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Synthesis of polyynes by laser ablation of diamond nanoparticles suspended in solution

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Abstract. We synthesized polyynes by laser ablation of diamond nanoparticles (about 5 nm in diameter) and graphite particles with two different sizes (about 5 nm and 10 μm) suspended in liquid ethanol. It was found that the ablation of diamond nanoparticles results in larger amounts of long polyynes compared to the ablation of graphite particles. It was also found that the chain length distribution of polyynes produced from diamond nanoparticles is dependent on the laser irradiation time and the fraction of long polyynes is higher when the irradiation time is shorter. These results allow us to conclude that the direct evaporation of carbon atoms from pristine diamond nanoparticles at the initial stage of laser irradiation results in the larger amounts of long polyynes.

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1 Introduction

Linear carbon chain structures such as hydrogen capped polyynes with the general structure H–(C≡C)$_m$–H (with an integer m) or C_nH_2 (with an even integer n) are known as the *sp*-hybridized carbon structure. These linear carbon chain structures are extremely interesting, because they are not only possible carriers of unidentified interstellar bands [1], but also offer a possibility of realizing one-dimensional conducting materials [2,3] and nonlinear optical materials [4]. However, they remain synthetically challenging and difficult to study. Up to now, formidable synthetic obstacles and instability have limited the study of their electronic and optical properties.

Recently, Tsuji and co-workers have reported successful formation of hydrogen-capped polyynes by laser ablation of graphite [5] or fullerene [6] particles suspended in organic solvents. Polyynes produced in solution were very stable at room temperature and the amount was sufficient to carry out several kinds of analysis including optical measurements. The extremely easy access to polyynes will have an enormous impact in the possibility to study the chemical and physical properties. However to date, polyynes produced by this production method is limited to the length of up to $n = 16$, and the yield decreases with the chain length. Therefore, it is still challenging to produce longer polyynes with high yields.

Very recently, we have carried out laser ablation experiments by using diamond nanoparticles 5 nm in diameter suspended in ethanol as a target material [7]. We confirmed the formation of polyynes from diamond nanoparticles as well as graphite and fullerene particles. It was found that the products obtained from diamond nanoparticles contain larger amounts of long polyynes than those from pristine graphite particles, although the diamond nanoparticles are graphitized by preceding laser irradiation. This result suggests that some diamond nanoparticles are directly evaporated without graphitization and the direct evaporation may result in larger amounts of long polyynes. In order to produce larger amounts of long polyynes and much longer polyynes, it is necessary to know the detailed mechanism of the polyyne formation from diamond nanoparticles.

In this work, we compare the chain length distributions of polyynes produced from diamond nanoparticles with those from graphite particles with two different sizes, and show that the chain length distribution depends on the atomic structure, i.e., diamond or graphite. We also show that the chain length distribution of the polyynes produced from diamond nanoparticles depends on the laser irradiation time, and demonstrate that the direct evaporation process from the diamond nanoparticles plays an important role in the effective formation of long polyynes.

2 Experiment

The experimental setup was described in reference [7]. As ablation targets we used diamond nanoparticles

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about 5 nm in diameter, carbon onions (∼5 nm) and graphite powder (∼10 μm). Diamond nanoparticles and graphite powder are commercially available. Carbon onions are produced by annealing the diamond nanoparticles (∼5 nm) at 1700 °C in high vacuum [8]. They consist of concentric curved graphitic shells with an interlayer distance close to that of bulk graphite. We approximately regard the carbon onions as graphite particles as small as diamond nanoparticles. Ablation targets of 5 mg were suspended in 5 ml ethanol in a transparent vial. The second harmonic (532 nm) of a Nd:YAG laser was used as an irradiation source. The pulse duration is ∼7 ns and the frequency is 20 Hz. The energy fluence of the incident beam was about 1.3 J/cm^2.

In order to estimate the amounts of polyynes in suspension, the ultraviolet-visible (UV-Vis) transmission spectra of the suspensions were recorded by a double-beam spectrometer (Shimadzu, UV-3101PC). For measurements, suspensions were diluted 50 times with ethanol. When the suspension contains residual target materials, they were separated by centrifugation.

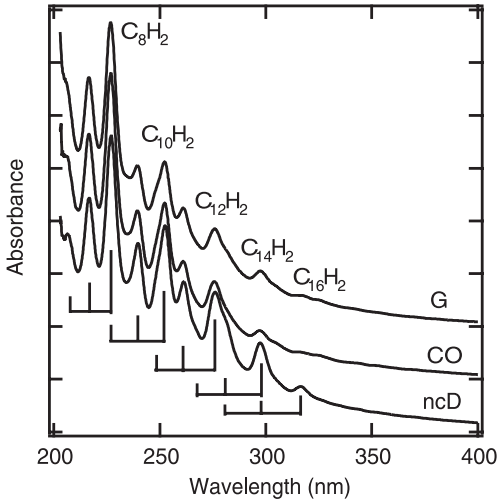

Fig. 1. Spectra of the suspension produced from diamond nanoparticles (ncD), carbon onions (CO) and graphite powder (G) respectively. All spectra are normalized and offset. The vertical lines indicate the position of the main three absorption bands of each polyyne (C_nH_2: $n = 8 \sim 16$).

3 Results and discussion

The initial suspension of diamond nanoparticles is light gray. By laser irradiation for 5 ∼ 10 minutes, the suspension is transformed into black. From the analysis of Raman spectrum and transmission electron microscopy (TEM) observation of the black products in the suspension, it was found that diamond nanoparticles are transformed into graphitic particles by laser irradiation. After 40 min irradiation, all particles in suspension disappear and the suspension turns into yellowish transparent solution. Similar results were obtained in the suspensions of graphite particles with different sizes.

Figure 1 shows the UV-Vis spectra of suspensions at the final stage. The vertical axis is the normalized absorbance. The curves denoted "ncD", "CO" and "G" are the spectra of the suspension of diamond nanoparticles, carbon onions and graphite particles, respectively. These spectra commonly exhibit many sharp bands in the UV region. The observed bands coincide well with those of a series of hydrogen-capped polyynes. From a close comparison of the wavelengths of the bands seen in Figure 1 with those in literatures [9], we conclude that the suspensions contain polyynes with $n = 8$, 10, 12, 14 and 16. As can be seen in Figure 1, it is clear that the amount of long polyynes in the suspension of the diamond nanoparticles is larger than that of the graphite particles.

In order to analyze more in detail the observed spectra, we deconvoluted the spectra into those of individual polyynes with different n. In the deconvolution, we assumed the spectra of polyynes with n ranging from 8 to 16 reported by Cataldo [10] and a continuous background representing the absorption by molecules produced other than polyynes. By fitting the observed spectra by a least square method, we obtained the absorbances for the most intense bands of polyynes. The absorbances for

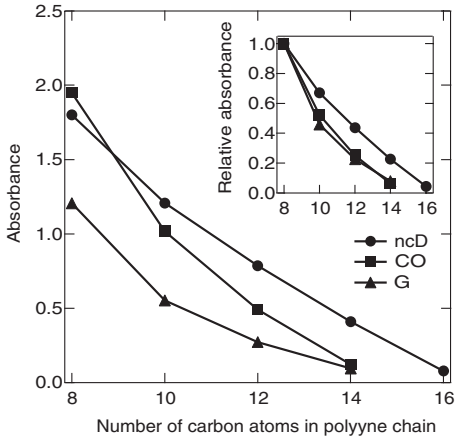

Fig. 2. Absorbances of the most intense bands of C_nH_2 produced from diamond nanoparticles (ncD, •), carbon onions (CO, ■) and graphite powder (G, ▲) as a function of the carbon atoms in the polyyne chain. The inset shows the relative absorbance of each polyyne normalized at the value of C_8H_2.

polyynes are proportional to the amounts of polyynes produced.

Figure 2 compares the value of the absorbances of the most intense bands of polyynes produced from diamond nanoparticles, carbon onions and graphite powder, when all particles in suspension are exhausted. The absorbance of the $C_{16}H_2$ in the suspensions of carbon onions and graphite powder are too small to be estimated. The total amounts of polyynes produced from equal amount of carbon sources depend on the kind of the target material. Smaller carbon particles such as diamond nanoparticles and carbon onions can produce larger amounts of polyynes than the larger size graphite powder. In the

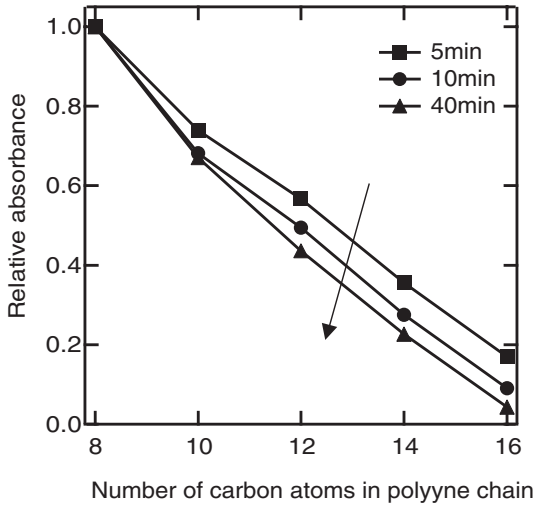

Fig. 3. Laser irradiation time dependence of length distribution of polyynes produced from diamond nanoparticles: 5 min (■), 10 min (•) and 40 min (▲), respectively.

inset of Figure 2 the absorbances of polyynes with $n = 8$ to 16 relative to that of $n = 8$ are plotted. It is found that the polyynes produced from diamond nanoparticles contain larger amounts of long polyynes than those from graphite particles. Furthermore, it is worth noting that the chain length distributions of the polyynes produced from carbon onions and graphite powder are very similar. This result indicates that the chain length distribution of the polyynes produced from graphite sources is intrinsic and independent of the particle size.

The polyynes produced from diamond nanoparticles are thought to be the mixture of polyynes, which are produced by the direct evaporation of carbon atoms from pristine diamond nanoparticles and those from graphitic particles transformed from diamond nanoparticles. Figure 3 shows the chain length distribution of polyynes produced from diamond nanoparticles for three different irradiation times 5, 10 and 40 min. The polyynes produced by a shorter irradiation contain larger fractions of long polyynes. After 5 min irradiation, particles in the suspension are still mainly diamond nanoparticles. Therefore, in this period the polyynes are mainly produced by the carbon atoms from pristine diamond nanoparticles. This indicates that the direct evaporation of carbon atoms from diamond nanoparticles plays an important role in effective formation of long polyynes. On the other hand, further irradiation transforms the diamond nanoparticles into graphitic particles and polyynes are produced mainly from them. Since polyynes produced from them may have the chain length distribution similar to that produced from pristine graphite particles, the relative fraction of the long polyynes decreases with the irradiation time. It is worth noting that the length distribution of polyynes from carbon onions was found to be independent of laser irradiation time.

In conclusion, the direct evaporation of carbon atoms from pristine diamond nanoparticles results in the formation of large amounts of longer polyynes. Further effective formation of long polyynes and much longer polyynes may be possible, if diamond nanoparticles could be evaporated more effectively, i.e., by using the laser beam with a higher power or with a photon energy larger than the band-gap of diamond.

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