Wavelength dependence of polyyne preparation by liquid-phase laser ablation using pellet targets

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Experimental

Methanol (4.0 ml, Wako Chemical) or *n*-hexane (4.0 ml, Wako Chemical) was put in a vitreous silica optical cell ($1 \times 1 \times 6.5$ cm^3) and a 70-mg fullerene pellet (7 mm in diameter and 1 mm thick), shaped from fullerene powder (Sigma-Aldrich) using a pellet molding press, was sunk to the bottom of the cell. Irradiation was performed by pulses of the fundamental (1064 nm) light from an Nd:YAG laser (Continuum Minilite II), and of the second (532 nm) and third (355 nm) harmonic lights from an Nd:YAG laser (Spectron Laser Systems SL454G) operating at a 10 Hz repetition rate. The beam size from SL454G was controlled with a lens, since its beam size was wider than the diameter of the pellet. The pulses were directed from the top of the cell, through the solvent, to the pellet target placed at the bottom of the cell. The ablation of fullerene was performed for 3 min at room temperature with an optimized laser power. Laser power for 1064, 532, and 355 nm was 40 mJ/pulse. After laser ablation, the diameter of the particle dispersed in the solution was measured by dynamic light scattering (DLS, Otsuka Electronics DLS-8000). After the solvent was evaporated, residual particles were observed by a field emission scanning electron microscope (FE-SEM, Hitachi S-4800), and also measured by a Fourier transform infrared spectrophotometer (FT-IR, Shimadzu FT-IR8600) using the KBr method. In addition, the solution was filtered with a filter of 0.2-μm hole diameter (Sartorius Minisart SPR25), and a UV-Vis absorption spectrum of the filtrate was measured using a UV-Vis spectrophotometer (Shimadzu UV-3600). After the ablation of fullerene was also performed for 60 min, the solution was filtered and analyzed with a high performance liquid chromatograph (HPLC, Shimadzu LC-20AT pump) equipped with a multichannel UV-Vis spectrometer. Polyynes produced were separated into individual components by HPLC equipped with an octadecylsilyl (ODS) column (Nacalai Tesque $5C_{18}$-AR-II, 4.6 mm × 150 mm) using ethanol (for methanol solution) or *n*-hexane (for *n*-hexane solution) as the mobile phase.

Characterization of the methanol or *n*-hexane solution after the fullerene was irradiated

In an FT-IR spectrum of the residual particle from the methanol solution (Figure 1S), four peaks of 527, 576 1181, and 1429 cm^{-1} were attributed to infrared allowed, dipole active vibrational modes of a C_{60} skeleton with icosahedral symmetry.[1] A UV-Vis-NIR spectrum of the methanol solution dispersed fullerene is shown in Figure 2S. Absorption bands were observed below about 600 nm, but not observed around 1064 nm.

The distribution of the diameter of the gains existing in the solvent is shown in Figure 3S. When the laser beam of 532 nm was used, the ratio of small particles was the highest, and large particles of 1 μm or more were not observed. Figure 4S shows SEM images of the particles obtained from the solutions. Particles of few hundred nanometers, though aggregated, were observed using the 355- or 532-nm laser beam, and large particles of few micro meters using the 1064-nm beam. The quantity of particles in the solutions was small using the 355- or 1064-nm laser beam, but large using the 532-nm beam.

When polyynes were prepared using the fullerene pellet and the *n*-hexane solvent, the presence of polyynes could barely be confirmed in the UV-Vis spectra since the fullerene was well soluble in *n*-hexane which has a strong absorption spectrum (Figure 5S) that almost covered the polyyne spectrum. The absorption peaks were in agreement with those of the fullerene, and weak peaks of polyynes C_8H_2 and $C_{12}H_2$ were also observed at 226 and 296 nm. UV-Vis spectra of both the methanol and *n*-hexane solutions containing polyynes separated using HPLC are given in Figure 6S. The solutions irradiated by the laser of 1064 nm were used for HPLC because of the large number of polyynes produced.

UV-Vis absorption spectra of polyynes up to $C_{20}H_2$ were obtained from the methanol and fullerene pellets as shown in Figure 6S(a). The production of polyynes has not yet been reported from methanol and fullerene using a laser beam of 1064 nm, only C_8H_2 and $C_{10}H_2$ have been produced by 355-nm irradiation.[3] UV-Vis absorption spectra of polyynes up to $C_{22}H_2$ were obtained from *n*-hexane and fullerene as shown in Figure 6S(b). However, in this system, polyynes up to $C_{12}H_2$ have previously been obtained.[2,3] Figure 6S shows that longer-chain polyynes were prepared from the *n*-hexane solution than the methanol one. This result agrees with that of the fullerene powder target.[2,3]

References

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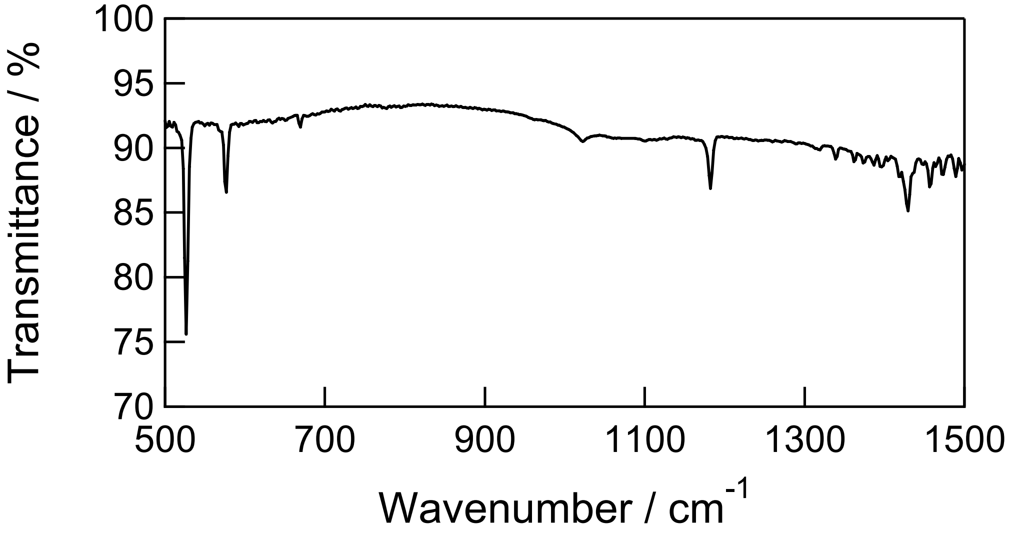

Figure 1S. FT-IR spectrum of residual particle from the methanol solution measured using KBr method.

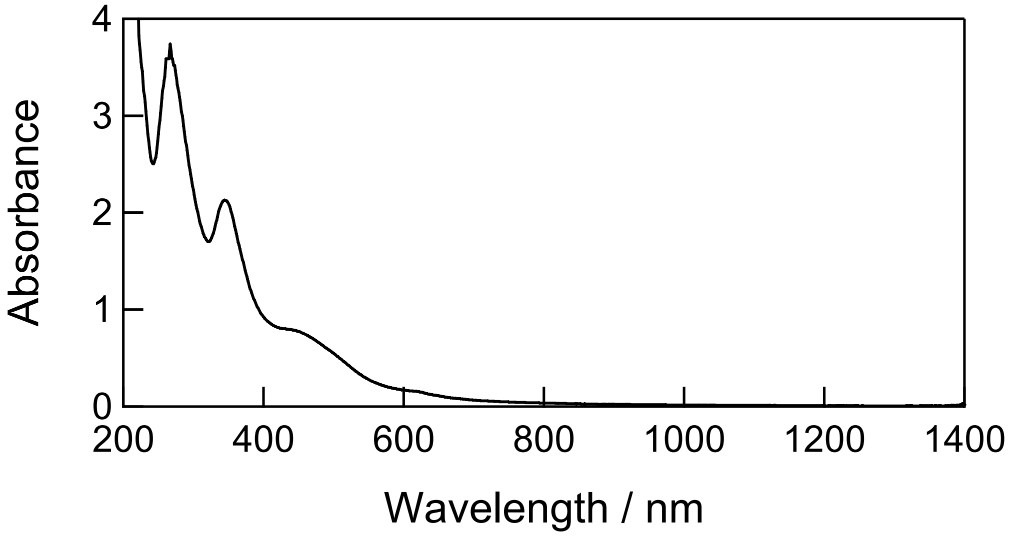

Figure 2S. UV-Vis-NIR spectrum of a methanol solution dispersed with fullerene.

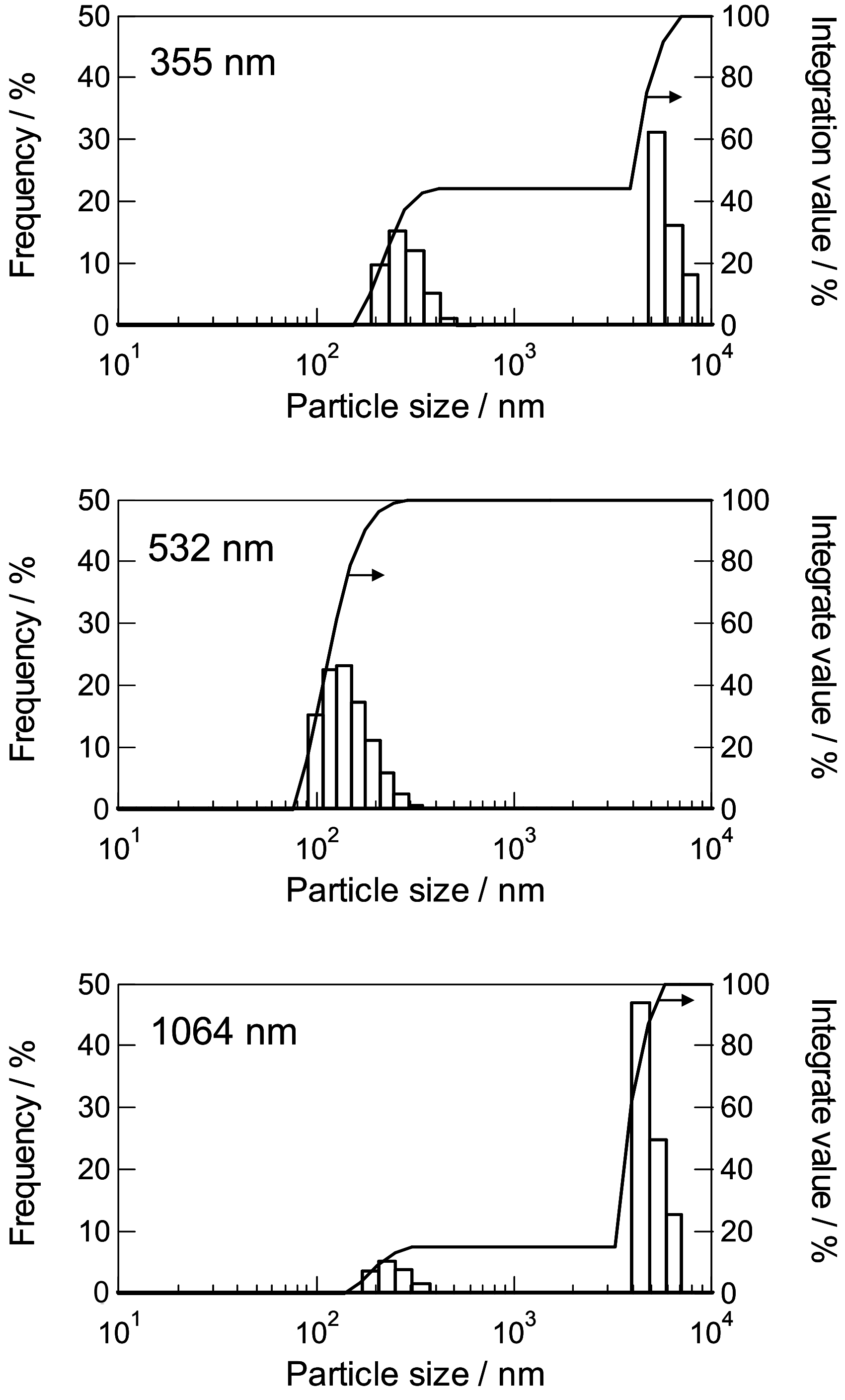

Figure 3S. Diameter distribution of grains in the solutions without filtration after laser ablation with different wavelengths.

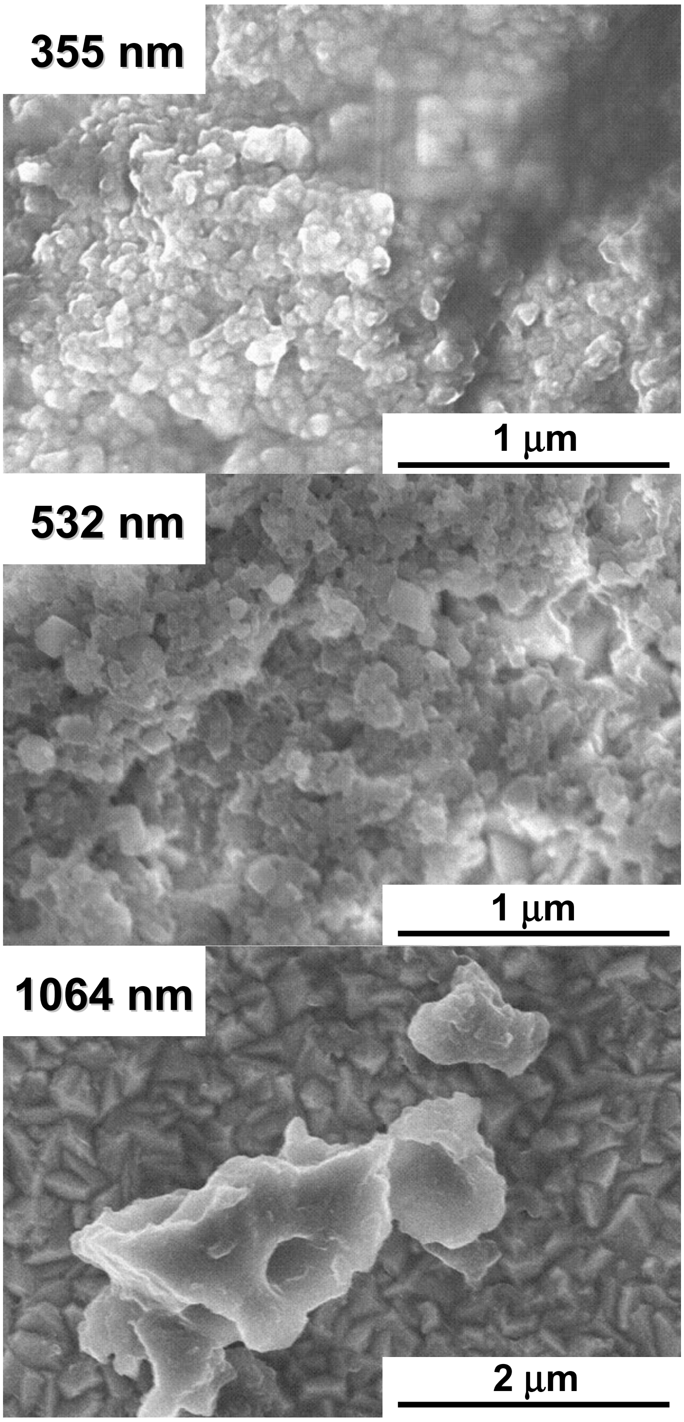

Figure 4S. SEM images of the particles separated from the solutions. In the bottom image (1064 nm), the surface of the fluorine-doped tin oxide (FTO) glass substrate is also observed.

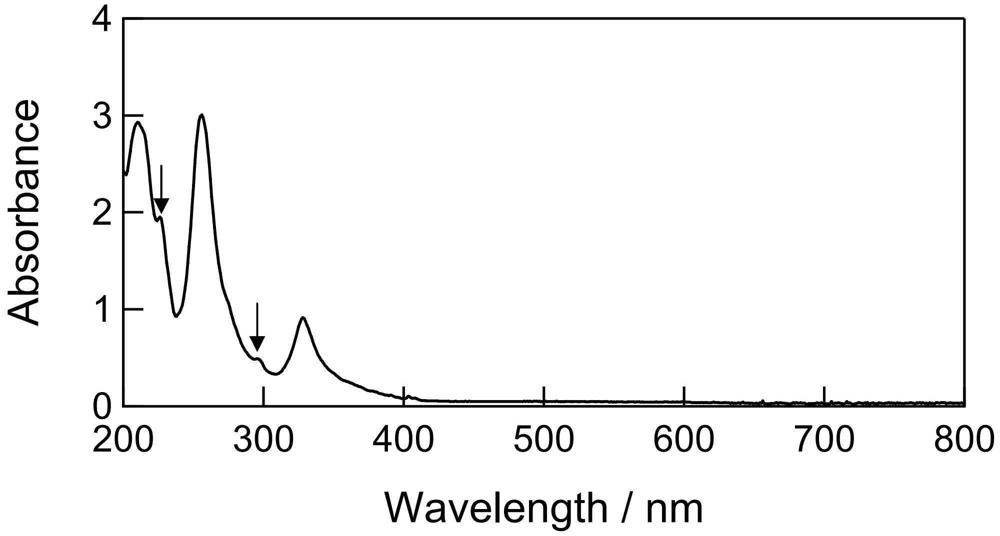

Figure. 5S. UV-Vis spectra of the *n*-hexane solutions obtained from the laser ablation of fullerene pellet. The solution has been diluted four times. The arrows show polyyne peaks.

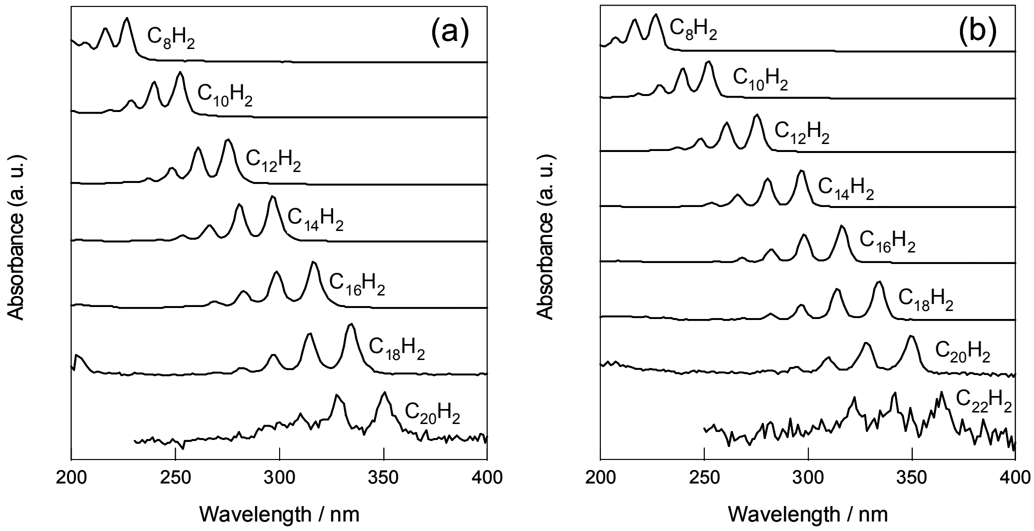

Figure 6S. UV-Vis spectra of polyynes produced from the fullerene pellet in methanol (a) and in *n*-hexane (b) after being separated by HPLC.