DIAMONDOID SYNTHESIS BY PULSED LASER MICROPLASMAS IN SUPERCRITICAL CARBON DIOXIDE

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ABSTRACT

Diamondoids [1] and their derivatives have been suggested as promising new materials for a wide range of applications including pharmaceuticals [2] and optoelectronic devices [3]. However, conventional chemical synthesis is impractical due to the large number of reaction pathways, intermediate compounds and low yields. This makes it necessary to develop alternative methods. Recently, higher order diamondoids were synthesized from lower diamondoids by our group and Dahl's group [4], independently. We have generated dielectric barrier discharge [5] and pulsed laser microplasmas [6] in supercritical xenon (scXe) using adamantane, the smallest diamondoid, as a precursor. However, the prohibitively high cost of Xe makes it unattractive as a supercritical medium. On the other hand, supercritical CO_2 ($scCO_2$) is a promising alternative to conventional organic solvents and more readily available compared to scXe. We synthesized diamondoids in $scCO_2$ by microplasmas produced by pulsed laser ablation on highly oriented pyrolitic graphite targets. The targets were placed in a high-pressure cell (inner volume 3 mL), then adamantane ($C_{10}H_{16}$) was added and the cell filled with CO_2, with and without cyclohexane as a cosolvent. The synthesis experiments were conducted close to the critical point of CO_2 (critical temperature T_c: 304.1 K; critical pressure p_c: 7.38 MPa) by focusing the beam of a Nd:YAG laser (wavelength 532 nm, pulse width 7 ns, repetition rate 10 Hz) on the surface of the targets, the high pressure of $scCO_2$ confining the size of the plasma plume. After the experiments (duration: 60 minutes), the synthesized materials were collected and analyzed by micro-Raman spectroscopy and gas-chromatography/mass spectrometry (GC/MS). Micro-Raman spectroscopy of the products revealed the presence of hydrocarbons possessing sp^3 hybridized bonds also found in diamond structures while molecular ion and fragment peaks in the GC/MS spectra indicate the synthesis of diamantane ($C_{14}H_{20}$) and possibly isomers of diamondoids consisting of up to twelve cages, dodecamantane. The synthesis of diamondoids in supercritical fluids using microplasmas generated by pulsed laser ablation might be advantageous compared to other processes such as plasma-enhanced chemical vapor deposition [4] because of the high-density medium, the highly non-equilibrium reaction field generated, and the resulting higher reaction rates. It is suggested that the present method is a first step to the simple and rapid synthesis of higher-order diamondoids.

***Keywords*:** diamondoids, supercritical CO_2, pulsed laser ablation

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