Synthesis of higher diamondoids by pulsed laser ablation plasmas in supercritical CO₂

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(Received 17 February 2011; accepted 12 May 2011; published online 24 June 2011)

Pulsed laser ablation (wavelength 532 nm; fluence 18 J/cm²; pulse width 7 ns; repetition rate 10 Hz) of highly oriented pyrolytic graphite was conducted in adamantane-dissolved supercritical CO₂ with and without cyclohexane as a cosolvent. Micro-Raman spectroscopy of the products revealed the presence of hydrocarbons possessing \( sp^2 \)-hybridized carbons similar to diamond structures. The synthesis of diamantane and other possible diamondoids consisting of up to 12 cages was confirmed by gas chromatography–mass spectrometry. Furthermore, gas chromatography–mass spectrometry measurements of samples before and after pyrolysis treatment indicate the synthesis of the most compact decamantane, namely, superadamantane. It is thought that oxidant species originating from CO₂ during pulsed laser ablation might lead to the selective dissociation of C-H bonds, enabling the synthesis of low H/C ratio molecules. Therefore, laser ablation in supercritical CO₂ is proposed as a practical method for synthesizing diamondoids. © 2011 American Institute of Physics. [doi:10.1063/1.3599887]

I. INTRODUCTION

Diamondoids are hydrogen-terminated molecules whose structure consists of \( C(sp^3) - C(sp^3) \) bonds. They can be described as diamond molecules because they can be superimposed on a diamond lattice. In contrast to diamondoids, other well-known carbon nanomaterials, namely fullerences, carbon nanotubes (CNTs), and graphenes, are comprised of \( sp^2 \)-hybridized bonds between carbon atoms; see Fig. I. Diamondoids and their derivatives have elicited considerable interest as possible next-generation nanomaterials for applications in various fields, including pharmaceuticals,1,2 nanotechnology,3 and optoelectronics.4 As for the availability of these molecules, it was reported that diamondoids with a number of cages \( n \) of up to 11 were isolated from crude oil.5 However, the synthesis of diamondoids with \( n \geq 4 \) cages by conventional chemical synthesis has not been pursued further because of the complexity of the thermodynamic rearrangement.6

On the other hand, plasmas generated in supercritical fluids (SCFs) can serve as highly advantageous media to synthesize nonequilibrium materials because of the combination of the high reactivity of the plasma and the superior transport properties of SCFs.7 For example, carbon nanomaterials with \( sp^2 \) bonds, e.g., CNTs, nanohorns, and nano-onions, were synthesized by generating either short pulse direct-current (pulse duration: 400 \( \mu \)s) plasmas or low-temperature dielectric barrier discharges (DBDs), especially in neat supercritical CO₂ (scCO₂; critical temperature \( T_{\text{crit}} = 304.1 \) K, critical pressure \( P_{\text{crit}} = 7.38 \) MPa) without any catalyst.8,9

Notwithstanding the intricacy of synthesizing higher diamondoids consisting of a minimum of four cages, our group10–13 and that of Dahl et al.14 independently reported the synthesis of higher diamondoids using lower diamondoids as precursors. In our previous studies, higher diamondoids consisting of up to 10 cages were synthesized by the generation of plasmas in supercritical Xe (scXe; \( T_{\text{crit}} = 289.7 \) K, \( P_{\text{crit}} = 5.84 \) MPa) with dissolved adamantane \( n = 1 \) as a precursor. DBDs10–12 or pulsed laser ablation (PLA) of highly oriented pyrolytic graphite (HOPG)15 was used to produce a highly dense plasma reaction field in scXe. The key factors for the artificial synthesis of diamondoids were considered to be the high-density and highly nonequilibrium reaction field of the plasmas generated in the SCF media, especially in the vicinity of the critical point, and the use of dissolved adamantane as a precursor.

Concerning the extension of this synthesis process to other applications, however, the prohibitively high cost of Xe, which is about 1000 times more expensive than other SCF media such as Ar and CO₂,15 makes Xe less attractive as a supercritical medium for both science and industry. On the other hand, scCO₂ is one of the most widely used SCFs. It is a promising alternative to conventional organic solvents in the fields of semiconductor and chemical processing and chemical analysis.16,17 Because CO₂ is a readily available, low-cost, and environmentally benign gas at ambient temperature and pressure, replacing Xe with CO₂ as a supercritical medium could enable more research groups to develop methods for synthesizing diamondoids and their derivatives or other nanomaterials using SCFs.

Unfortunately, the as-collected products from plasmas generated in SCFs are expected to be a mixture of hydrocarbons, including many kinds of nondiamondoid materials. As
a result, micro-Raman spectra showed signs of mixed materials. Accordingly, the analysis of the micro-Raman spectra only allowed a confirmation of the presence of diamondoids, but it was not possible to identify individual ones. Moreover, in the gas chromatography–mass spectrometry (GC-MS) analyses, nondiamondoids and other unresolved complex mixtures co-eluting with the diamondoids affected their resolution. On the other hand, in studies of the isolation of diamondoids from petroleum, it was reported that the extremely high thermal stability of diamondoids was used to separate them from nondiamondoids. According to Ref. 5, all higher diamondoids are thermally stable up to a temperature of 723 K, which is high enough to decompose most other non-diamondoid hydrocarbons. In Ref. 5, the authors used different separation techniques (distillation, pyrolysis, column chromatography, and high-performance liquid chromatography, HPLC) to purify and isolate the individual diamondoids. For identifying the separated diamondoids, the authors of Ref. 5 used GC-MS. In addition, HPLC fractions of the separated samples were crystallized and then analyzed by X-ray diffraction (XRD). In another paper, Dahl et al. isolated one type of the 6th diamondoid member, cyclohexamantane, and in addition to GC-MS conducted both XRD and nuclear magnetic resonance spectroscopy on the crystallized sample.

The aim of this study was to synthesize diamondoids by generating plasmas in scCO₂ instead of scXe. PLA was the chosen method to generate the plasma because of the following advantages with respect to DBDs: (i) Easier plasma generation, regardless of the supercritical medium, which allows for more variation of parameters such as temperature, pressure, and supercritical medium; (ii) higher reproducibility of the process, its control, and the monitoring of the pulsed laser, i.e., fluence, pulse width, and repetition rate; and (iii) reduced contamination because of the electrode-free setup. Accordingly, PLA of highly oriented pyrolytic graphite (HOPG) was conducted in scCO₂, including dissolved adamantane. Cyclohexane, which dissolves adamantane easily, was also used in some experiments as a cosolvent of scCO₂ to improve the solubility of adamantane. Moreover, thermal treatment (pyrolysis) was conducted on the collected samples to increase the concentration of the diamondoid fraction. Due to the small quantities of synthesized materials, the samples were analyzed by GC-MS and micro-Raman spectroscopy.

II. EXPERIMENTAL PROCEDURE

Figure 2 shows a schematic of the experimental setup. The HOPG (mosaic spread 3.5–5°; NT-MDT Co.) target was placed in a batch-type high-pressure cell (inner volume: 3 cm³; Taiatsu Techno Co.). Adamantane (purity > 99.0%; Tokyo Chemical Industry) was dissolved in scCO₂ with and without cyclohexane as a cosolvent; see the experimental conditions listed in Table I. The temperature and the pressure in the inner cell were monitored by a thermocouple and pressure sensor, respectively. The outer cell temperature was controlled by a thermostat. The high density of CO₂ was realized by condensation of the CO₂ gas (purity > 99.995%; Japan Fine Products) in a liquefaction loop cooled by liquid nitrogen before introducing it into the inner cell. A second-harmonic neodymium-doped yttrium aluminum garnet (Nd:YAG) laser (λ = 532 nm; Spectra-Physics, Quanta-Ray Lab-150) was used for the ablation of the HOPG targets in both scXe (Ref. 13) and scCO₂. The maximum energy was 7 mJ per pulse, giving a maximum fluence of approximately 18 J/cm² on the surface of the HOPG target. The pulse width was 7 ns, with a repetition rate of 10 Hz. The ablation experiments were conducted for periods of 60 min. The synthesized products were retrieved by evacuating the gas through a collection trap containing 10 ml of cyclohexane. In addition, the cyclohexane solutions used for cleansing the cell...
were also collected. The HOPG target was dipped in the collection trap and sonicated. The concentration of the products was then increased by partial evaporation of the collected organic solvents.

A schematic of the experimental setup for the pyrolysis experiments is shown in Fig. 3. A small amount (0.5 ml) of the sample solution was dropped into the high-temperature high-pressure batch-type cell (Taiatsu Techno Co., inner volume: 11 cm³; maximum temperature: 723 K; maximum pressure: 40 MPa). The temperature was monitored and controlled by a microring heater, a proportional-integral-derivative controller (Chino, LT370), and thermocouples placed inside and between the cell, respectively. To remove cyclohexane, the solution was first heated up to 348 K and then increased by partial evaporation of the collected or-

TABLE I. Experimental conditions for the pulsed laser ablation in scCO₂ with and without cyclohexane.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>scCO₂</th>
<th>scCO₂ with cyclohexane</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adamantane concentration (mol/l)</td>
<td>(1.2–12) × 10⁻²</td>
<td>(3.1–6.2) × 10⁻²</td>
</tr>
<tr>
<td>Cyclohexane concentration (mol/l)</td>
<td>-</td>
<td>7.7 × 10⁻¹</td>
</tr>
<tr>
<td>Temperature T (K)</td>
<td>304.5–305.2</td>
<td>304.5–304.8</td>
</tr>
<tr>
<td>Reduced temperature (T/T_{crit})</td>
<td>1.001–1.004</td>
<td>1.001–1.002</td>
</tr>
<tr>
<td>Pressure P (MPa)</td>
<td>7.42–7.59</td>
<td>7.54–7.56</td>
</tr>
<tr>
<td>Reduced pressure (P/P_{ox})</td>
<td>1.005–1.028</td>
<td>1.022–1.024</td>
</tr>
</tbody>
</table>

spectroscopy were prepared by spotting small volumes (~0.1 ml) of the suspensions on aluminum substrates. Micro-Raman spectroscopy was performed using a second-harmonic Nd:YAG laser (λ = 532 nm) with an excitation power of 1–2 mW and a spatial resolution of around 1 μm. Spectra were measured using an acquisition time of 1 min. For the GC-MS measurements, the GC was setup in splitless sample injection mode. The GC capillary column was a 15 m (inner diameter 0.25 mm) Durabond DB-1HT (J & W Scientific, Agilent Technologies) with a 100% dimethylpolysiloxane stationary phase (film thickness 0.10 μm). Helium served as carrier gas at a flow rate of 1.46 ml/min (constant flow mode). The GC oven had an initial hold time of 3 min at 323 K, followed by a linear temperature ramp at 20 K/min to 633 K and a final hold time of 15 min. Consequently, the total retention time monitored was 33.5 min. The MS measurements were conducted by electron-impact mass spectrometry at 70 eV, both in selected ion monitoring (SIM) mode and scan mode on the products dissolved in 1 μL of cyclohexane. In SIM mode, the dwell time was 360 ms. SIM ions included combinations of mass-to-charge ratio (m/z) varying from 188 to 590 that correspond to diamondoids with cage numbers varying between n = 2 and 12. Mass scans were acquired over an m/z range from 40 to 1000 at 1.79 scans/s.

![FIG. 3. Experimental setup for pyrolysis treatment of the samples.](Image)

III. RESULTS AND DISCUSSION

A. Micro-Raman spectroscopy

The characteristics of the Raman spectra of diamondoids can be summarized by dividing them into the following three regions: (i) Strong peaks in the low-energy region below 500 cm⁻¹, due to vibrational modes of the CCC structure such as CCC bend and deformation modes; (ii) well-resolved peaks in the range 1000–1500 cm⁻¹ due to CH twist and wagging modes; and (iii) strong and broad peaks in the high-energy region. For the high-energy region, it is reported that the stretching mode of sp²-bonded CH₃ shows peaks in the region of 2800–2950 cm⁻¹, while sp³-bonded CH₃ shows peaks in the region of 2890–3060 cm⁻¹. Comparing the measured spectrum with these characteristics might help to identify the synthesized products, even though these characteristics are common in not only diamondoids but also other hydrocarbons such as paraffin.

In Fig. 4, the Raman spectra of the products obtained by PLA in scCO₂ with and without cyclohexane as a cosolvent (both before and after pyrolysis) are presented together with the Raman spectrum of the material obtained in our previous work using PLA in scXe. For illustrating the effect of increasing cage numbers on the Raman spectra, in Figs. 4(f) and 4(g) the spectra of commercial adamantane and [12312] hexamantane are shown. The Raman spectra of the products obtained by PLA in scCO₂, regardless of the presence of cyclohexane, presented almost the same features that are known to be characteristic of Raman spectra of diamondoids, i.e., well-resolved peaks in the range 1000–1500 cm⁻¹ and strong peaks in the high-energy region, 2800–2950 cm⁻¹. On the other hand, the peaks in
the measured Raman spectra are supposed to originate from a mixture of different hydrocarbons. Moreover, it is known that the Raman-scattering signal varies largely for each material, e.g., sp\(^2\)-hybridized carbon shows a much stronger Raman signal compared to that of sp\(^3\)-hybridized carbon.\(^{24,26}\) Therefore, it is possible that the peaks from synthesized diamondoids and those from other hydrocarbons such as paraffin and aromatics get balanced out, which could explain the lack of strong peaks in the low-energy region below 500 cm\(^{-1}\). The features in the wavenumber region between 1000–1500 cm\(^{-1}\) and the peaks ranging between 2800–2950 cm\(^{-1}\), which are characteristic of sp\(^3\) CH\(_x\) stretching modes,\(^{24}\) indicate the presence of diamond-structured hydrocarbons in the synthesized products. The existence of diamond-structured hydrocarbons in the synthesized products was also indicated for PLA in scCO\(_2\), both with and without cyclohexane.

In all the Raman spectra of the synthesized materials, no indication of the precursor adamantane could be found. This is attributed to the fact that adamantane sublimes even at room temperature and that for increasing the concentration of the samples, the solutions collected after PLA were evaporated. Interestingly, the Raman spectra collected from the products obtained by PLA in scCO\(_2\) with and without cyclohexane showed similar characteristics. Thus, even when cyclohexane was added as a cosolvent, the synthesized materials, which possess relatively high Raman-scattering cross sections, seemed to be almost identical for the products obtained by PLA in neat scCO\(_2\). Smaller differences that are found in the Raman spectra for the samples obtained in scCO\(_2\) with cyclohexane as a cosolvent are attributed to the possible synthesis of additional species, which could be formed by the dissociation of cyclohexane. In contrast, the differences between the products obtained by PLA in scCO\(_2\) and scXe (Ref. 13) were bigger. For example, the strongest intensities in the low-energy region (300–1500 cm\(^{-1}\)) appeared around 1440 cm\(^{-1}\) for PLA in scCO\(_2\) with and without cyclohexane, while the most intense Raman peaks appeared around 1050 cm\(^{-1}\) for PLA in scXe. Moreover, the shapes of the strong peaks in the high-energy region (2800–3000 cm\(^{-1}\)) vary considerably. These dissimilarities indicate that the synthesized materials were different for PLA in scCO\(_2\) and scXe. The effects of pyrolysis for the samples obtained by PLA in scCO\(_2\) and in scCO\(_2\)/cyclohexane are shown in Figs. 4(a) and 4(b) and 4(c) and 4(d), respectively. Compared to the spectra before pyrolysis, the biggest difference can be observed in the high-wavenumber region between 2980 and 3000 cm\(^{-1}\). The intensity of the peaks that are attributed to sp\(^2\) CH\(_x\) stretching modes\(^{24}\) was lower after pyrolysis. In addition, the peaks in the high-wavenumber region become better resolved. From this we conclude that pyrolysis permitted a reduction of the number of non-diamondoid hydrocarbons. However, we assume non-diamondoid hydrocarbons to persist in the samples even after pyrolysis and that more separation steps are necessary to separate diamondoids from non-diamondoids.

FIG. 4. (Color online) Micro-Raman spectra of synthesized products obtained by PLA (a) in scCO\(_2\) before pyrolysis and (b) after pyrolysis; (c) in scCO\(_2\) with cyclohexane before pyrolysis, and (d) after pyrolysis, (e) in scXe before pyrolysis,\(^{13}\) For illustrating the effect of increasing cage number, the Raman spectra of (f) commercial adamantane and (g) [12312] hexamantane (taken from Ref. 22) are also included as examples.

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FIG. 5. (Color online) GC-MS mass spectra at \(t = 7.3\) min: (a) the synthesized product obtained in neat scCO\(_2\), (b) scCO\(_2\) with cyclohexane, and (c) diamantane of the standard sample, with the inset showing the structure of diamantane.
B. Gas chromatography–mass spectrometry

1. Synthesis of diamantane

The retention times for \( m/z \) 136 and \( m/z \) 188, which correspond to the molecular weights (MWs) of adamantane and diamantane (\( n = 2 \)), respectively, were compared for products obtained by PLA in scCO\(_2\) with and without cyclohexane, and the standard solution with dissolved commercial adamantane and diamantane (\( n = 2 \)). The standard solution was prepared by dissolving both commercially available adamantane and diamantane (purity > 98.0%; Tokyo Chemical Industry) in cyclohexane, each with a concentration of 5.0 mg/l. The comparison revealed the same time lag, 3.5 min, for all experimental conditions. Moreover, the mass spectra of the GC-MS measurements at the retention times of SIM for \( m/z \) 188 for both products from PLA in scCO\(_2\) with and without cyclohexane presented almost the same fragments as those of the standard diamantane; see Fig. 5. Hence, it was concluded that diamantane had been synthesized.

A calibration curve was applied to estimate the production rate of diamantane. Cyclohexane solutions with diamantane concentrations of 0.0, 1.0, 2.0, 4.0, and 10.0 mg/l were prepared. Figure 6 shows the comparison of the SIM peak areas as a function of the concentration of diamantane. By comparing the SIM peak areas of the synthesized products, the production rate of diamantane was estimated to be 0.2 \( \mu \)g/h for PLA in scCO\(_2\) both with and without cyclohexane; see Table II.

2. Possible synthesis of diamondoids with \( n \geq 3 \)

SIM curves and mass spectra indicated the possible synthesis of diamondoids consisting of three or more cages by PLA in scCO\(_2\). At first, however, only triamantane (\( n = 3 \)) was observed in addition to diamantane for PLA in pure scCO\(_2\). We suggest that this might be due to the poor solubility of adamantane in scCO\(_2\). To improve the signal-to-noise ratio in the GC-MS measurements, the sample solution was enriched by using a smaller amount of solvent (20 l of cyclohexane instead of 1 ml). As a result, more peaks were observed that could be attributed to diamondoids consisting of up to 12 cages. The cage numbers of eluted diamondoids obtained by PLA in scCO\(_2\) with and without cyclohexane as a function of the experimentally determined GC-MS retention times are listed in Tables III and IV, and Fig. 7, respectively. The relative retention times were calculated by dividing the individual retention times by the retention time of diamantane in the range 7.148–7.157 min.

We assigned the GC-MS signals to the following diamondoids: triamantane at \( m/z \) 240, tetramantane at \( m/z \) 292, hexamantanes at \( m/z \) 342, 382, and 396, heptamantane at \( m/z \) 394, octamantane at \( m/z \) 446, decamantanes at \( m/z \) 456 (\( C_{45}H_{46} \)) and 590, and dodecamantane at \( m/z \) 586. In principle, the GC-MS retention time increases with the number of cages, which is in agreement with previous work. Further- more, the relative retention times of the diamondoids obtained by PLA in scCO\(_2\) both with and without cyclohexane showed good agreement: triamantane (1.188–1.189); tetramantane (1.509–1.510); hexamantanes (1.986–1.987 for a dual graph code); and dodecamantane (2.495–2.496).

### Table II. SIM peak area and estimated diamantane concentration of the product obtained by PLA in scCO\(_2\).

<table>
<thead>
<tr>
<th>Supercritical medium for PLA</th>
<th>Solution for GC-MS analyses</th>
<th>SIM peak area (a. u.)</th>
<th>Diamantane concentration (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>scCO(_2)</td>
<td>Sample contained 1 ml cyclohexane</td>
<td>2100</td>
<td>0.23</td>
</tr>
<tr>
<td>scCO(_2) with cyclohexane</td>
<td>Sample contained 1 ml cyclohexane</td>
<td>1900</td>
<td>0.21</td>
</tr>
</tbody>
</table>

### Table III. List of possibly synthesized diamondoids by PLA in scCO\(_2\), with their molecular formulae, MWs, GC-MS relative retention times, and dual graph codes.

<table>
<thead>
<tr>
<th>Cage number (( n ))</th>
<th>Molecular formula</th>
<th>( M^+ ) (( m/z )) base peak</th>
<th>GC-MS relative retention time</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>( C_{14}H_{20} )</td>
<td>188</td>
<td>1.000</td>
<td>Diamantane</td>
</tr>
<tr>
<td>3</td>
<td>( C_{16}H_{24} )</td>
<td>240</td>
<td>1.189</td>
<td>Triamantane</td>
</tr>
<tr>
<td>4</td>
<td>( C_{18}H_{28} )</td>
<td>292</td>
<td>1.509</td>
<td>e.g., [121]</td>
</tr>
<tr>
<td>6</td>
<td>( C_{22}H_{34} )</td>
<td>382</td>
<td>1.986</td>
<td>e.g., [12(1)31]</td>
</tr>
<tr>
<td>7</td>
<td>( C_{26}H_{36} )</td>
<td>396</td>
<td>2.038</td>
<td>e.g., [12121]</td>
</tr>
<tr>
<td>10</td>
<td>( C_{35}H_{36} )</td>
<td>394</td>
<td>1.843</td>
<td>e.g., [123121]</td>
</tr>
<tr>
<td>12</td>
<td>( C_{45}H_{46} )</td>
<td>586</td>
<td>2.495</td>
<td>e.g., [1213431234]</td>
</tr>
</tbody>
</table>
MW of 382 and 2.038–2.039 for a MW of 396); and dodecama-
tanate (2.493–2.495). In addition, some of the observed
diamondoids, corresponding to MWs of 382, 586, and 590,
were not found in previous works in which the diamondoids
were isolated from petroleum.\(^5\) These molecules were
detected at high GC temperature, higher than the maximum
GC temperature used by another group (593 K). For exam-
ple, molecular ion peaks corresponding to a MW of 586
appeared when the GC oven temperature was raised to
620 K.

In GC-MS measurements, each diamondoid is expected
to elute at a distinct retention time. In contrast, for higher
diamondoids, there are MW groups that have many structural
isomers. For example, MW 292 (tetramantane) has 4 possi-
bile isomers and MW 396 (hexamantane) has 28. Therefore,
in the GC-MS measurements, diamond molecules corre-
sponding to the same MW group but possessing different
structures are expected to elute at different retention times.
However, each MW group of diamondoid had only one or a
few points per analysis in this study, even for those with a
large number of possible structural isomers. Considering the
relatively fast heating rate of GC-MS (20 K/min) and the
slow scan rate at 1.79 scans/s compared to those of other
groups (10 K/min and 2.94 scans/s),\(^5\) the resolution of the
GC-MS analyses was about 30% of the other groups’ analy-
yses. Therefore, it is expected that different isomers could
appear at the same scan times, even if they elute at different
times. Slower heating rates or faster scan rates will be used
in future studies to improve the resolution of GC-MS
analyses.

Figure 8 shows an example of mass spectra correspond-
ing to a MW of 456. The diamondoid corresponding to
MW 456 is the most compact decamantane \((n = 10),\)
\([1231241(2)]\) decamantane, which is also known as supera-
damantane. The spectrum shows a typical feature of unsub-
stituted higher diamondoids, i.e., a strong molecular ion peak
\(M^+\) at \(m/z\) 456 with a few fragment ions including the \(M^+/2\)
peak at \(m/z\) ~228, which corresponds to the doubly charged
molecular ion. Strong peaks at low \(m/z\) in Fig. 8 are supposed
to be due either to other hydrocarbon molecules such as par-
affin and aromatics that co-elute at the same retention time,
or to other materials that originated from the GC column
and the septum that appear in the entire GC-MS analysis.

The results of the GC-MS analyses can be summarized
as follows: (i) There were many possible diamondoids syn-
thesized, and their GC-MS retention times generally increase
with the number of cages; (ii) some of the synthesized dia-
mondoids have not been reported before, which might be

![Figure 7](https://example.com/figure7.png)

**FIG. 7.** (Color online) Number of cages in diamondoids obtained by scCO\(_2\) with and without cyclohexane plotted as a function of the GC-MS relative
retention time, taking the retention time of diamantane as a standard.

![Figure 8](https://example.com/figure8.png)

**FIG. 8.** GC-MS mass spectra of possible superadamantane (MW 456)
obtained by PLA in scCO\(_2\). The inset shows the molecular structure.

<table>
<thead>
<tr>
<th>Cage number ((n))</th>
<th>Molecular formula</th>
<th>(M^+) ((m/z)) base peak</th>
<th>GC-MS relative retention time</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>(C_{14}H_{20})</td>
<td>188</td>
<td>1.000</td>
<td>Diamantane</td>
</tr>
<tr>
<td>3</td>
<td>(C_{18}H_{24})</td>
<td>240</td>
<td>1.188</td>
<td>Triamantane</td>
</tr>
<tr>
<td>4</td>
<td>(C_{22}H_{28})</td>
<td>292</td>
<td>1.510</td>
<td>e.g., [121]</td>
</tr>
<tr>
<td>6</td>
<td>(C_{26}H_{30})</td>
<td>342</td>
<td>1.627</td>
<td>[12312]</td>
</tr>
<tr>
<td></td>
<td>(C_{26}H_{30})</td>
<td>382</td>
<td>1.987</td>
<td>e.g., [12131]</td>
</tr>
<tr>
<td></td>
<td>(C_{30}H_{36})</td>
<td>396</td>
<td>2.039</td>
<td>e.g., [12121]</td>
</tr>
<tr>
<td>8</td>
<td>(C_{34}H_{40})</td>
<td>446</td>
<td>2.156</td>
<td>e.g., [121312]</td>
</tr>
<tr>
<td>10</td>
<td>(C_{45}H_{46})</td>
<td>590</td>
<td>2.423</td>
<td>e.g., [1233123]</td>
</tr>
<tr>
<td>12</td>
<td>(C_{58}H_{50})</td>
<td>586</td>
<td>2.493</td>
<td>e.g., [1213143123]</td>
</tr>
</tbody>
</table>
due to the high GC oven temperature of up to 633 K; (iii) all MW groups of diamondoids had only one or a few points per analysis, which could be explained by the lower scanning resolution of the GC-MS analyses; and (iv) the mass spectra showed features that were similar to those of previously reported diamondoids with high MW, i.e., a large molecular ion peak and a small number of fragment peaks.

C. Effects of pyrolysis on the synthesized products

The mass spectra acquired after the pyrolysis experiments and corresponding to possible higher diamondoids are listed in Tables V and VI. The observed peaks were different before and after pyrolysis. However, the molecular ion peak with a MW of 456 was observed both before and after pyrolysis. Moreover, the relative retention times of GC-MS were very close to one another. This result suggests that the synthesized products with a MW of 456 survived after pyrolysis. It is expected that nondiamondoid hydrocarbons of high MW will decompose after thermal treatment at 723 K. Therefore, the present results suggest that the peak corresponding to a MW of 456 originated from superadamantane.

Many MW groups of diamondoids, such as those with \( n = 5 \) and 7 cages, were not found before pyrolysis, although they were found after the pyrolysis experiments; see Fig. 9. In scCO\(_2\), species originating from the decomposition of CO\(_2\) could possibly participate in the formation of new materials. Assuming those materials were nondiamondoid hydrocarbons and were decomposed after pyrolysis, this might explain why the observed GC-MS spectra contained peaks corresponding to diamondoids with 5 and 7 cages only after pyrolysis.

D. Comparison between PLA in scCO\(_2\) and scXe

There are MW groups that were only synthesized in scXe and not in scCO\(_2\). Moreover, the production rate of diamantane by PLA in scCO\(_2\) was 0.2 \( \text{µg/h} \), which is lower than that of PLA in scXe. This could be attributed to the lower solubility of adamantane in scCO\(_2\) compared with that of scXe. The production rate of diamantane is approximately the same in neat scCO\(_2\) and in the scCO\(_2\)/cyclohexane mixture. Therefore, while the solubility of adamantane in scCO\(_2\) can be enhanced using cyclohexane as a co-solvent, this is probably not the only factor for increasing the production rate. In the case of scXe, the molecules of the medium do not participate in the reaction, whereas in the case of scCO\(_2\), CO\(_2\) itself can also dissociate and form reaction products. Consequently it is suspected that the lower reaction yield of diamantane in scCO\(_2\) is due to both the lower solubility of adamantane and competing reactions resulting in the formation of non-diamondoids.

In contrast, the mass spectrum showing a MW of 456 was only obtained by PLA in pure scCO\(_2\). C-C and C-H bonds must be dissociated to allow the formation of successive diamondoids from adamantane. In the previous work where diamondoids were synthesized by DBD in scXe, it was suggested that the absence of oxidants resulted in a preferential dissociation of C-C bonds and led to the synthesis of diamondoids with a high H/C ratio. On the contrary, the products from PLA in scCO\(_2\) include relatively low H/C ratio diamondoids compared with those in scXe. It is supposed that oxidant species originating from scCO\(_2\) might lead to selective dissociation of C-H bonds, enabling the synthesis of low H/C ratio diamondoids, such as superadamantane.

IV. CONCLUSION

PLA was performed in scCO\(_2\) with and without cyclohexane as a cosolvent. Raman spectra of the synthesized

<p>| TABLE V. List of observed higher diamondoids for PLA in scCO(_2) after pyrolysis. |
|---------------------------------|------------------|-----------------|------------------|</p>
<table>
<thead>
<tr>
<th>Cage number ((n))</th>
<th>Molecular formula</th>
<th>( M^+ ) (m/z) base peak</th>
<th>GC-MS relative retention time</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>( C_2H_{25} )</td>
<td>330</td>
<td>1.70–2.25</td>
</tr>
<tr>
<td>5</td>
<td>( C_2H_{25} )</td>
<td>344</td>
<td>2.30–2.31</td>
</tr>
<tr>
<td>7</td>
<td>( C_6H_{34} )</td>
<td>394</td>
<td>2.02</td>
</tr>
<tr>
<td>7</td>
<td>( C_7H_{36} )</td>
<td>448</td>
<td>2.45</td>
</tr>
<tr>
<td>9</td>
<td>( C_8H_{40} )</td>
<td>444</td>
<td>1.66</td>
</tr>
<tr>
<td>9</td>
<td>( C_9H_{40} )</td>
<td>484</td>
<td>2.20</td>
</tr>
<tr>
<td>10</td>
<td>( C_{10}H_{36} )</td>
<td>456</td>
<td>2.12–2.13</td>
</tr>
<tr>
<td>10</td>
<td>( C_{10}H_{48} )</td>
<td>576</td>
<td>2.57</td>
</tr>
</tbody>
</table>

<p>| TABLE VI. List of observed higher diamondoids for PLA in scCO(_2) with cyclohexane after pyrolysis. |
|---------------------------------|------------------|------------------|------------------|</p>
<table>
<thead>
<tr>
<th>Cage number ((n))</th>
<th>Molecular formula</th>
<th>( M^+ ) (m/z) base peak</th>
<th>GC-MS relative retention time</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>( C_2H_{28} )</td>
<td>292</td>
<td>1.34</td>
</tr>
<tr>
<td>5</td>
<td>( C_2H_{32} )</td>
<td>344</td>
<td>1.83</td>
</tr>
<tr>
<td>6</td>
<td>( C_6H_{36} )</td>
<td>396</td>
<td>1.67</td>
</tr>
<tr>
<td>7</td>
<td>( C_7H_{36} )</td>
<td>420</td>
<td>2.01</td>
</tr>
<tr>
<td>7</td>
<td>( C_7H_{40} )</td>
<td>448</td>
<td>2.45</td>
</tr>
</tbody>
</table>

FIG. 9. GC-MS mass spectra of possible diamondoids after pyrolysis: MW 448 (heptamantane, \( C_{34}H_{40} \)) obtained by PLA in scCO\(_2\) with cyclohexane. The inset shows \([121212]\) heptamantane, which is one of the possible isomers possessing MW of 448.
products indicated the presence of $sp^3$-hybridized materials, including diamondoids. From GC-MS measurements, this indicates the synthesis of diamantane and possibly other, higher-order diamondoids, including those with a number of cages larger than that reported so far ($n = 10$) and superadamantane ($n = 10$). Because oxidant species originating from scCO$_2$ might lead to the selective dissociation of C-H bonds, synthesis of low H/C ratio higher-order diamondoids, such as superadamantane, could be realized. Moreover, there were more newly found higher-order diamondoids with $n = 5$–10 for PLA in scCO$_2$. It is expected that the fraction of non-diamondoid hydrocarbons might be effectively removed by pyrolysis. Therefore, PLA in scCO$_2$ is considered to be a promising approach for the facile synthesis of higher-order diamondoids.

**ACKNOWLEDGMENTS**

This work was supported financially in part by a Grant-in-Aid for Scientific Research on Innovative Areas (Frontier Science of Interactions between Plasmas and Nano-interfaces, Grant No. 21110002) from the Ministry of Education, Culture, Sports, Science, and Technology of Japan. The authors thank the Materials Design and Characterization Laboratory, Institute for Solid State Physics, University of Tokyo for providing access to the pulsed laser facility, and Professor M. Suzuki for assistance with the GC-MS measurements and helpful discussions.