG with wavelength of 532nm. Furthermore, we have noticed a hole-doping effect which was demonstrated in the synthesis of diamond from graphite [9]. A mixture of C<sub>60</sub> and I<sub>2</sub> was also studied in comparison with the case of pure C<sub>60</sub> as pristine powder was irradiated.

Hereinafter, the developed photon-assisted process is introduced and the possibility of synthesis of 3D C<sub>60</sub> polymers by laser irradiation will be demonstrated.

### 2. EXPERIMENTAL

Figure 1 shows the schematic apparatus for the synthesis of C<sub>60</sub> polymers. The vacuum chamber was evacuated to *ca.* 10<sup>-4</sup> Pa by a turbo molecular pump and was pre-annealed at *ca.* 400K for 3h. The two kinds of pristine powder were studied. The pure C<sub>60</sub> (99.95%) was a commercial product. The C<sub>60</sub> was also mixed with I<sub>2</sub> in the mole ratio, 1:4. Iodine was adopted for the enhancement of polymerization reactions expected from the hole doping effect as stated before. The effect is expected to be applicable to polymerization reactions of C<sub>60</sub> molecules because of the mutually similar structures of carbon networks in graphite and C<sub>60</sub>. Here we aimed to promote electron transfers from C<sub>60</sub> to iodine atoms by the photon-excitation because the electron affinity of the C<sub>60</sub> is high.

The powder was set in an anvil which was placed in the vacuum and was pressed via a bellows by a hydraulic press. The pressure, the maximum of *ca.* 600MPa, was applied to the sample powder by the quartz window.

Laser was introduced to the surfaces of the compressed powder by aluminum cold mirrors which reflect only lights with the wavelength less than, *ca.* 700nm. When the wavelength of FEL was chosen by changing the fundamental wavelength, laser was guided to specimen surfaces through the band pass filter (BPF).

Infrared (wavelength of few tens μm) FEL has been developed and applied to many researches of the

laser-solid interaction [10]. On the other hand we adopted here a newly developed FEL system which generated a tunable near-infrared laser and the higher harmonics with comparatively high power. The details of the FEL system used appeared in the elsewhere [11]. A few tens microsecond macro-pulse, which included few hundreds picosecond micro-pulses, was repeated in 2Hz. The power of the fundamental macro-pulse was *ca.* 0.5mJ/pulse. Since the FEL can supply a laser with a tunable wavelength, the fundamental wavelength was changed arbitrarily in this work. The laser mainly used was the third harmonics (*ca.*450nm) of *ca.* 1350nm fundamental FEL or the fifth harmonics (*ca.*345nm) of *ca.* 1700nm. The wavelength of about 450nm of which the value is evaluated from the difference of the bonding energy of C=C double bond and C-C bond. The irradiation time was 60–180 min.

Furthermore, YAG laser (*ca.*532nm) was irradiated as the second harmonics of *ca.*1064nm fundamental laser. The irradiation power was 1.6mJ/pulse and the irradiation time was 60min.

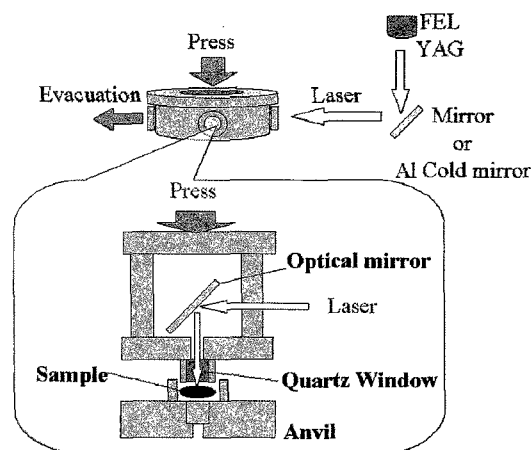


Figure 1. Schematic apparatus constructed for synthesis of C<sub>60</sub> polymers. The compressed surfaces of the sample were irradiated using a laser by the quartz window. Aluminum cold mirrors were used for high reflectance of visible laser (wavelength less than *ca.*700nm) and for cutting near-infrared lights. The quartz ensures high transmittance of greater than 95% of visible light.

The obtained samples were 5-mm-diameter disks with thickness of less than 0.5mm. They were brought in a vacuum case to prevent contamination from air. Raman microscopic spectroscopy (Renishaw plc. SYSTEM1000) was used to study molecular vibration spectra. The light source for excitation was Ar ion laser with wavelength of 514.5nm. Crystalline

structures were studied using reflective X-ray diffraction (XRD) (Rigaku Corp. RAD-C) with CuK $\alpha$ 1 x-rays.

### 3. RESULT & DISCUSSION

Figure 2 shows the change of the lattice parameter of (111) planes of samples irradiated by 350–600nm FEL through the BPF under atmospheric pressure. The lattice parameter of C<sub>60</sub> and C<sub>60</sub>+I<sub>2</sub> samples irradiated by 500nm FEL decreased by *ca.* 1.1 $\times$ 10<sup>-2</sup>nm and *ca.* 1.2 $\times$ 10<sup>-2</sup>nm, respectively. These results revealed that the polymerization reactions were effectively induced by irradiation of FEL with wavelength of about 500nm. Then covalent binding between C<sub>60</sub> molecules took place and the decline of the crystal structure proceeded.

Figure 3 shows Raman peaks of the Ag(2)-derived mode in the case of 532nm YAG laser irradiation. The wave number of the peak of the non-irradiated pristine C<sub>60</sub> was 1466.1cm<sup>-1</sup>, whereas that of the irradiated C<sub>60</sub> changed to 1462.9cm<sup>-1</sup> with decrement by *ca.* 3cm<sup>-1</sup>. On the other hand, the irradiated mixture of C<sub>60</sub>+I<sub>2</sub> revealed the peak wave number of 1460.0cm<sup>-1</sup>. The Raman shift was as large as *ca.* 6cm<sup>-1</sup>. The half-width of the Raman peak also increased in correspondence to the amount of the peak shift.

Figure 4 shows typical Raman peaks of the Ag(2)-derived mode in the case of 450nm FEL irradiation. The wave number of the peak of the non-irradiated pristine C<sub>60</sub> was 1463cm<sup>-1</sup>. The irradiated C<sub>60</sub> showed the wave number of 1460cm<sup>-1</sup> with a decrement by *ca.* 3cm<sup>-1</sup>. The irradiated mixture of C<sub>60</sub>+I<sub>2</sub> revealed the larger Raman shift as large as *ca.* 8cm<sup>-1</sup>. The half-width of the Raman peak increased by irradiation.

The ultraviolet laser caused somewhat different changes of the Raman spectrum. Figure 5 shows Raman peaks of the Ag(2)-derived mode in the case of 345nm FEL irradiation. Double splitting of the peak was observed. Since the optical absorption of C<sub>60</sub> at 345nm is about three times higher than that at 450nm, polymerization reactions proceeded better in the thinner region of sample surfaces by 345nm irradiation than by 450nm. Consequently, the Raman peak from non-polymerized C<sub>60</sub> also remained in this case. The maximum amount of the Raman shift attained up to *ca.* 10cm<sup>-1</sup> in the C<sub>60</sub>+I<sub>2</sub> sample. Then the large decrease and broadening of the peak were also observed.

The results of these Raman shifts were summarized in Table 1. As well known the Raman peak broadens and shifts to the lower-energy side according to the progress of polymerization. Then the Ag(2)-derived mode is noted as an index of the polymerization reaction progress. It is suggestive that the change of the Raman peak of the C<sub>60</sub>+I<sub>2</sub> sample was definitely larger than that of pure C<sub>60</sub>. This result indicates that some additional

Table 1. The conditions of laser irradiation and observed the Raman peak shift.

Pristine Powder	Laser	Wavelength [nm]	Laser Power [mJ/Pulse]	Irradiation Time [min]	Ag(2) peak shift [cm <sup>-1</sup> ]
C <sub>60</sub>	FEL	450 (3rd)	0.5	300	3.0
C <sub>60</sub> +I <sub>2</sub>	FEL	450 (3rd)	0.5	300	7.6
C <sub>60</sub>	FEL	345 (5th)	2	120	7.6
C <sub>60</sub> +I <sub>2</sub>	FEL	345 (5th)	2	120	9.7
C <sub>60</sub>	YAG	532 (2nd)	1.6	60	3.2
C <sub>60</sub> +I <sub>2</sub>	YAG	532 (2nd)	1.6	60	6.0

mechanisms work for promotion of polymerization by addition of  $I_2$ . It can be interpreted that photo-excited electrons of  $C_{60}$  molecules transfer to iodine atoms: hole doping into  $C_{60}$  molecules takes place.

The hole-doping effect was also confirmed through crystalline structure analyses. Figure 6 shows typical XRD patterns of samples irradiated using 450nm FEL. After the irradiation the main diffraction peak (111) markedly decreased and broadened in the case of the  $C_{60}+I_2$  sample. Especially the lattice spacing of (111) planes of the irradiated  $C_{60}$  and  $C_{60}+I_2$  sample were smaller by  $ca.7 \times 10^{-3} nm$  and  $ca.8 \times 10^{-3} nm$ , respectively, than that of the non-irradiated  $C_{60}$ . The results suggest that covalent bondings between  $C_{60}$  molecules took place and the decline of the crystalline structure progressed according to polymerization reactions induced by laser irradiation and/or addition of iodine.

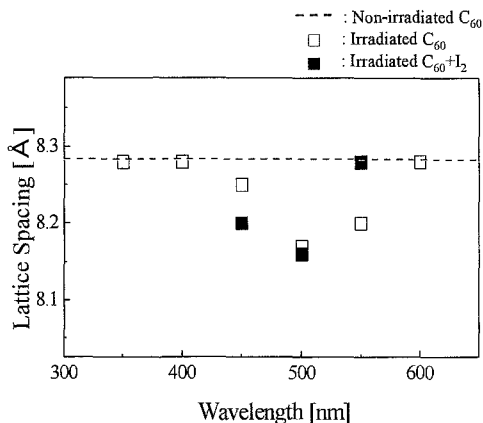


Figure 2. Observed lattice spacing of  $C_{60}$  (111) of the sample after 350~600nm FEL irradiation under atmospheric pressure in vacuum. The open square and closed one show the results of  $C_{60}$  and  $C_{60}+I_2$  sample, respectively.

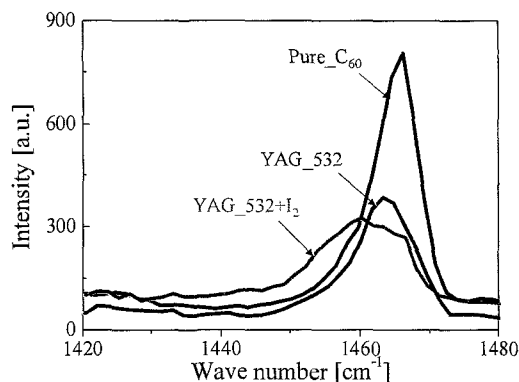


Figure 3. Raman peaks of the  $Ag(2)$ -derived vibration modes observed in the three samples: non-irradiated pristine  $C_{60}$ ,  $C_{60}$ , and  $C_{60}+I_2$  irradiated by 532nm YAG laser.

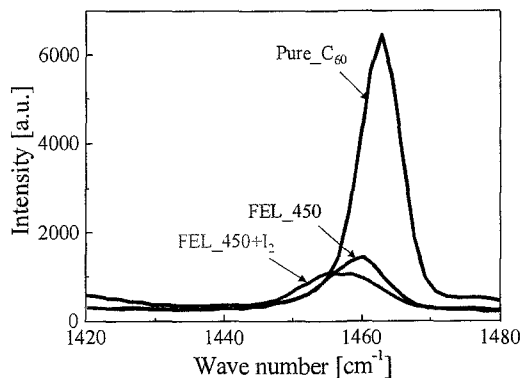


Figure 4. Raman peaks of the  $Ag(2)$ -derived vibration modes observed in the three samples: non-irradiated pristine  $C_{60}$ ,  $C_{60}$ , and  $C_{60}+I_2$  irradiated by 450nm FEL.

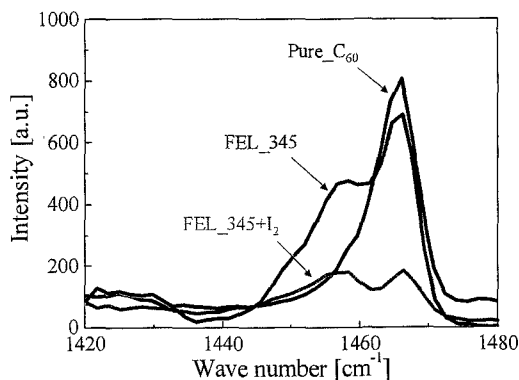


Figure 5. Raman peaks of the  $Ag(2)$ -derived vibration modes observed in the three samples: non-irradiated pristine  $C_{60}$ ,  $C_{60}$ , and  $C_{60}+I_2$  irradiated by 345nm FEL.

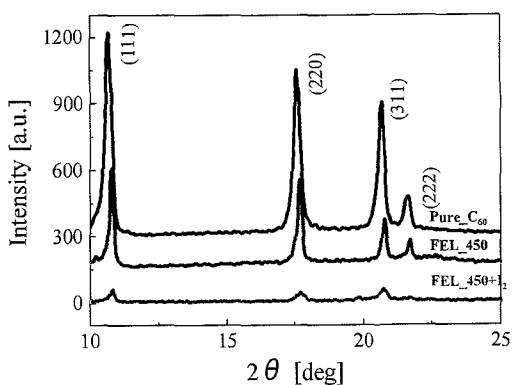


Figure 6. XRD patterns of the three samples: non-irradiated pristine  $C_{60}$ ,  $C_{60}$ , and  $C_{60}+I_2$  irradiated by 450nm FEL. The inset index corresponds to each fcc plane of  $C_{60}$ . The (111) peak intensity of the irradiated  $C_{60}+I_2$  decreased remarkably.

#### 4. CONCLUSION

The 450nm or 345nm FEL and 532nm YAG laser were irradiated to surfaces of compressed  $C_{60}$  or  $C_{60}+I_2$  powder in vacuum. After laser irradiation the  $C_{60}$  Raman peak of the  $A_g(2)$ -derived mode clearly shifted to the lower energy side and/or the half-width of the peak became broad. Also the lattice parameter of  $C_{60}$  decreased and the crystalline structure was declined by 450nm FEL irradiation. These characteristic changes in the  $C_{60}+I_2$  sample were more distinct than those in  $C_{60}$  powder. Conclusively the obtained results suggest that the 3D polymerization of  $C_{60}$  was effectively promoted using laser irradiation and/or the effect of the photon-assisted hole-doping from iodine to  $C_{60}$  molecules. The detailed characterization of the obtained samples is a subsequent work.

#### ACKNOWLEDGEMENTS

This work is partly supported by "Academic Frontier" Project for Private Universities: matching fund subsidy from MEXT, 200-2007.

The authors would like to thank the staff members of Laboratory for Electron Beam Research and Application of Nihon University for their helps of FEL operations.

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(Received January 10, 2007; Accepted August 23, 2007)