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Supplementary Information for

A new phase transformation path from nanodiamond to new-diamond via an intermediate carbon onion

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S1. Theoretical model of laser-induced high temperature in amorphous carbon and carbon onion

The basis of heating model is that amorphous carbon and carbon onion without a band gap can absorb light and be heated. In contrast, nanodiamonds have a large band gap of about 5.5 eV and transparent to visible light[1], in other words, they cannot be heated. The schematic diagram of various materials interacting with light is shown in Figure S1.

We use the particle heating modal proposed by the Wang *et al.*[2]. The energy absorbed by a particle from the laser pulse is spent in the particle heating process, which is described as following equation

$$J\sigma_{abs}^{\lambda} = m\int_{T_0}^{T} C_p(T)dT \quad (1)$$

where $m = \rho\frac{\pi d^3}{6}$ is the particle mass, d is the diameter of particle, ρ is the density, J is laser fluence, T_o is fixed to 300 K, σ_{abs}^{λ} is the particle absorption cross section, which strongly depends on the laser wavelength. C_p (T) is heat capacity. It is known that the heat capacity is the function of temperature. The different data points about the relationship between heat capacity and temperature are adopted from Ref. [3], which are shown in Figure S2, the exponential function is used for fitting these data points, which is expressed as follows

$$C_p = A_1 \exp(-T/t) + C_o \quad (2)$$

And the relationship between heat capacity and temperature can be described as follows (red curve in Figure S2)

$$C_p = -30.7 \exp(-T/486.7) + 25.4 \quad (3)$$

For a spherical particle, this absorption cross section can be calculated as[4]

$$\sigma_{abs}^{\lambda} = \frac{\pi d^2 Q_{abs}^{\lambda}}{4} \quad (4)$$

Where Q_{abs}^{λ} denotes absorption efficiency, the index λ indicates that both Q and σ depend on laser wavelength. In fact, Q_{abs}^{λ} can be expressed as the function of relative refractive index m[4]

$$Q_{abs}^{\lambda} = 4x \,\mathrm{Im}\{\frac{m^2-1}{m^2+2}\}[1+\frac{4x^3}{3}\mathrm{Im}\{\frac{m^2-1}{m^2+2}\}] \quad (5)$$

$$x = ka = \frac{2\pi \tilde{n}_1 a}{\lambda} \quad (6)$$

$$m = \frac{\tilde{n}}{\tilde{n}_1} \quad (7)$$

x is size parameter, a is radius of particle, $\tilde{n}$ and $\tilde{n}_1$ are the refractive indices of particle and medium (in this case, alcohol, ~1.36), respectively. In order to calculate the absorption efficiency of a spherical particle, we must know two optical characteristics of the particle materials: refractive index n (λ) and extinction coefficient k (λ), or the real and imaginary parts of the complex refractive indices:

$$\tilde{n}(\lambda) = n(\lambda) + ik(\lambda) \quad (8)$$

Their values as function of the wavelength n (λ) and k (λ) for many materials can be found in the reference book[5]. In our case, we take amorphous carbon and 532 nm as the reference material and wavelength:

$$\tilde{m}(532nm) = 2.32626 + 0.85359i \tag{9}$$

Note that, for equation (5), if

$$(4x^3/3)\,\mathrm{Im}\{(m^2-1)/(m^2+2)\} = 1 \tag{10}$$

a condition that will be satisfied for sufficiently small d (d = 5 nm in this case), the absorption efficiency express approximately as:

$$\mathrm{Q_{abs}} = 4x\,\mathrm{Im}\{\frac{m^2-1}{m^2+2}\} \tag{11}$$

In addition, the density difference should be taken into account. The density of amorphous carbon is relative stable value ~2.1 g/cm[3, 6]. Combining above equations, the rising temperature of amorphous carbon is calculated to approximately linear increase with laser fluence, as shown in Figure S3. However, the density of carbon onion is concerned with temperature [7]. Figure S4 shows the rising temperature versus laser fluence absorbed by carbon onion.

S2. Theoretical model of carbon onion as nanoscaled temperature and pressure cell under laser irradiation in liquid

Carbon onion as nanoscaled temperature and pressure cell upon laser irradiation is attributed to the mechanism as follows. Laser can firstly induced a high temperature in carbon onions by carbon onions absorbing laser energy. Then the laser-induced-high temperature will compress the interlayer distance of carbon onions. Finally, interlayer distance reducing results in a high pressure inside carbon onions. A detailed theoretical model for this issue is provided below.

Taking into account a carbon onion containing *N* carbon cages with different radii, each carbon cage (*CC*) under high temperature will be expansion and the volume thermal coefficient (α_V) is related with the Debye temperature based on the Lindemann's equation [8] and Gründisen's theory of the solid state [9,10], i.e., $\alpha_V = c/\left(\theta_D^2\ V^{2/3} A_r\right)$, where *c*, *V* and A_r denote a constant, the mole volume and the atomic weight compared to C^{12}, respectively. According to this relation, one may calculate the $\alpha_V\left(\infty\right)$of each carbon cage from the Debye temperature data. On the basis of the proportional relationship of $\alpha_V\left(\infty\right) \propto\ \theta_D\left(\infty\right)$ and assuming the size in this equation can be extended to nanoscale regime, we have

$$\frac{\alpha_V\left(CC\right)}{\alpha_V\left(G\right)} = \frac{\theta_D^2\left(G\right)}{\theta_D^2\left(CC\right)} \qquad (1)$$

Here $\alpha_V\left(G\right)$ is the volume thermal coefficient of graphite. Knowing that $\theta_D^2 \propto E_c \propto \gamma$ [11,12], where E_c and γ are the cohesive energy and the surface energy. Thus, one has

$$\frac{\alpha_V(CC)}{\alpha_V(G)}=\frac{\gamma(G)}{\gamma(CC)} \tag{2}$$

As an approximation, the size-dependent surface energy of nanosolids can be expressed as: $\gamma(G)/\gamma(CC)=1\big/_{1+2h/R}$, where h and R represent the size of a carbon atom and the radius of carbon cage. Combining Eqs. (2) and (3) yields

$$\alpha_V(CC)=\alpha_V(G)(1-2h/R) \tag{3}$$

Furthermore, based on the relation of thermal volumetric expansion coefficient $\alpha_V=(1/V)(dV/dT)$[13], we can obtain the size and temperature dependence of volume of CC in carbon onion, i.e.,

$$V(CC)=V_0\left(1+\alpha_V(G)(1-2h/R)T\right) \tag{4}$$

Apparently, the volume change of each CC in carbon onion is nonuniform and will lead to the variation of interlayer distance and further result in the change of van der Waals (vdW) interaction between carbon layers. Considering a double-layer carbon onion consisting of an inner cage with radius R_1 and a outer cage with radius R_2 (see the inset of Figure S7), the pressures (p) acting on the inner and the outer carbon cages are [14]

$$p_{inner}=-\frac{\rho_\infty^2}{4\pi R_1^2}\int_{S_{inner}^{(0)}}\left(\int_{S_{outer}^{(0)}}F_1 dS_{outer}^{(0)}\right)dS_{inner}^{(0)} \tag{5}$$

$$p_{outer}=\frac{\rho_\infty^2}{4\pi R_2^2}\int_{S_{outer}^{(0)}}\left(\int_{S_{inner}^{(0)}}F_2 dS_{inner}^{(0)}\right)dS_{outer}^{(0)} \tag{6}$$

where ρ_∞ is the atom density of plane graphene, $S_{inner}^{(0)}$ and $S_{outer}^{(0)}$ denote the areas of inner and outer carbon cages in the undeformed state which is used as a reference configuration, F_1 and F_2 are the vdW forces acting on each of the atoms (positive for the attraction) , which can be gained from the first derivative of the Lennard-Jones (LJ) potential ($V(d) = 4\varepsilon\left[\left(\sigma/d\right)^{12} - \left(\sigma/d\right)^{6}\right]$, with ε and σ being the LJ parameters) with respect to *d*.

Noticeably, the carbon onion in our case are perfect crystalline without considering any defect effect. From Eq. (3), the size- and temperature-volume thermal expansion coefficients of carbon cages have been calculated, as shown in Figure S5. Note that the volume thermal expansion coefficient of graphite can be depicted as $\alpha_V(G) = 2\alpha_a + \alpha_c$, with α_a and α_c being the thermal expansion coefficients of graphite in *a*-axial and *c*-axial directions, which are related with the heat capacity and the Debye functions. The inset in Figure S5 is the heat capacity of graphite in *a*-axial and *c*-axial directions. It is shown that the volume thermal expansion coefficient of different carbon cages increases with decreasing size and increasing temperature, implying that the smallest carbon cage within carbon onion has the largest expansion velocity at fixed temperature.

Considering a double carbon onion containing two perfectly spherical layers such as C_{60} in C_{180}, we can predict the temperature-dependent interlayer distance based on Eq. (4). In Figure S6, the interlayer distance between C_{60} and C_{180} becomes smaller with increasing temperature. Therefore, it is concluded that the interlayer pressure will be altered due to the changes of carbon cages' radii. Figure S7 shows p_1 as a function of the interlayer distance. Evidently, the smaller interlayer distance leads to the larger pressure.

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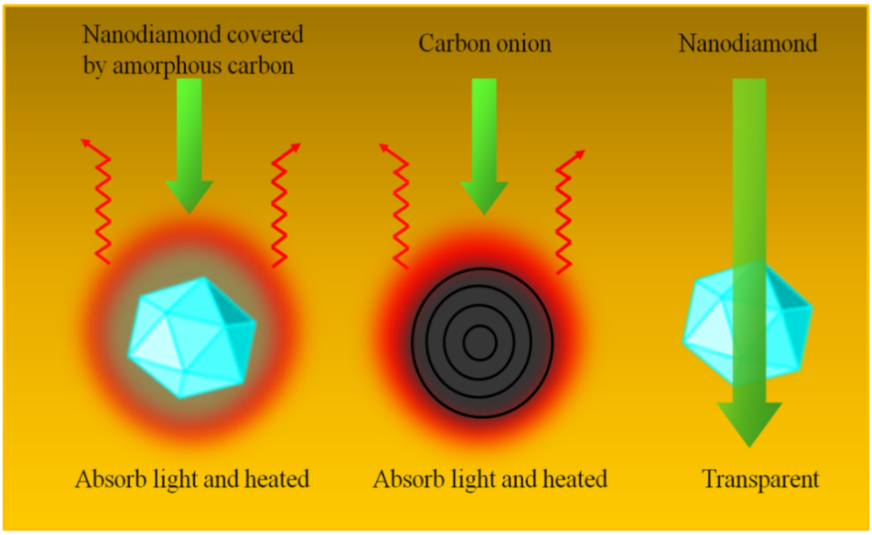

Figure S1. The interaction between various materials and light. Nanodiamond covered by amorphous carbon (left) and carbon onion (middle) irradiated by the visible light can be heated due to absence of band gap. However, the pure nanodiamond (right) without cover is transparent to green light owing to a large bandgap of 5.5 eV, which is hardly to be heated and keep still.

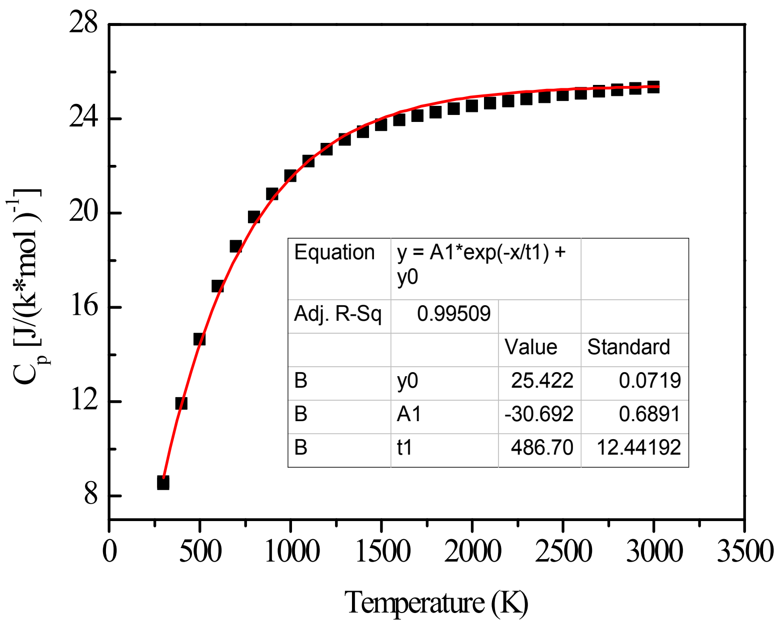

Figure S2. The function of $C_p(T)$. The square points adopted from Ref. [3], the red curve is the fitting curve. Note that, the degree of fitting is over 0.99.

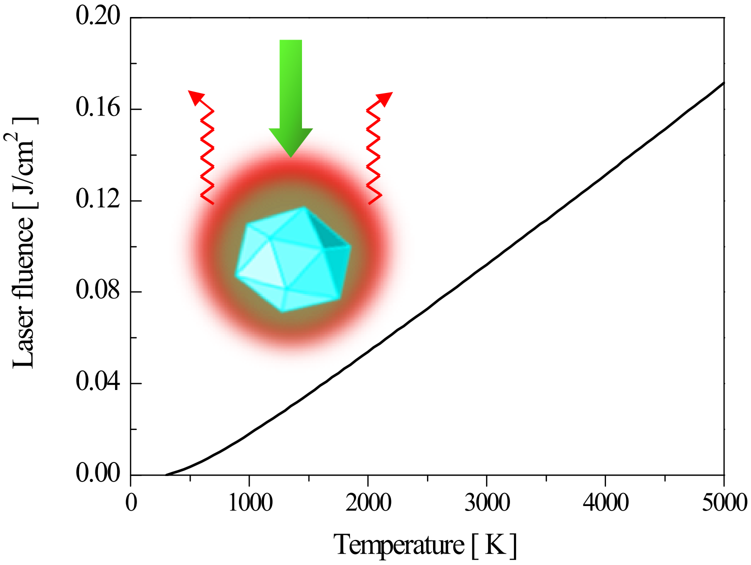

Figure S3. Relationship between laser fluence and temperature rising result from the nanodiamonds covered by amorphous carbon absorbing the power of laser, the inset is the schematic plot of nanodiamonds covered by amorphous carbon irradiated by laser.

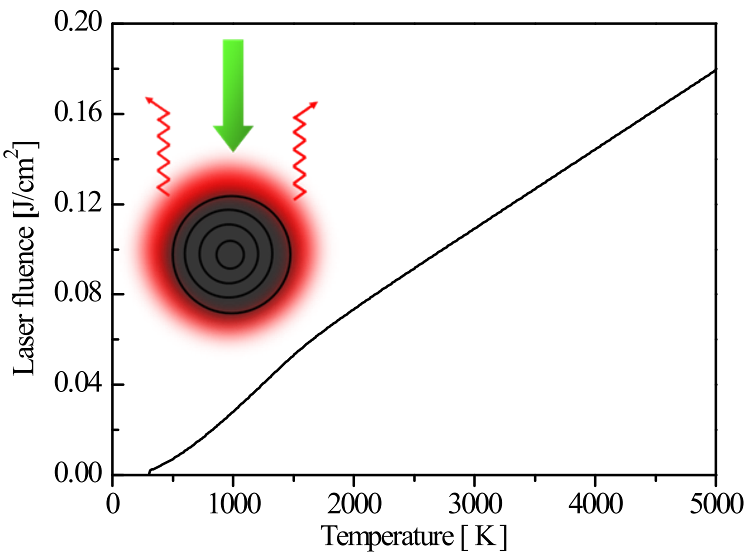

Figure S4. Relationship between laser fluence and temperature rising result from carbon onion absorbing the power of laser, the inset is the schematic plot of carbon onion irradiated by laser.

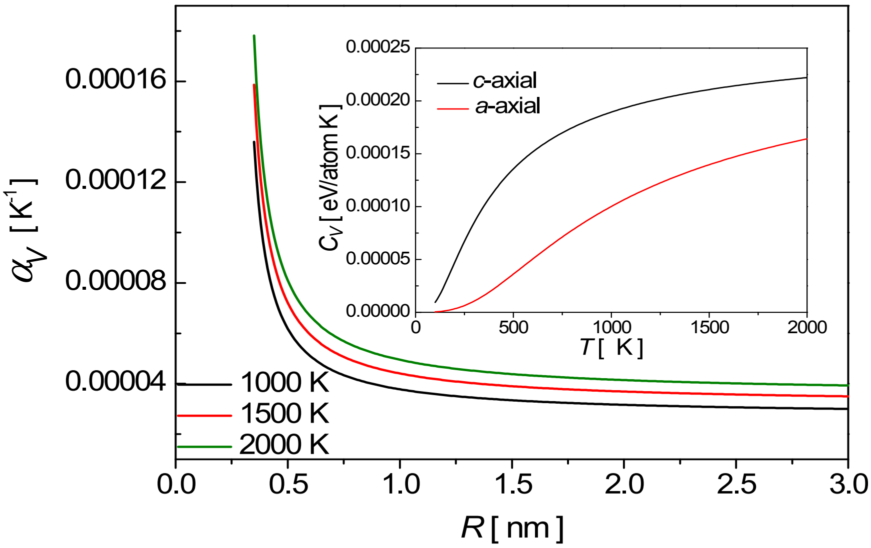

Figure S5. Size and temperature dependence of volume thermal expansion coefficient in carbon cages. The inset is the heat capacity of graphite in *c*-axial and *a*-axial directions.

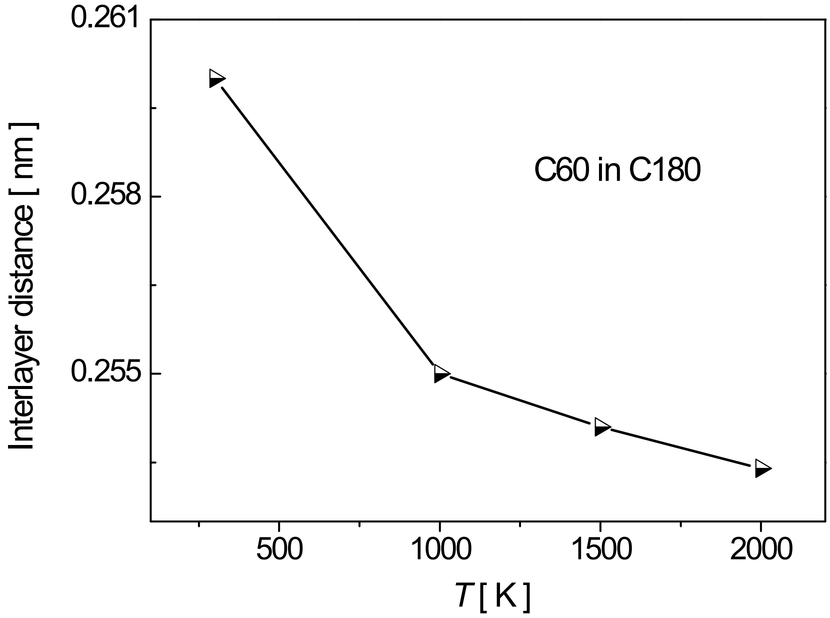

Figure S6. Temperature-dependent interlayer distance of C_{60} in C_{180}.

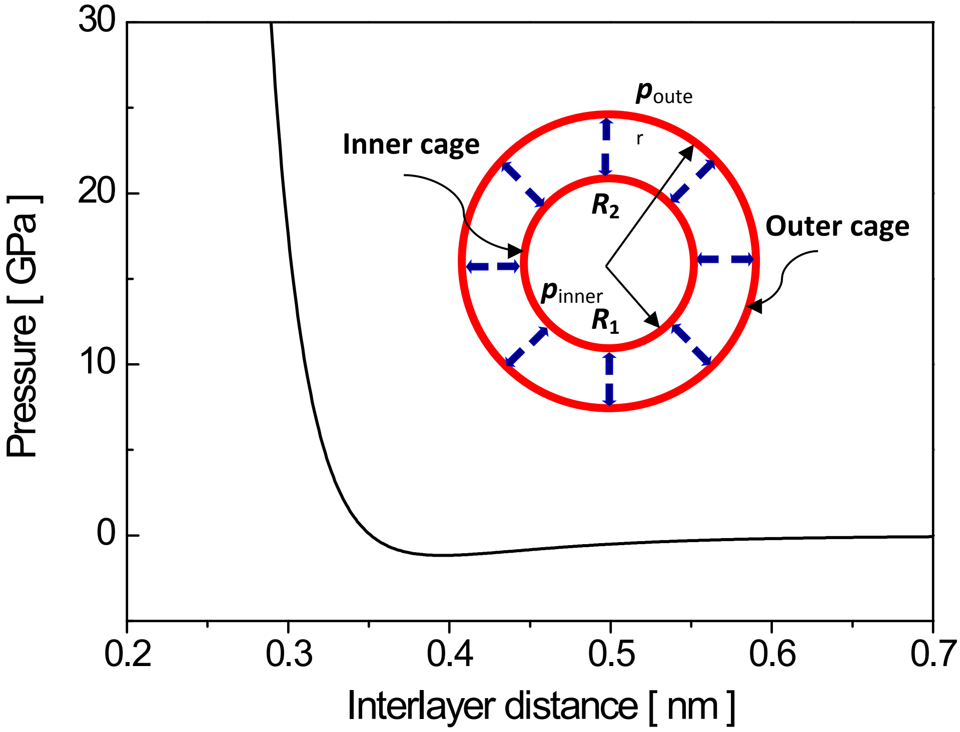

Figure S7. Dependence of pressure (p_{inner}) on interlayer distance in a double-layer carbon onion. Note that the inset is a double-layer carbon onion (C_{60} in C_{180}) considered in our case.