

## Size Tunable Synthesis of Solution Processable Diamond Nanocrystals

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Supporting information:

**Synthesis of periodic mesoporous carbon.** Soft-assembled periodic mesoporous carbon (SBA-15 type) was synthesized following published procedure (Wang et al., *Langmuir*, **2008**, 24, 7500). In a typical synthesis procedure, 1.0 g of resorcinol and 1.0 g of Pluronic F127 (BASF Corporation) block copolymers were dissolved in 4.5 ml of absolute ethanol in a plastic vial (50 ml) followed by magnetic stirring at room temperature. After stirring for 1h, 4.5 ml of 3.0 M HCl solution was added to the solution. To this mixture, 1.3 g of formaldehyde (37 wt%) solution was added after 1h. After stirring for 10 min, the whole reaction mixture (polymeric gel) was centrifuged and the supernatant was discarded. Then, 2 ml of a 1:1 ethanol/THF mixture was added to the gel followed by stirring for 30 min. Then the gel was aged overnight for the removal of the solvent under ambient conditions. The whole gel-mixture was then cured at 100 °C for 2 days. Finally, the obtained material was carbonized under nitrogen atmosphere by heating from room temperature to 400 °C (heating ramp 1 °C/min) for 2 h, followed by increasing the temperature to 850 °C (heating ramp 5 °C/min) for 3 h to obtain the mesoporous carbon material. Yield of the mesoporous carbon was ~ 0.50 g from each batch of synthesis.

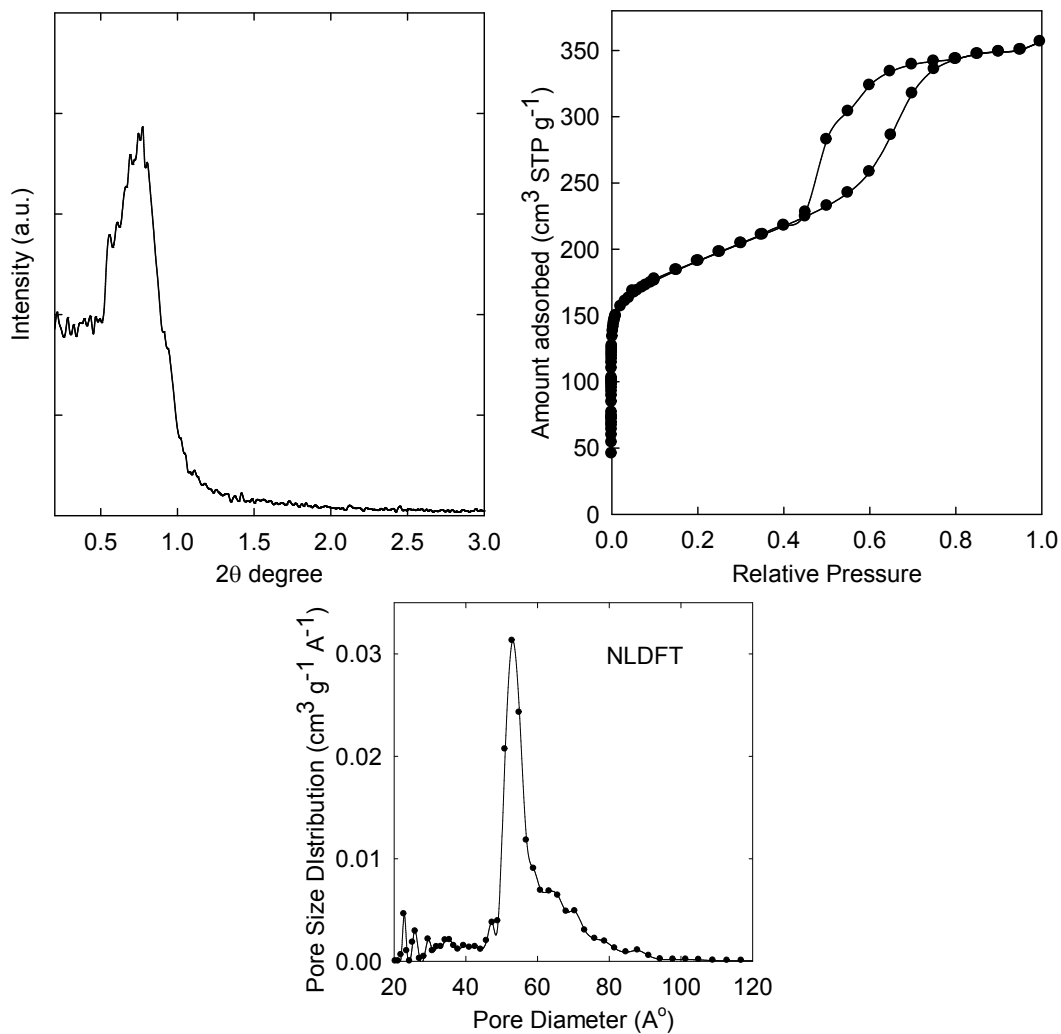
**High pressure and temperature experiment with multi-anvil apparatus.** The high pressure and high temperature (HPHT) experiments were carried out using a multi-anvil apparatus with a 1500 ton press. The sample was encapsulated in a 2.5 x 3 mm platinum capsule. The capsule was welded and placed inside an alumina sleeve, a cylindrical Re heater, and a zirconia sleeve for thermal insulation. The whole assembly was placed inside a Cr<sub>2</sub>O<sub>3</sub> doped MgO octahedron with an edge length of 14 mm. The temperature was measured using a W5%Re-W26%Re wire as thermocouple (C-type) which was implemented into the assembly. The octahedron was placed inside eight corner truncated tungsten carbide cubes with edge length 8 mm. Pyrophyllite gaskets were used to separate the tungsten carbide cubes from each other. The sample was compressed to the desired pressure at a rate of 2 GPa/h at room temperature and then heated to final temperature at a rate of 50 °C/min. After the final temperature was reached, the temperature was kept constant for 3 h (or other time). Then, the pressure was released at a rate of 2 GPa/h. After ambient pressure was reached, the sample was extracted from the capsule for characterization and analysis.

**Yield of nanodiamond.** For each HPHT experiment, ~ 7.5 mg of mesoporous carbon precursor was put into a platinum capsule and welded shut. The estimated amount of diamond recovered is ~ 5.5 mg. Therefore, mass yield of nanodiamond is = (5.5/7.5) X 100= 73.3%. There was some loss of weight of nanodiamond due to extraction process from the capsule. In a typical HPHT experiment, 5-6 mg of nanodiamond was recovered.

**Characterizations.** X-ray diffraction (XRD) patterns were acquired on an imaging plate using Rigaku D/MAX-RAPID microdiffraction system with Mo K<sub>α</sub> as radiation source ( $\lambda = 0.071073$  nm). The sample was mounted in a 0.5 mm diameter capillary tube. Raman spectra were acquired on Horiba-Jobin Yvon LabRam-HR Spectrometer equipped with a confocal microscope (Olympus BX-30), a 325 nm notch filter, and a single stage monochromator. The spectrum was collected with 325 nm excitation (20 mW YAG laser) at ambient conditions. Transmission electron microscopy (TEM) images were recorded on JEOL 2000FX instrument operated at an accelerating voltage of 200 kV. The samples were first sonicated in ethanol, and then drop-casted on carbon coated copper grid. The solvent was evaporated in air before analysis. SEM was carried out using a Hitachi S4200 instrument at an operating voltage of 3 kV.

The average nanocrystals size and size distributions of the diamond nanocrystals in the colloidal diamond suspensions were obtained by performing dynamic light scattering (DLS) measurements. A BI-9000 AT digital time correlator was used to monitor the intensity-intensity time correlation function. The constrained regularized CONTIN method was used to analyze the field correlation function  $G(\Gamma)$  and to get the characteristic line width  $\Gamma$ . The hydrodynamic radius ( $R_h$ ) of the nanocrystals can be calculated using Stokes-Einstein relation:  $R_h = kT/(6\pi\eta D)$ , where  $k$  is boltzman constant and  $\eta$  is the viscosity of the solvent at temperature  $T$ . The translational diffusion coefficient  $D$  was converted to  $\Gamma$

using the following equation:  $D = \Gamma/q^2$ , where  $q = 4\pi n/\lambda \sin(\theta/2)$  with  $n$ ,  $\lambda$ , and  $\theta$  are the refractive index of the sample, the incident laser wavelength, and the scattering angle respectively. From a plot of  $\Gamma G(\Gamma)$  vs  $R_h$ , the particle size distribution in solution was measured.



**Figure S1.** Small-angle X-ray scattering (top left), nitrogen gas adsorption isotherm (top right), and NLDFT (adsorption branch) pore size distribution (bottom) of synthesized periodic mesoporous carbon.

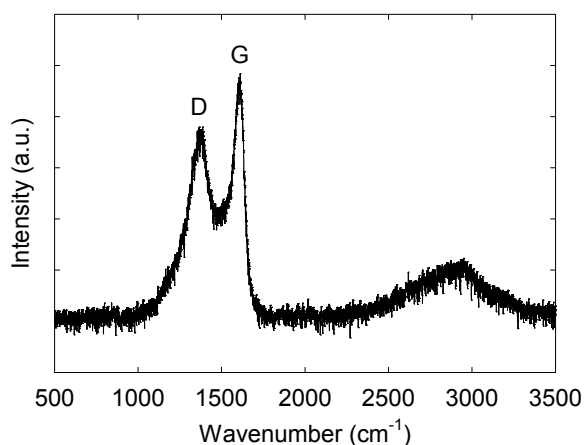
**Chemical composition of mesoporous carbon:**

Chemical composition of mesoporous carbon was analyzed by Elemental analysis and Raman spectroscopy. We analyzed five different areas of mesoporous carbon in the TEM grid and performed EDX analysis from which atomic weight percent of carbon and oxygen was calculated (Table S1). From the Table S1, an average value of 95.31 atomic weight percent for carbon and 4.69 weight percent for oxygen was calculated.

**Table S1.** EDX analysis of mesoporous carbon at different areas:

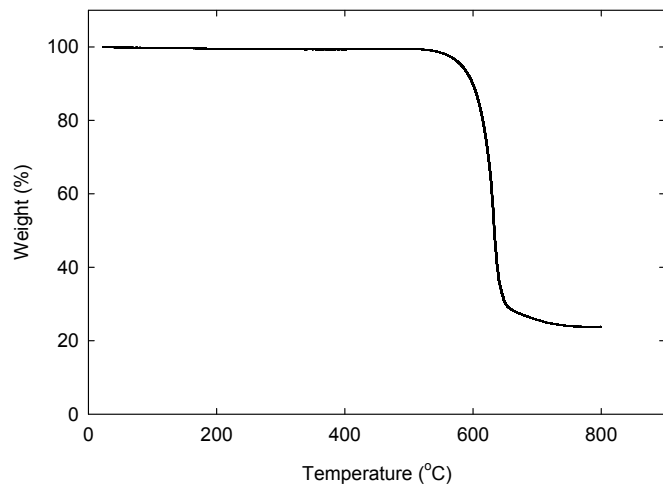
Area	Carbon	Oxygen
1	94.67	5.33
2	95.01	4.99
3	95.48	4.52
4	95.08	4.92
5	96.30	3.70
Average	95.31	4.69

Raman spectrum showed D and G bands corresponding to  $sp^2$  bonded carbon (Figure S2). A broad band at  $\sim 2930\text{ cm}^{-1}$  could be related to C-H stretching from terminal C-H bonds on the pore surface of the carbon material.

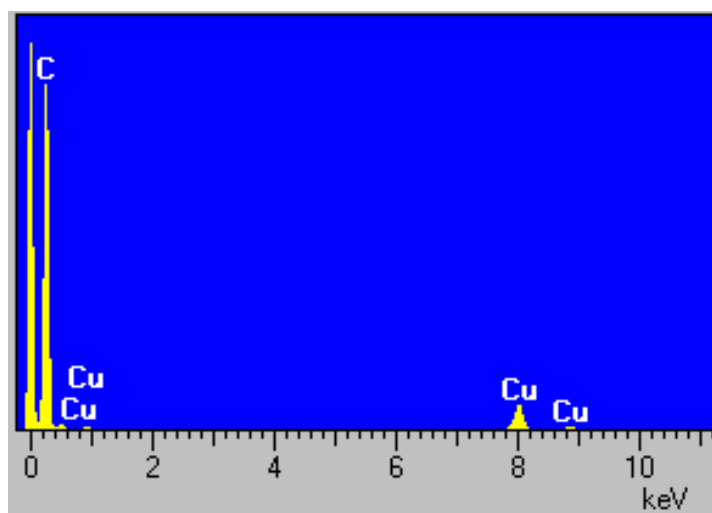


**Figure S2.** Raman spectroscopy of mesoporous carbon material obtained at 850 °C.

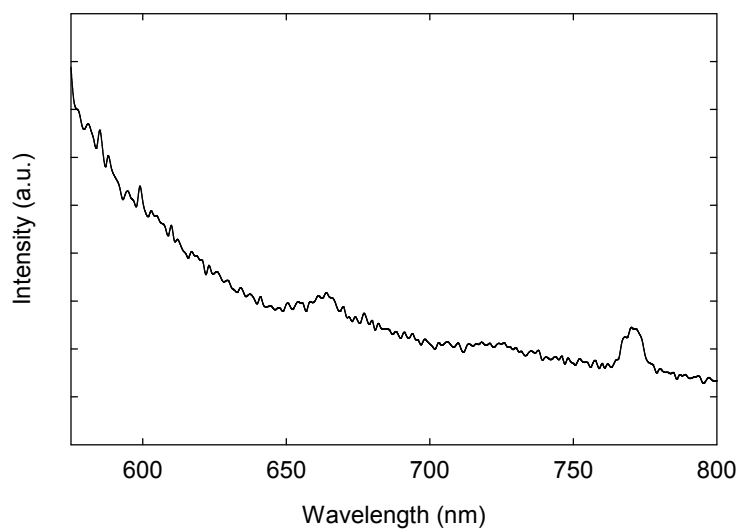
From EDX analysis and FTIR spectroscopy, we calculated the chemical composition of mesoporous carbon as  $C_{95}O_5H_0$ .



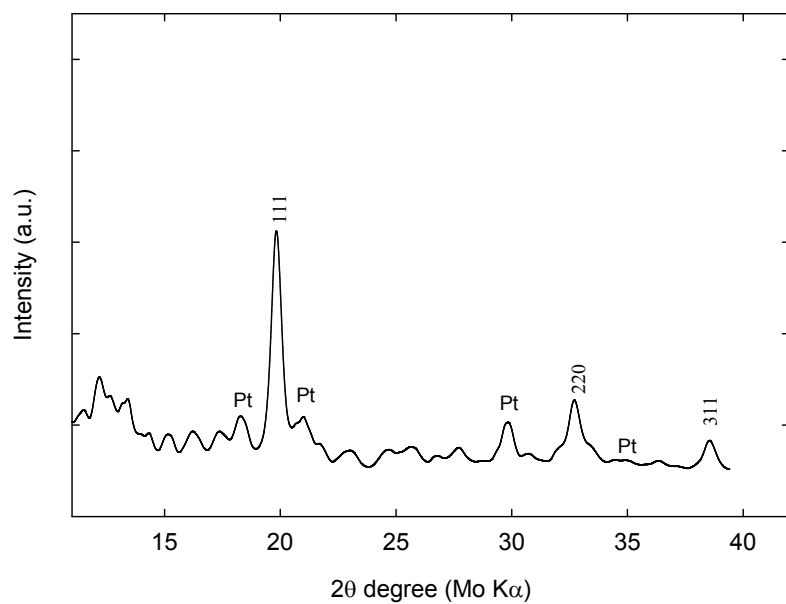
**Figure S3.** TGA analysis of product materials obtained at a pressure of 14 GPa and temperature of 1300 °C for 3 h. A single weight loss at ~ 630 °C was observed.



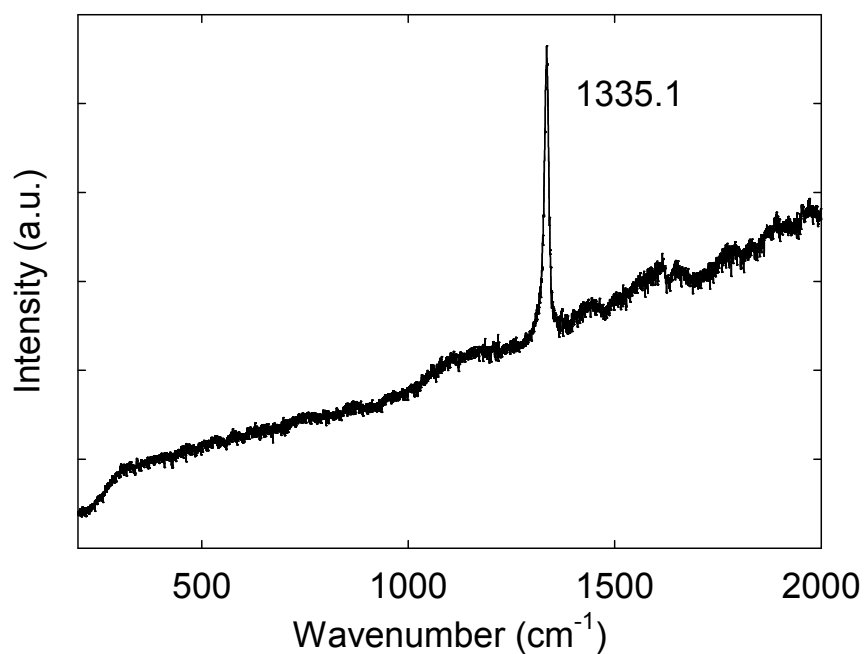
**Figure S4.** EDX analysis of synthesized diamond nanocrystals.



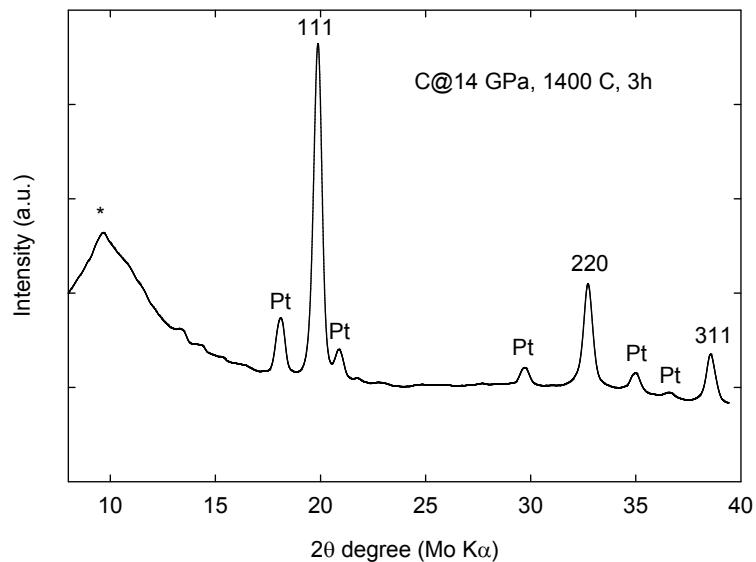
**Figure S5.** Photoluminescence spectrum of diamond solution in acetone excited at  $\lambda=488$  nm.



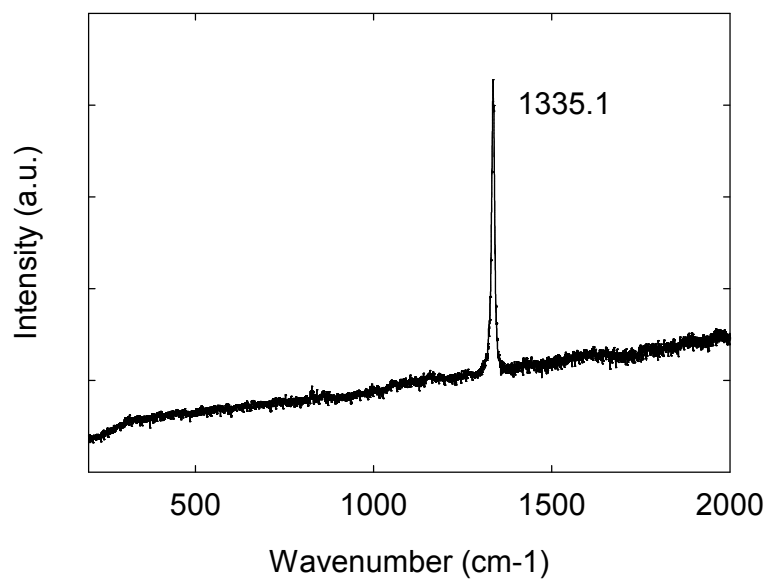
**Figure S6.** XRD of product materials obtained at a pressure of 14 GPa and temperature of 1400 °C for 30 min. Peaks for Pt were from the capsule and some smaller peaks were also observed which are due to presence of graphite.



**Figure S7.** Raman spectrum of product materials obtained at a pressure of 14 GPa and temperature of 1400 °C for 30 min. Band at 1335.1  $\text{cm}^{-1}$  is due to formation of diamond.

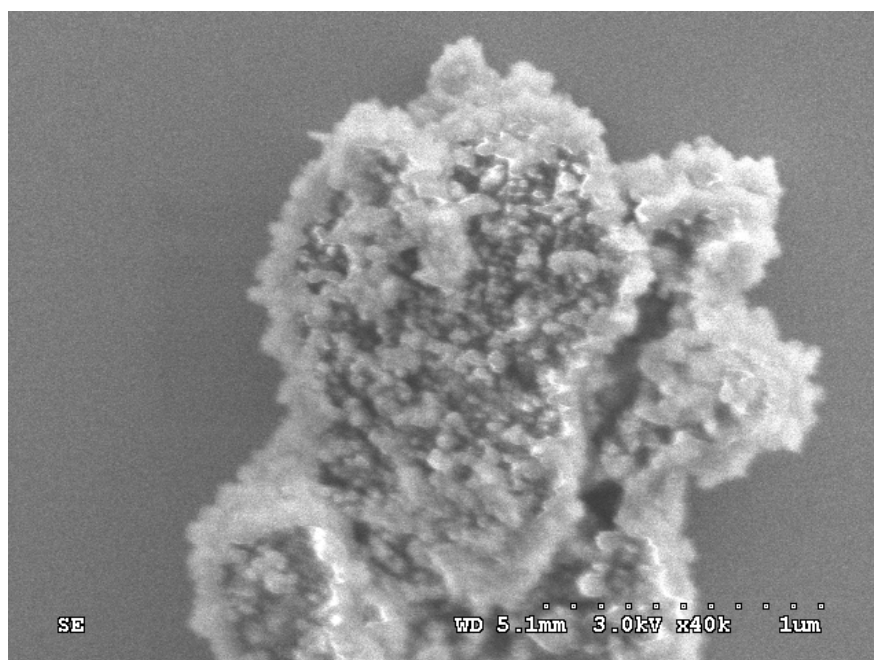


**Figure S8.** XRD of product materials obtained at a pressure of 14 GPa and temperature of 1400 °C for 3h. Peaks for Pt were from the capsule.

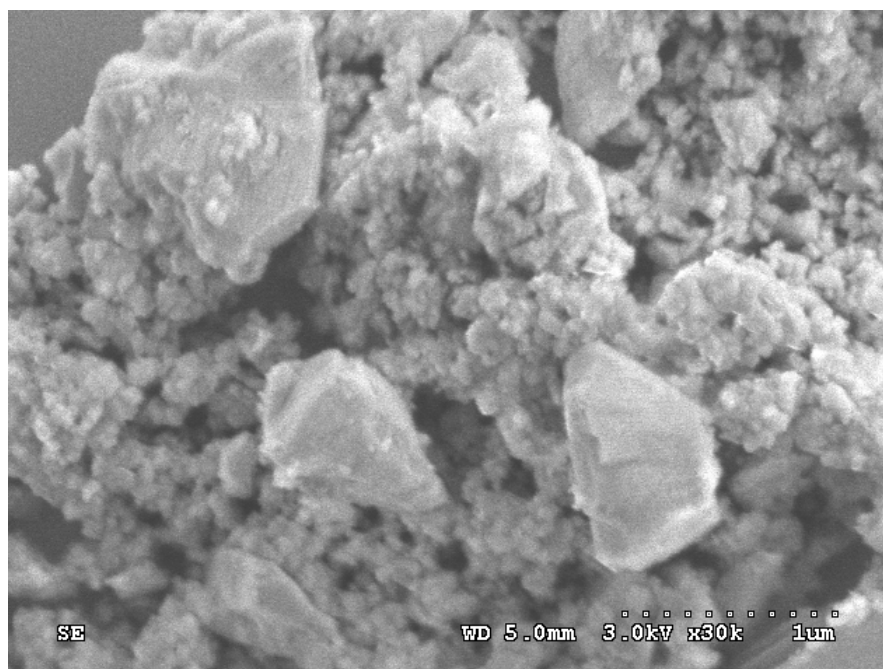


**Figure S9.** Raman spectrum of product material obtained at a pressure of 14 GPa and temperature of 1400 °C for 3 h. Band at 1335.1  $\text{cm}^{-1}$  is due to formation of diamond

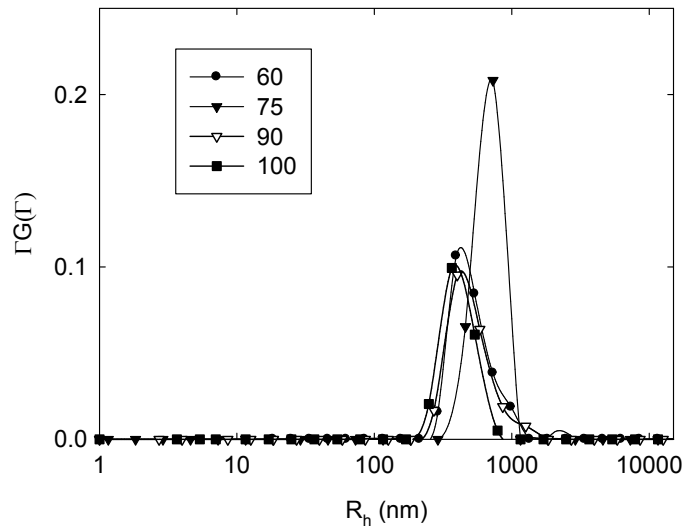




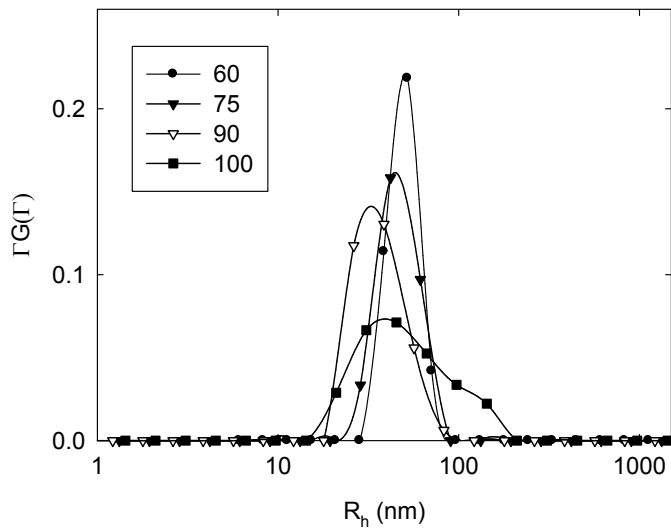
**Figure S10.** SEM (bottom) images of product material obtained at a pressure of 14 GPa and temperature of 1400 °C for 30 min. The large particle is composed of many smaller particles of size ~ 50 nm.



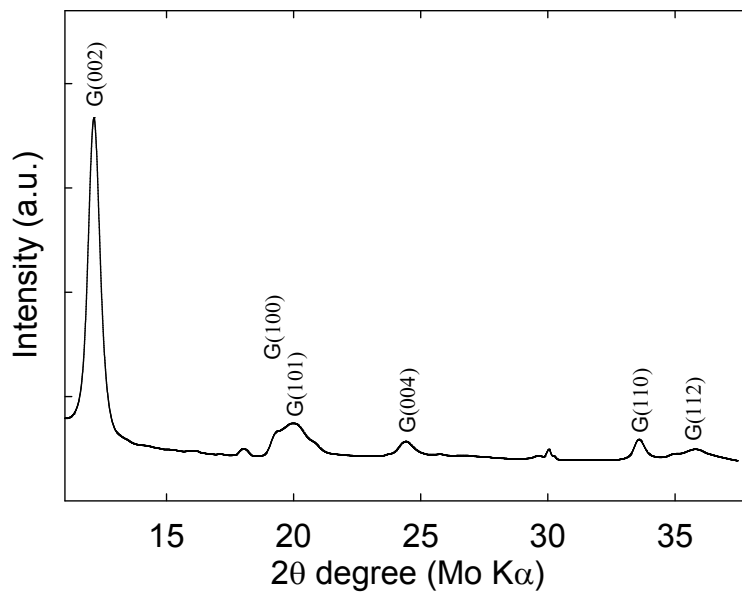
**Figure S11.** SEM (bottom) images of product material obtained at a pressure of 14 GPa and temperature of 1400 °C for 3 h.



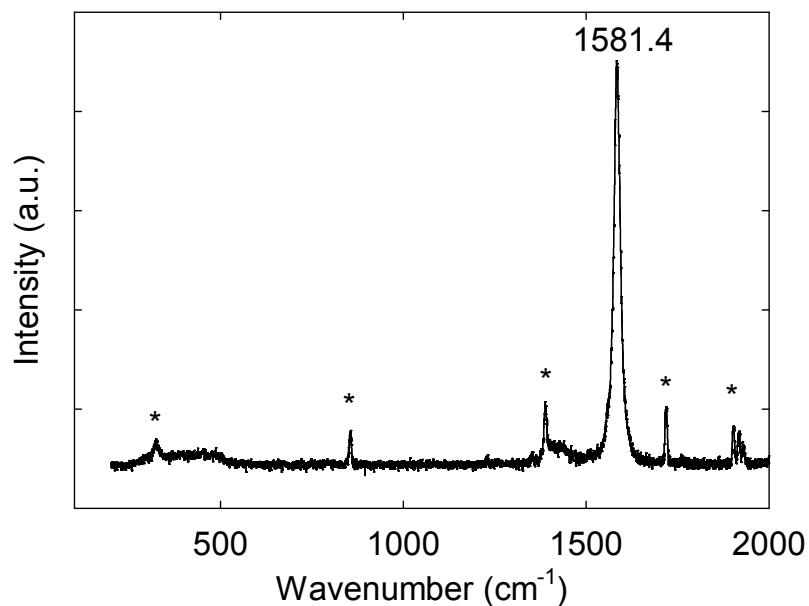
**Figure S12.** CONTIN analysis of Dynamic light scattering data of product material obtained at a pressure of 14 GPa and at temperature of 1400 °C for 30 min at different scattering angles of diamond nanocrystals dispersed in acetone.



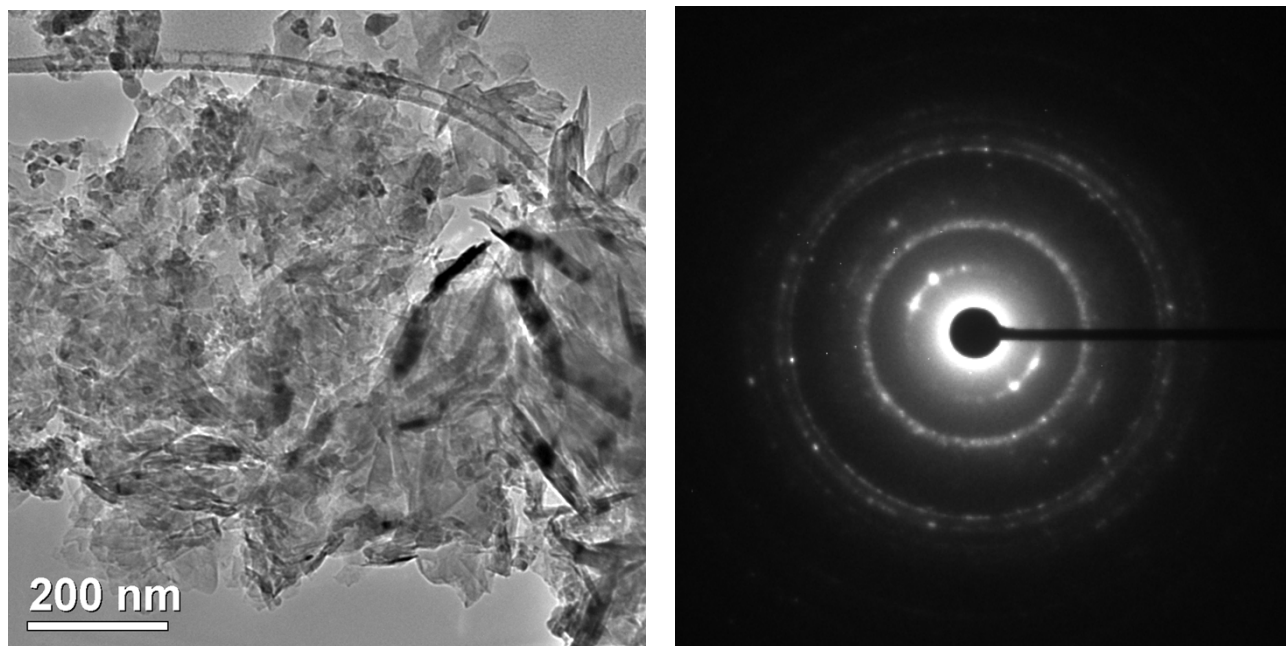
**Figure S13.** CONTIN analysis of Dynamic light scattering data of product material obtained at a pressure of 14 GPa and at temperature of 1400 °C for 3 h at different scattering angles of diamond nanocrystals dispersed in acetone.



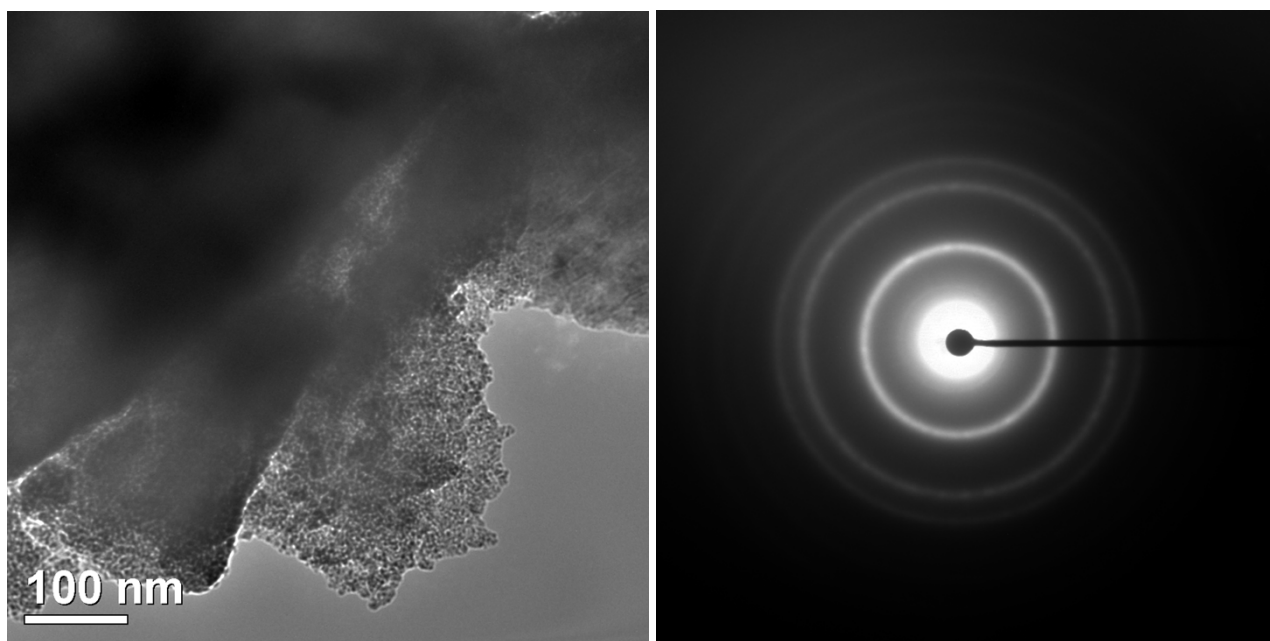
**Figure S14.** XRD of product material at a pressure of 12 GPa and a temperature of 1300 °C for 3h.



**Figure S15.** Raman spectra of product material obtained at different pressures of 12 GPa at a temperature of 1300 °C for 3h. Band at 1581 is due to graphitic G band. Asterisk (\*) indicates impurity that originates from the ceramic wool used during Raman spectrum measurements.



**Figure S16.** TEM image and SAED of product material obtained at a pressure of 12 GPa and at a temperature of 1300 °C for 3h.



**Figure S17.** TEM image and SAED of product material obtained at a pressure of 21 GPa and at a temperature of 1300 °C for 3h.