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## Communications

### Laser-Induced Intracluster Reactions of Oxygen-Containing Nanodiamonds

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The synthesis of nanometer-sized diamond clusters by shock wave compression using explosive compounds such as TNT and RDX is a well-established technique.<sup>1</sup> With proper explosive mixture ratios, the shock wave can produce nanodiamonds with a remarkably narrow particle size distribution of  $5 \pm 1$  nm in diameter.<sup>2</sup> Recent experiments<sup>3</sup> demonstrated that such synthesized nanodiamonds can be readily converted to carbon onions at 1800 K, as diamond-to-graphite phase transformation initiates on {111}-faceted surfaces. While these novel materials are potentially useful in nanotechnology, elemental analysis showed that the detonation-synthesized diamonds contain only 87% C. The rest of the components are 10% O, 2% N, and 1% H, nearly randomly distributed in the crystal lattices.<sup>4</sup> It is conceivable that the presence of these elements as defects can substantially change the rigidity and reactivity of the nanocrystals in their purest forms. Here

we report the unusual photochemical behaviors of the detonation-synthesized diamonds as they are subjected to intense pulsed Nd:YAG laser excitation at 1064 nm and its harmonics via multiphoton absorption.

The diamond nanocrystals, obtained from Toron, were synthesized from TNT/RDX (50/50) mixtures in a detonation chamber.<sup>5</sup> After being thoroughly cleaned using concentrated and oxidative acids,<sup>4</sup> the sample was grayish and contained less than 2% graphitic carbon, as determined by Raman spectroscopy employing an Ar<sup>+</sup> laser.<sup>6</sup> Elemental analysis showed a sample composition essentially identical to that reported in the literature.<sup>4</sup> The high density of defects (10% O) is also indirectly confirmed by X-ray diffraction<sup>4</sup> and optical absorptivity<sup>7</sup> measurements, which revealed marked heterogeneous band broadening and considerable sub-band-gap light absorption. Upon thermal annealing, the sample yielded large quantities of CO and CO<sub>2</sub>, which were identified using a quadrupole mass spectrometer in an ultrahigh vacuum (UHV) chamber with a typical base pressure of  $5 \times 10^{-8}$  Torr. Figure 1 illustrates a temperature-programmed desorption (TPD) spectrum of CO as the sample was resistively heated in a tantalum tube up to 1800 K. The spectrum exhibits two well-separated peaks at 950 and 1380 K, indicating two structurally unique sites for oxygen. In accord with previous studies on graphite<sup>8</sup> and diamond<sup>9</sup> surfaces, they are identified as CO originating from the surface- and lattice-bonded O, respectively. The identification

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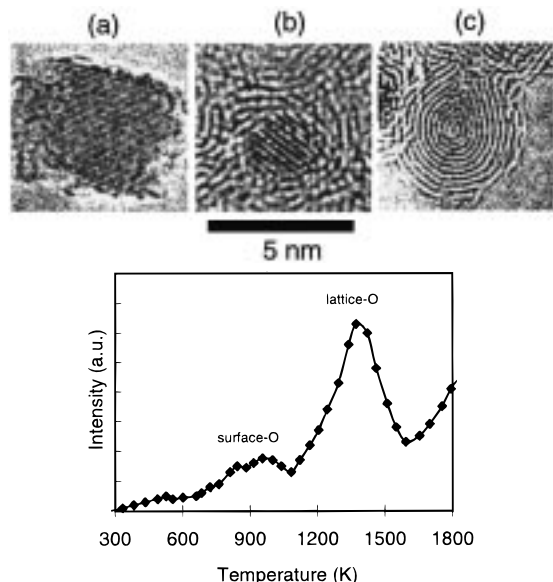
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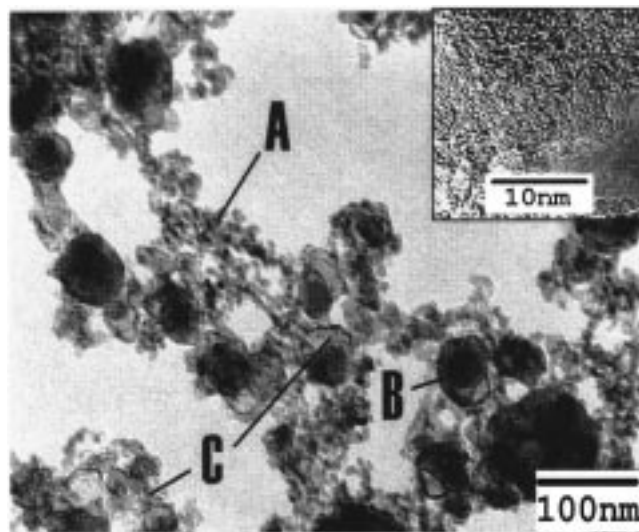


**Figure 1.** Typical temperature-programmed desorption diagram of CO emanating from O-containing nanodiamonds. The applied constant heating rate was 0.7 K/s. The appended HREM images are those of nanodiamonds (a) and nanodiamonds which were annealed at 1800 K for 4 h to obtain graphite-shelled nanodiamonds (b) and carbon onions (c). The fringes in panel a are spaced by 0.205 nm due to the (111) planes of the nanodiamonds, but are spaced by 0.335 nm in panel c due to the graphitic layers of carbon onions.

is corroborated by the band area comparison, which suggests an intensity ratio of roughly 1:4 between the low- and high-temperature features.<sup>10</sup> At 1800 K, the nanodiamonds readily transform to onion-like carbon after 4 h of thorough annealing.<sup>3</sup>

Figure 1 also displays the corresponding images of the diamond and carbon onion nanoclusters taken by a 400-kV high-resolution electron microscope (HREM) at different annealing stages. The intermediate states with multiple graphitic shells formed on diamonds can be clearly observed after desorbing interior oxygen atoms at 1800 K.<sup>3</sup> The observation of the graphitic shell formation excellently agrees with recent molecular dynamics simulations<sup>11</sup> which predict that diamond-to-graphite phase transition begins at surfaces. It should be emphasized that carbon onions, typically formed by annealing soot at 2500–2700 K via thermal heating or electron beam irradiation,<sup>12</sup> can be synthesized at a much lower temperature (1800 K) here by thermally annealing the detonation-synthesized diamonds.<sup>3</sup> Figure 1 features this event and demonstrates that this synthesis is possible, predominantly, due to facile desorption of gaseous carbon oxides.<sup>13</sup>

When exposed to unfocused Nd:YAG laser photons (400 mJ at 1064 or 532 nm in an 8-ns pulse) with a typical power density of  $1 \times 10^8$  W/cm<sup>2</sup>, the oxygenen-



**Figure 2.** Transmission electron micrograph of O-containing nanodiamonds after exposure to 1064 nm photons with a power density of  $1 \times 10^8$  W/cm<sup>2</sup> at 10 Hz for 10 min. The images indicated are those of diamond residues (A), coalesced carbon nanospheres (B), and amorphous carbon ribbons (C). Inset: HREM images of the photofragments.

containing nanodiamonds decomposed violently. The crystals immediately blackened and graphitized, which can be vividly visualized as the sample was irradiated in a sealed, evacuated quartz tube. Close examination upon irradiation at 532 nm indicates that the sample fluffed with an apparent volume increase by almost 3-fold in 60 s of exposure. The dramatic volume expansion is accompanied by abrupt gas evolution. In situ mass spectrometric measurements under UHV identified the evolved gas to be mainly CO and CO<sub>2</sub>. The gas evolution can occur on a single-shot basis, strongly suggesting that the nanoclusters burst as in photofragmentation of polyatomic molecules.<sup>14</sup> It is interesting to notice that the surface-O-desorbed, graphitic-C-covered nanodiamonds also burst, although the reaction occurs more mildly than the original samples. This bursting, initiated primarily by laser-induced decomposition of O-containing diamond cores, resembles corn popping.

In analyzing the photofragments by HREM and electron diffraction, we found that structures of the laser-irradiated nanodiamonds are nearly completely shattered in 10-min exposure (Figure 2). While the structures of the carbon fragments are fairly irregular, some similarities between them and those of distorted graphitic onions and platelets<sup>15</sup> can be discerned. In Figure 2, we denote specifically the large spheroidal carbon clusters (B) that are shaped like cotton balls with diameters of more than 50 nm. These are newly formed via C–C recombination, fragment coalescence, and thermal annealing in the high-temperature laser plasmas.<sup>16</sup> The generation of these spheroidal particles with

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large internal voids adequately accounts for the sample fluffing observed macroscopically. As an important contrast to the nanodiamonds, the thoroughly annealed onion-like carbon clusters [Figure 1(c)] are rather inert to the laser treatment with their particle sizes virtually unchanged in 30-min exposure.

The laser-induced intracluster reactions should be closely associated with the content of O in the nanodiamonds, since the O-depleted carbon onions show little volume expansion. To further elucidate this point, we repeated the same experiment on diamond nanocrystals (100 nm in size) fabricated by standard high-temperature and high-pressure methods<sup>17</sup> but found no significant volume expansion and gas evolution. Reference experimentation on pure carbon black and graphite powders also gave negative results. We argue that the violent decomposition observed for the O-containing diamonds should be triggered by multiphoton excitations of interstitial carbonyl, ether, peroxide, or other  $\pi$ -bonded lattice defects by the laser photons. The excitation is not expected to drive  $sp^3$ -carbon electronic transitions,<sup>18</sup> since diamond is a wide band gap material with  $E_g = 5.4$  eV.<sup>19</sup> Among the many possible forms of carbon-oxygen bonding, the most likely candidate is  $-C-O-C-$ , as O is directly embedded in the diamond lattice. In the gas phase, the typical energy required to break the ether bond of alkyl ethers is about 80 kcal/mol.<sup>20</sup> Assuming a comparable bonding energy of 80 kcal/mol for  $-C-O-$  in the lattice, one expects these bonds to be easily ruptured by 1064- or 532-nm laser photons via multiphoton excitation.<sup>21</sup> Conceivably,

(17) The diamond powders were obtained from Kay Industrial Diamond.

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subsequent radical recombination and further photon absorption can supply sufficient energy for CO and CO<sub>2</sub> desorption via explosive decomposition or rapid thermal annealing.

The present observations correlate with the recent demonstration<sup>22</sup> that diamond nucleation can be induced in the cores of carbon onions by intense electron irradiation. The prevailing pressure inside the carbon onions, while heating the sample to 1000 K, can be so high that the onions in effect act as a nanoscopic pressure cell for diamond formation. Our experiment concerning the graphite-shelled nanodiamonds is particularly relevant to that work since the annealing intermediates have closed shells with diamond cores as well. With these intriguing materials, one can explore the dependence of the photofragmentation process on excitation wavelength, energy, cluster size, and oxygen content. Additionally, how the shape, structure, and geometry of the photofragments vary with external pressures can be analyzed. One attractive feature of the nanodiamonds is that they can be rapidly and violently decomposed by lasers but not by heat. Their potential use could be found in engineering and biomedical applications where micromachinery and microsurgery are becoming more important.<sup>23</sup>

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