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Rapid Heating Transformation of Nanodiamonds to Carbon Spiroids and Onions in Quantum Chemical Molecular Dynamics Simulations

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【序】 Diamonds are precious materials and rarely would one want to see them wasted by transformation into much lower valued graphitic structures. Nevertheless, this is exactly what Qiao *et al.* have recently demonstrated,[1] they transformed nanodiamonds (NDs) into bucky diamonds → carbon onions → graphitic ribbons at 1400°C for 20 min, 60 min, and 120 min, respectively, in that order. Accompanied with this transformation is obviously a continuous increase of sp^2 carbon at the expense of sp^3 carbon, and one can think of this process as the reversal of fullerene formation from carbon vapor, where sp-hybridized C_2 and C_3 molecules are converted into sp^2 carbon cages. The latter process has been clarified recently by our groups in quantum chemical molecular dynamics (QM/MD) simulations,[2] where we had postulated a "Shrinking Hot Giant" road of fullerene formation, according to which at first giant fullerenes with moderate curvatures are formed, that continuously shrink during annealing by C_2 evaporation, finally arriving at C_{60} as the smallest, IPR-obeying fullerene cage (see Figure 1).

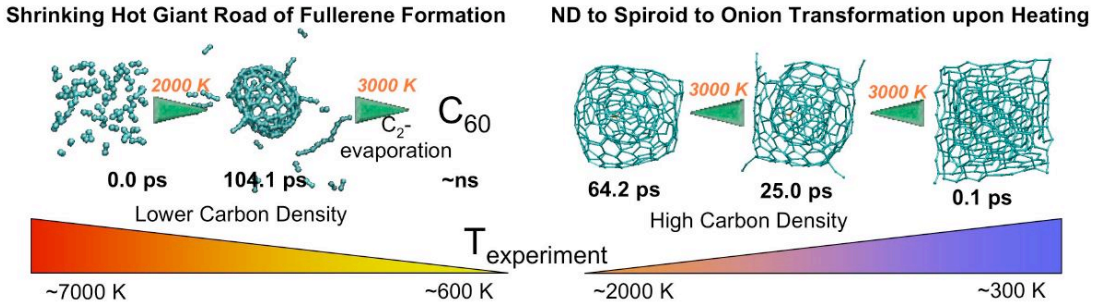

Figure 1

【理論】 The density functional tight binding (DFTB) method is the central method employed in this study to compute on-the-fly potential energy surfaces (PESs) and energy gradients for direct trajectory calculations. All DFTB calculations were carried out with the program package developed by Frauenheim, Seifert, and Elstner.[3] The excellent performance of DFTB for fullerene systems relative to B3LYP/6-31G(d)

geometries and energies has recently been demonstrated by our groups.[4] We have employed the non-charge consistent (NCC) as well as self-consistent charge (SCC) formalism of DFTB, and used a scaling of velocities and Andersen thermostat for the maintenance of temperatures ranging between 1000 to 3000 K. Time steps for trajectory integration were chosen to be 1.2 fs.

【結果と考察】 We present direct QM/MD simulations for the transformation of NDs during rapid heating. Interestingly, in these simulations, we found that an additional intermediate step can be described that lies in between NDs and carbon onions, namely the formation of carbon spiroids which can be thought of as spherical carbon nanoscrolls. Such spiroid structures and *ad hoc* chemical reaction mechanisms for their transformations to carbon onions have first been described by Ozawa *et al.*[5] As it turns out, the transformation seems to be dependent on the initial $sp/sp^2/sp^3$ ratio, i.e. the edge/surface-to-bulk ratio, as well as on the annealing temperature, according to our simulations. Clusters with sizes ranging between 67 and 377 atoms were studied, being subjected to temperatures between 1000 K and 3000 K for up to 600 ps simulation time. Snapshots for a representative trajectory at 3000 K for a C_{286} ND are shown in Figure 2. According to these simulations, spiroid structures seem short-lived and occur only briefly at higher temperatures. We analyze transformation pathways and compare our results with experimental data reported by Zhao *et al.*[1]

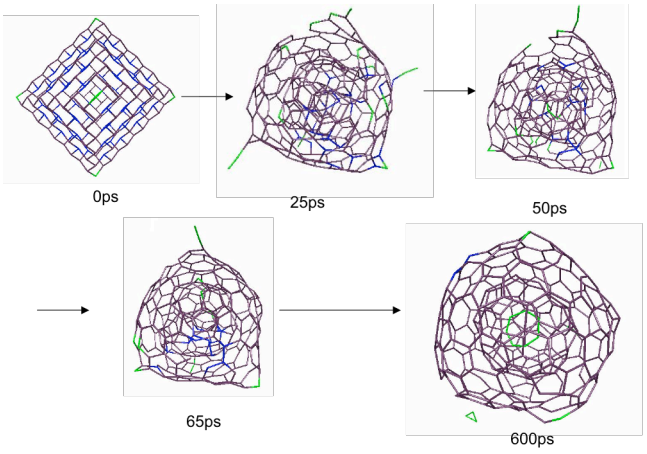

Figure 2. Green: sp, purple: sp^2, blue: sp^3

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