

Production of Hydrogen-Capped Polyynes by Laser Ablation of Graphite in Neat Water

Yeong Kyung Choi, Jae Kyu Song,* and Seung Min Park*

Department of Chemistry, Kyunghee University, Seoul 130-701, Korea

*E-mail: jaeksong@khu.ac.kr (JKS); smpark@khu.ac.kr (SMP)

Received July 15, 2009, Accepted August 24, 2009

Key Words: Polyynes, Liquid laser ablation, Graphite

Laser ablation of a solid graphite target has been a topic of utmost research interest since the advent of lasers in 1960s.¹ Carbon clusters of various sizes were formed simply by irradiating a graphite surface in vacuum or gas-phase and remained highly stable due to their high binding energies.^{2,3} Accordingly, laser ablation of graphite has been widely employed as an effective tool for the synthesis of carbon clusters and it has ultimately brought about the discovery of C₆₀.

Recently, there has been a growing interest in laser ablation of a graphite target in *liquid phase* aiming at the growth of polyynes,^{4,9} which are hardly produced employing conventional organic synthesis methods. Hydrogen-capped polyynes, (H(C \equiv C)_nH), are linear carbon chain molecules consisting of *sp* hybridized orbitals, being observed in the interstellar space. Due to their typical one-dimensional electronic structures, polyynes have attracted considerable attention in their size-dependent band gap¹⁰ and nonlinear optical properties.⁹

Large polyynes with $n \geq 5$, in particular, have been prepared by laser ablation of graphite mostly in *organic solvents*,⁶ while we present experimental results on the formation of C₁₀H₂ (namely $n = 5$) by laser irradiation of a graphite target in *neat water*. Although larger polyynes can be formed in organic solvents, laser ablation in water has a unique advantage in that it can greatly reduce the contaminant carbon materials including graphite and graphite-like carbon particulates (in short, carbon contaminants hereafter) compared to the organic solvents.

The key feature of laser ablation of a solid target in liquid phase is certainly the formation of a dense plasma which generates local and temporal non-equilibrium conditions. Therefore, physical parameters including laser fluence, wavelength, and ablation time as well as chemical parameters including solvent undoubtedly determine the characteristics of the resultant polyynes significantly. In this Note, we discuss the effects of aging and post-irradiation on the polyynes solution, together with the influence of laser fluence on the formation rate and size of polyynes.

Experimental

Polyynes were produced by laser ablation of a graphite target (diameter = 20 mm, thickness = 6.0 mm, 99.99%) placed on the bottom of a glass vessel filled with 30 mL of deionized water. The graphite target was irradiated vertically by a Q-switched Nd-YAG laser (QuanteI 980C, $\lambda = 1064$ nm) operating

at 10 Hz. The laser energy ranged from 60 to 200 mJ/pulse. The laser beam was loosely focused using a lens with a focal length of 300 mm. The spot size of the focused laser beam was 2.0 mm in diameter. The vessel was continuously rotated to minimize the target aging effect and to give some stirring effect. The optical properties of the nascent polyynes solution was examined at room temperature by a UV-Vis absorption spectrophotometer (HP 8452A). The irradiation time and laser fluence were varied to investigate the influence on the optical properties. The post-irradiation was performed using pulsed UV laser ($\lambda = 266$ nm, pulse duration = 7 ns) for 30 min. The laser beam diameter was 7 mm and energy was 2 mJ/pulse.

Results and Discussion

The UV absorption spectrum of a solution prepared by laser ablation of a graphite target in neat water and that of a graphite powder solution are displayed in Figure 1. The laser energy was 160 mJ/pulse (5.1 J/cm²) and the ablation time was 5 min. Unlike the graphite powder solution, there appear distinctive features in the spectrum for the solution containing laser-generated species. The peaks at 205 nm, 215.5 nm, and 226 nm represent C₈H₂ and those at 239.5 nm and 251.5 nm belong to C₁₀H₂.⁹ It is gratifying that polyynes as large as C₁₀H₂ can be generated by laser ablation of graphite in neat water, for the first

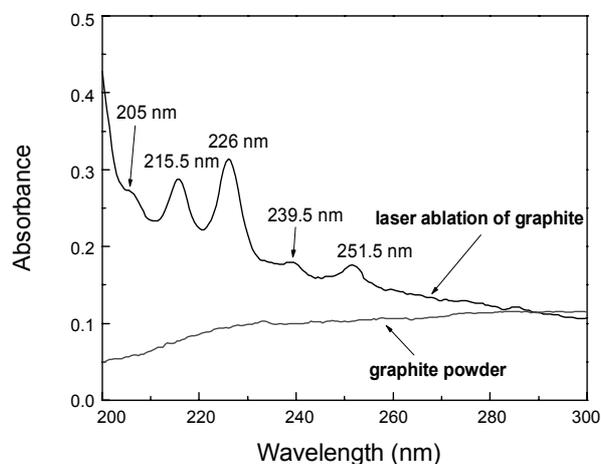


Figure 1. The UV absorption spectrum of a solution prepared by laser ablation of a graphite target in neat water at 1064 nm (160 mJ/pulse) and that of a graphite powder solution.

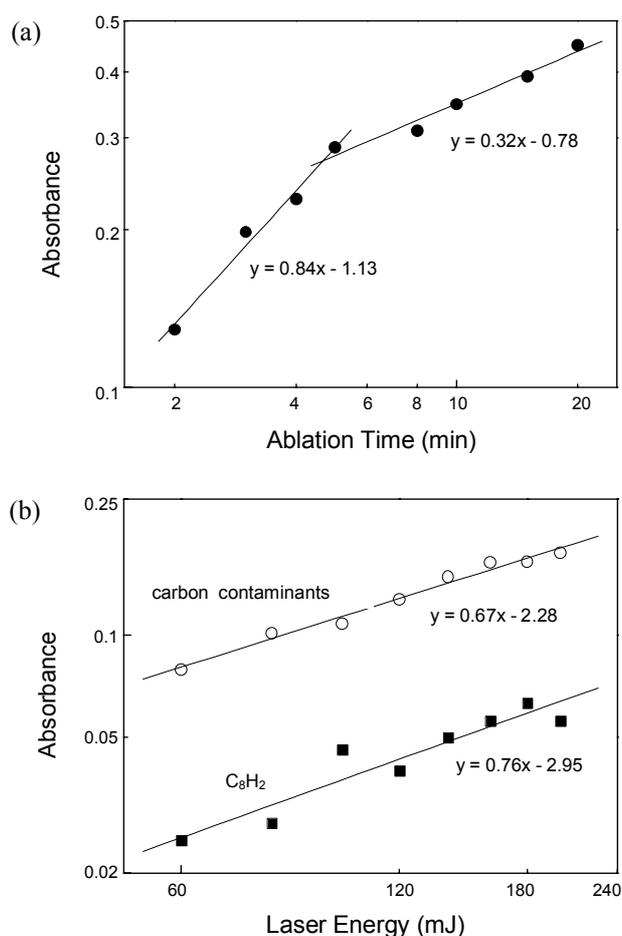


Figure 2. The effects of (a) the irradiation time, and (b) the laser energy on the formation of polyynes (log-log plots). In Fig. 2(b), the base line was subtracted when the absorbance at 215.5 nm was measured to select contribution from C_8H_2 only, while this still may include some intensities from smaller or larger polyynes. Since the concentration of polyynes larger than $C_{10}H_2$ is negligible, the absorbance at 300 nm is loosely indicative of the content of the carbon contaminants.

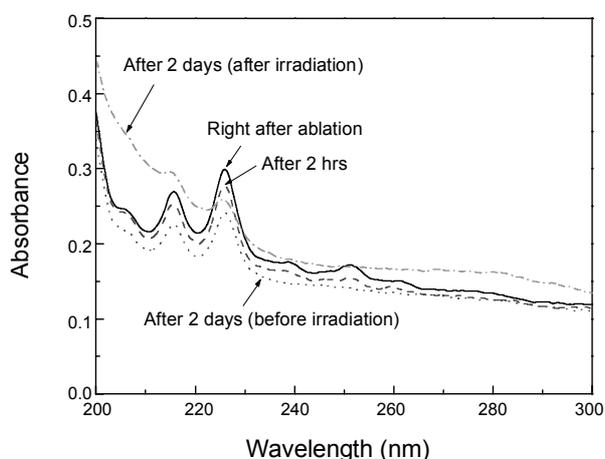


Figure 3. The aging and post-radiation effects on the polyyn solution.

time to our knowledge. While Compagnini *et al.*⁶ reported synthesis of C_8H_2 by laser ablation of graphite in water at 532 nm, they could not detect any larger polyynes at the laser fluence of

0.4 J/cm^2 . Since the density of C_2 , which is considered to be the major building block of polyynes, determines in essence the size of polyynes, the shorter ablation laser wavelength was often preferred to enrich C_2 molecules in liquid laser ablation of graphite.⁴ It is, however, of note that the laser fluence as well as the laser wavelength is a critical parameter for the growth of large polyynes.

Figure 2 shows the effects of the irradiation time and laser energy on the formation of polyynes using log-log plots. The absorbance of the polyyn (more strictly, polyyn plus other carbon contaminants) solution at 215.5 nm increased with ablation time as shown in Fig. 2(a), but the rate was drastically reduced after 5 min. This indicates that the self-absorption by the solution diminishes the effective laser fluence on the target surface. Figure 2(b) illustrates the relative concentrations of a polyyn (\blacksquare), C_8H_2 , and carbon contaminants (\circ), which were estimated from the absorbance data at 215.5 nm (after the correction of baseline to eliminate the contribution of carbon contaminants) and 300 nm, respectively, as a function of laser energy. At first glance, polyynes and carbon contaminants show similar trend in their absorption intensities as the laser energy increases. Nevertheless, the slight difference in the slope may possibly imply that polyynes are preferably produced at higher laser energies. This is in line with the result of Fig. 1, which shows the effect of laser fluence on the growth of large polyynes.

The aging and post-radiation effects on the polyyn solution are depicted in Fig. 3. Two days after the preparation of polyyn solution by laser ablation, the absorption peaks representing C_8H_2 decreased as little as $\sim 25\%$ while those belong to $C_{10}H_2$ were not quite detectable. This leads us to conclude that the larger polyynes are less stable in liquid environment containing carbon-containing species. As the polyyn solution was irradiated for 30 min at 266 nm, the peak intensities related to polyynes were drastically reduced. Since the band gap energies of C_8H_2 and $C_{10}H_2$ are larger than the photon energy of $\lambda = 266 \text{ nm}$,¹⁰ the disappearance of polyynes by irradiation at 266 nm is presumably related with a 2-photon absorption process. Details are to be further investigated by more elaborate studies.

Acknowledgments. This work was supported by a grant from the Kyung Hee University in 2008. (KHU-20080381)

References

1. *Pulsed Laser Deposition of Thin Films*; Chrisey, D. B.; Hubler, G. K., Eds.; Wiley-Interscience: New York, U. S. A., 1994.
2. Park, S. M.; Moon, J. Y. *J. Chem. Phys.* **1998**, *109*, 8124.
3. Park, S. M.; Chae, H.; Wee, S.; Lee, I. *J. Chem. Phys.* **1998**, *109*, 928.
4. Tsuji, M.; Tsuji, T.; Kuboyama, S.; Yoon, S.-H.; Korai, Y.; Tsujimoto, T.; Kubo, K.; Mori, A.; Mochida, I. *Chem. Phys. Lett.* **2002**, *355*, 101.
5. Kitazawa, S.-i.; Abe, H.; Yamamoto, S. *J. Phys. Chem. Solid.* **2005**, *66*, 555.
6. Compagnini, G.; Mita, V.; Cataliotti, R. S.; D'Urso, L.; Puglisi, O. *Carbon* **2007**, *45*, 2445.
7. Nishide, D.; Wakabayashi, T.; Sugai, T.; Kitaura, R.; Kataura, H.; Achiba, Y.; Shinohara, H. *J. Phys. Chem. C* **2007**, *111*, 5178.
8. Matsutani, R.; Kakimoto, T.; Wada, K.; Sanada, T.; Tanaka, H.; Kojima, K. *Carbon* **2008**, *46*, 1091.
9. Matsutani, R.; Ozaki, F.; Yamamoto, R.; Sanada, T.; Okada, Y.; Kojima, K. *Carbon* **2009**, *47*, 1659.
10. Yang, S.; Kertesz, M. *J. Phys. Chem. A* **2006**, *110*, 9771.