

Novel Method of Producing Carbon Nanoparticles on Benzene/Water Interface with Femtosecond Laser Plasma Filament

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The irradiation of NIR femtosecond laser pulses to a benzene/water bilayer dramatically enhanced the formation of carbon nanoparticles compared with that in neat benzene. The focusing-position-dependent chemistry and the oxidative mechanism of nanoparticle formation are discussed.

Extensive and intensive studies on the formation of nanoparticles or nanocrystals on a liquid/solid interface by pulsed laser irradiation have been reported.¹ As for carbon nanoparticles, laser ablation of a variety of solid carbon materials in water has been well studied. In contrast, nanoparticle formation from other carbon sources, such as liquid organic molecules, has rarely been examined. Wesolowski et al. reported the precipitation of soot from neat benzene by NIR femtosecond laser pulse irradiation.² However, it is not certain whether photo-reaction or ionization plays an important role in soot formation. In this study, we report the first example of the preparation of carbon nanoparticles by NIR femtosecond laser irradiation to a benzene/water (B/W) bilayer. The production of nanoparticles was strongly dependent on where the laser was focused. Irradiation on a water layer resulted in the efficient formation of carbon nanoparticles.

Benzene was added onto a water layer in a quartz cuvette with a 1-cm optical path length slowly to maintain a stable B/W bilayer. The irradiation conditions such as wavelength, pulse duration, energy, chirp, focusing length, and temperature were fixed to investigate the focusing-position-dependent chemistry. The B/W bilayer was exposed to femtosecond laser pulses (0.8 μm, 40 fs fwhm, 1 kHz) under aerated conditions at 296 K.³ The laser beam was focused on the benzene or water layer using a plano-convex quartz lens with a focusing length of 50 mm. The appearance of each layer after laser irradiation depended strongly on where the laser was focused, as shown in Figure 1. When the laser irradiated to the bottom of the water layer, the black colloidal particles appeared not from the laser focus spot but from the B/W interface and sank into the water layer like Indian ink. Finally, the water layer became a homogeneous black colloidal solution, whereas the benzene layer was transparent (Figure 1a). The nanoparticle formation was enhanced when the laser irradiated close to the B/W interface, and large aggregated particles were visible in the benzene layer (Figure 1b). In addition, the B/W interface was covered by a black sheet-like structure, and the curvature of the B/W interface became larger than that of the initial B/W interface. In contrast, the water layer stayed transparent, and the benzene layer became only pale yellow when the laser was focused on

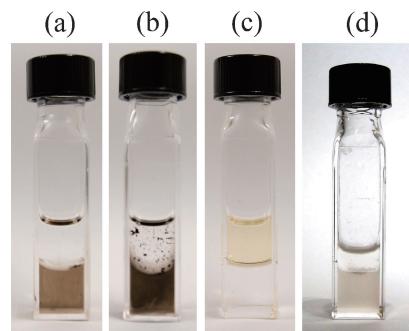


Figure 1. Cuvette after 25-min laser irradiation. The laser beam was focused on (a) the bottom of the water layer, (b) the benzene layer through the benzene/water interface (meniscus), and (c) the benzene layer. (d) The laser beam was focused on the bottom of the water layer, which was deaerated prior to and during the irradiation by bubbling argon through the cuvette. Laser energy was 0.4 mJ/pulse.

the benzene layer (Figure 1c). During the laser irradiation, bubbles continuously formed from the laser focal spot accompanying the white light.

After 25-min irradiation, each layer was collected and dropped onto a copper grid covered with amorphous carbon film. The drop was allowed to dry to prepare specimens for TEM observations, which were performed with a Hitachi H-7100 electron microscope operated at 75 kV. A large quantity of nanoparticles was observed in the water layer when the laser was focused on the bottom, whereas almost nothing was found in the benzene layer. A small but nonnegligible quantity of dispersed nanoparticles was found in the benzene layer that was irradiated, and a rod-like nanostructure was found in the water layer. Figure 2 shows representative TEM images of nanoparticles collected from the water layer when the laser was focused on the bottom of the water layer or benzene through the B/W interface (meniscus). Fine particles smaller than 10 nm in diameter were observed as well as their agglomerates, which have amorphous structures.

The origin of the black colloidal particles that appeared on the B/W interface should unquestionably be benzene, but it is surprising that such nanoparticles were formed even when the water layer was irradiated solely by femtosecond laser pulses. In addition, the nanoparticle generation in the B/W bilayer was quite efficient compared with that in benzene under our experimental conditions. Therefore, it is concluded that quite a different nanoparticle generation mechanism is operative in the

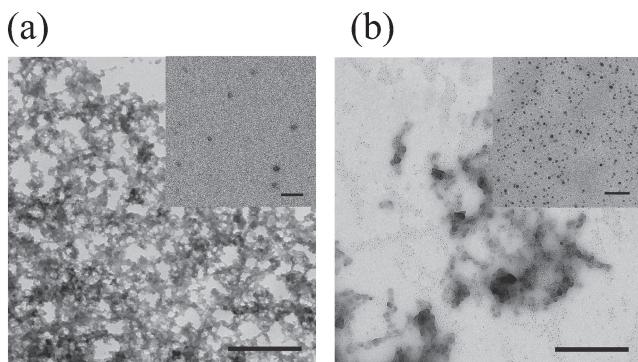


Figure 2. Representative TEM images of carbon nanoparticles collected from the water layer (scale bar: 500 nm; inset, 50 nm.). Laser pulses (40 fs, 0.8 μ m, 0.4 mJ) were focused on (a) the bottom of the water layer, and (b) the benzene layer through the benzene/water interface (meniscus).

B/W bilayer than in benzene and is also different from the build-up process of nanoparticles and polyynes⁴ from graphite in water. It is well known that once the solvent is ionized, filament is created by the propagation of femtosecond laser pulses in bulk transparent media. Filament formation is a result of the balance between self-focusing by the nonlinear refractive index and defocusing by plasma (electrons).⁵ White light is generated when the self-focusing is stopped by free-electron generation.⁶ As white light was generated during irradiation on either water or benzene in this study, electrons and cation radicals of solvent molecules should form. However, the recombination of an electron and a benzene cation may be the dominant process leading to the excited state, and the violent fragmentation leading to nanoparticles may not occur efficiently when benzene was solely irradiated. Benzene turned to pale yellow due to the photochemical reaction as was reported.⁷ The prolonged irradiation to benzene resulted in the formation of soot, as reported,² however, the yield was relatively very low under our experimental conditions. The shorter pulses used in this study would make both the subsequent excitation of radicals and the following fragmentation and nanoparticle formation difficult compared with the long pulse used in the previous reports.² In the case of B/W bilayer, mutual solubility between benzene and water should be considered; however, recombination and dimerization may precede the bimolecular reaction with water in the benzene layer due to the low solubility of water in benzene. Flash photolysis of aqueous benzene results in the formation of aldehyde via benzvalene;⁸ however, the ionization of water should precede such a reaction under filamentation conditions in our experiments.

As the colloidal particles formed even though the laser was focused on the bottom of the water layer, the reactive species that attack benzene to finally form nanoparticles should be generated in the water layer. Chemically reactive species, such as e^-_{aq} , H^\bullet , $\cdot O^\bullet$, and OH^\bullet are generated as a result of the primary reaction in the self-focusing region. The recombination of those radicals and the reaction with dissolved oxygen form H_2 , O_2 , H_2O_2 , and $O_2^\bullet^-$.⁹ We have succeeded in reducing europium ions under degassed conditions in methanol by solvated electrons whenever white light appears.¹⁰ However, the most probable candidates to survive from the bottom of the water layer to the

B/W interface were superoxides (H_2O_2 and $O_2^\bullet^-$), based on the lifetimes of those species under aerated conditions.¹¹ To confirm the contribution of $O_2^\bullet^-$ to nanoparticle formation, the B/W bilayer was deaerated prior to irradiation by bubbling argon through the cuvette. However, the black colloidal particle formation was not affected. On the other hand, bubbling argon prior to and during the laser irradiation resulted in the formation of an immiscible interface without black colloidal particles, and the water layer turned to an emulsion after shaking, as shown in Figure 1d. The generation of O_2 under filamentation conditions has already been published;⁹ hence, $O_2^\bullet^-$ formation may not be affected strongly in a static argon atmosphere. In contrast, bubbling argon during laser irradiation purged generated oxygen, and thus the nanoparticle generation process was inhibited to some extent due to the deficiency of $O_2^\bullet^-$. Supposing that the sequential oxidation process leads benzene to nanoparticles, the initial oxidized products are benzene oxide or phenol followed by further oxidation and aromatic ring cleavage. By the use of GC-MS, we were able to identify the low-molecular-weight products such as phenol, catechol, hydroquinone, biphenyl, phenylphenol, and a variety of oxidized products. Thus, the origin of immiscible species in water would be some insoluble intermediates during the oxidation process. We concluded that the nanoparticle formation is initiated by the oxidative decomposition of benzene, similar to photocatalysis on TiO_2 ¹² as well as to metabolism in plants.¹³ It should be mentioned that superoxides (H_2O_2 and $O_2^\bullet^-$) are relatively weak oxidizers, thus OH^\bullet , which is generated by further reactions between H_2O_2 and $O_2^\bullet^-$, would be an actual oxidizer.

No colloidal particles appeared when cyclohexane or *n*-hexane was used as an organic layer instead of benzene by exposing the water layer to a laser beam. We can conclude that π -conjugated molecules are necessary as a source of nanoparticles. Functionalization may occur in saturated hydrocarbons, but unsaturated chemical bonds should be necessary to recombine and enlarge carbon frameworks leading to nanoparticles. It has been reported that polyyne was incorporated in nanoparticles of amorphous carbon that was generated, aggregated, and precipitated as a soot in benzene.² In contrast, solution in this study was colloidal, thus carbon nanoparticles should be hydrophilic.¹⁴ The hydrophilicity would be due to hydrophilic functional groups on the surface of carbon nanoparticles. Further functionalization of the initially generated nanoparticles soluble in water may occur by the excitation and oxidization with filament in water. Our results indicated that we can synthesize hydrophilicity-controlled nanoparticles by using substituted benzene as a starting material for further applications.

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References

- 1 A. Fojtik, A. Henglein, *Ber. Bunsenges. Phys. Chem.* **1993**, 97, 252; J. Neddersen, G. Chumanov, T. M. Cotton, *Appl. Spectrosc.* **1993**, *47*, 1959; F. Mafuné, J.-y. Kohno, Y. Takeda, T. Kondow, H. Sawabe, *J. Phys. Chem. B* **2000**, *104*,

- 8333.
- 2 M. J. Wesolowski, S. Kuzmin, B. Moores, B. Wales, R. Karimi, A. A. Zaidi, Z. Leonenko, J. H. Sanderson, W. W. Duley, *Carbon* **2011**, *49*, 625.
 - 3 T. Yatsuhashi, Y. Nakahagi, H. Okamoto, N. Nakashima, *J. Phys. Chem. A* **2010**, *114*, 10475.
 - 4 M. Tsuji, T. Tsuji, S. Kuboyama, S.-H. Yoon, Y. Korai, T. Tsujimoto, K. Kubo, A. Mori, I. Mochida, *Chem. Phys. Lett.* **2002**, *355*, 101.
 - 5 S. L. Chin, S. A. Hosseini, W. Liu, Q. Luo, F. Théberge, N. Aközbek, A. Becker, V. P. Kandidov, O. G. Kosareva, H. Schröder, *Can. J. Phys.* **2005**, *83*, 863; A. Couairon, A. Mysyrowicz, *Phys. Rep.* **2007**, *441*, 47; L. Bergé, S. Skupin, R. Nuter, J. Kasparian, J.-P. Wolf, *Rep. Prog. Phys.* **2007**, *70*, 1633.
 - 6 A. Brodeur, S. L. Chin, *J. Opt. Soc. Am. B* **1999**, *16*, 637; A. Brodeur, S. L. Chin, *Phys. Rev. Lett.* **1998**, *80*, 4406.
 - 7 N. Nakashima, M. Sumitani, I. Ohmine, K. Yoshihara, *J. Chem. Phys.* **1980**, *72*, 2226.
 - 8 N. Shimo, N. Nakashima, K. Yoshihara, *Bull. Chem. Soc. Jpn.* **1983**, *56*, 389.
 - 9 S. L. Chin, S. Lagacé, *Appl. Opt.* **1996**, *35*, 907.
 - 10 D. Nishida, E. Yamade, M. Kusaba, T. Yatsuhashi, N. Nakashima, *J. Phys. Chem. A* **2010**, *114*, 5648; D. Nishida, M. Kusaba, T. Yatsuhashi, N. Nakashima, *Chem. Phys. Lett.* **2008**, *465*, 238.
 - 11 D. N. Nikogosyan, A. A. Oraevsky, V. I. Rupasov, *Chem. Phys.* **1983**, *77*, 131.
 - 12 T. D. Bui, A. Kimura, S. Ikeda, M. Matsumura, *Appl. Catal., B* **2010**, *94*, 186.
 - 13 T. Mithaishvili, R. Scalla, D. Ugrelkhelidze, B. Tsereteli, T. Sadunishvili, G. Kvesitadze, *Z. Naturforsch., C* **2005**, *60*, 97.
 - 14 M.-Y. Choi, D.-S. Kim, D. S. Hong, J. H. Kim, Y.-T. Kim, *Chem. Lett.* **2011**, *40*, 768.