

HPHT Synthesis and Compressibility of Hydrogen-Terminated Nanodiamonds

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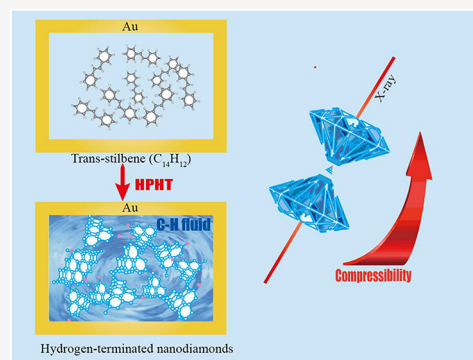


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Supporting Information

ABSTRACT: Hydrogen-terminated nanodiamonds are new functional nanodiamonds that have many applications, particularly in the field of catalysis. However, their elastic properties have not yet been investigated. In this study, hydrogen-terminated nanodiamonds were synthesized at 15.5 GPa and 1200–1600 °C using *trans*-stilbene ($C_{14}H_{12}$) as the starting material in a relatively closed carbon–hydrogen system by using a gold capsule. Raman spectroscopy revealed characteristic diamond peaks, with a set of peaks around 2900 cm^{-1} indicating hydrogen termination. The extent of hydrogenation and unit-cell volume are negatively correlated to the synthetic temperature, while the grain size is positively correlated to it. The size of the synthesized hydrogen-terminated nanodiamonds at 15.5 GPa and 1600 °C was confirmed to be $\sim 6\text{--}15\text{ nm}$ by synchrotron-based X-ray diffraction and transmission electron microscopy. Their equation of state was determined by synchrotron-based X-ray diffraction combined with the diamond anvil cell up to 33.6 GPa. The bulk modulus was determined to be 424(12) GPa, lower than the bulk moduli of the bulk diamond and conventional nanodiamonds. It indicates that hydrogen termination softens nanodiamonds and may play a vital role in modifying their elastic behavior.



1. INTRODUCTION

Hydrogen-terminated diamonds and nanosized diamondoid hydrocarbons form a series, including lower/higher diamondoids, nanocrystalline/CVD diamonds, and macroscopic diamonds.¹ In the context of increasingly severe environmental and energy problems, hydrogen-terminated nanodiamonds, as an important member of functional nanodiamonds, have a large reduction potential to trigger the photocatalytically initiating reactions,^{2,3} and their low cytotoxicity⁴ and environmental friendliness light up the application of the degradation of recalcitrant organic compounds in water.⁵

The design and synthesis of hydrogen-terminated nanodiamonds are of great importance. Synthesizing nanoscale hydrogen-terminated diamond molecules can be generally approached from two perspectives: synthesizing higher diamondoids or nanoscale CVD diamonds. The stable cage structures of diamondoids make them hard to synthesize. The synthesis of higher classes of adamantanes presents extremely complex reaction dynamics, with countless side reactions and isomers.^{6,7} Ahmed et al. reported the hydrogen termination dynamics of nanodiamond particles annealed at 500 °C in H_2 , revealing C_3 -radical desorption leading to H_2 dissociation and C–H adsorption on the surface.⁸ The hydrogen-terminated diamond layer synthesized through a hydrogen atmosphere and CVD method always contains a mixture of sp^2 -hybridized amorphous carbon phases.^{8–10} The previous work on CVD

diamond films synthesized using CH_4/H_2 mixtures showed that the concentration of hydrogen appears to be proportional to the sp^2 bond ratio.¹¹ Nanodiamonds synthesized by the laser impact method in the C–H and C–H–O systems, however, were found to be not hydrogen-terminated, making surface functionalization difficult.^{12,13}

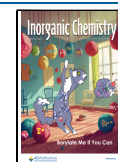
Since Wentorf et al. first synthesized diamond using hydrocarbons at high temperature and pressure, hydrocarbons have become a highly promising starting material to synthesize micron- and nano-sized diamonds free of metal impurities.¹⁴ Various types of C–H and C–H–X multinary compounds with different structures have been studied in diamond synthesis since then.^{15–17} Organic compounds from different categories such as saturated hydrocarbons (paraffin, polyethylene) and cyclic compounds with carbon bridges and sp^3 hybridized carbon atoms (adamantane, camphene) have been explored.^{18–21} In addition, hydrocarbons with different atomic ratios of H/C have been further investigated as the starting materials to synthesize diamond.^{22,23} Hydrocarbons could

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provide hydrogen in the system during the synthesis processes of diamond, potentially promoting the formation of a hydrogen-terminated diamond. However, among various studies using hydrocarbons as starting materials to synthesize nanodiamonds, only a few have investigated and reported that the synthetic nanodiamonds were hydrogen-terminated. Kudryavtsev et al. first reported the synthesis of hydrogen-terminated diamonds from adamantane at 8–9 GPa and 1700 K.²⁴ The Raman signatures of this kind of hydrogen-terminated diamond were investigated in detail subsequently.²⁵ Compared with the simple C–H system, Ekimov et al. and Kondrin et al. synthesized the hydrogen-terminated nanodiamond from halogenated adamantanes and polyvinyl chloride at a pressure range of 8–9 GPa and a temperature range of 727–1427 °C^{15,26–28} and found a correlation between synthetic temperature, grain size, and lattice parameters.²⁷ However, the properties of the hydrogen-terminated nanodiamonds synthesized from a simple C–H system including lattice parameters, grain sizes, spectroscopic characteristics, and their relations with synthetic conditions remain unclear, and whether they are similar to those synthesized from halogenated hydrocarbons still needs to be investigated. It is equally important to determine the compressibility of the hydrogen-terminated diamond, which reveals how hydrogen affects the stiffness of the synthesized nanodiamonds. Extensive theoretical and experimental studies have been conducted on the elasticity of diamond under high pressure;²⁹ however, research on hydrogen-terminated nanodiamonds remains limited.

In this study, *trans*-stilbene (C₁₄H₁₂) was used to synthesize hydrogen-terminated nanodiamonds in Au capsules at high pressures and temperatures using a multi-anvil press (MAP). Raman spectroscopy, synchrotron-based X-ray diffraction (XRD), and transmission electron microscopy (TEM) were employed to characterize the vibrational modes, crystallographic structure, and particle morphology of the nanodiamonds, respectively. In addition, the diamond anvil cell (DAC) combined with the synchrotron-based XRD was utilized to study the compressibility of the synthesized hydrogen-terminated nanodiamond.

2. MATERIALS AND METHODS

2.1. Selection of Capsule Material. In the synthesis of nanodiamonds, graphite sample capsules have been extensively utilized owing to their permeability. Several studies have suggested that the inherent low gas tightness of graphite may not enclose the gaseous products of thermal conversion of hydrocarbons inside the sample capsule.^{21,23} The confinement of small hydrocarbon molecules within the sample capsule may exert a positive influence on the quality of the synthesized nanodiamonds. Among noble metals considered for capsule materials, Au demonstrates the lowest hydrogen permeability.³⁰ The superior confinement and noncatalytic attributes of Au capsules employed in the research enable the investigation of hydrogen's role in the synthesis and growth of nanodiamonds within a confined environment.

2.2. Sample Synthesis. Nanodiamond samples were synthesized in a 1000-ton Walker-type MAP at the University of Hawaii at Manoa (UHM). *trans*-Stilbene (C₁₄H₁₂) as the starting material was loaded in an Au capsule (1.5 mm inner diameter × 1.45 mm height) and then put in the COMPRES 10/5 cell assembly.³¹ In the three runs of synthesis experiments, the samples were compressed to 15.5 GPa first and then heated to 800, 1200, and 1600 °C at a rate of 50 °C per minute, respectively. The samples were kept at the target temperature for 1 h and quenched to ambient temperature by shutting down the power. The quenched samples were mounted in epoxy and ground

longitudinally to expose their cross section. No uncommon hazards are noted.

2.3. Raman Spectroscopy. Raman spectral characterization of the synthetic samples was carried out using a HORIBA XploRa Plus/LabRAM HR Evolution Raman spectrometer at the School of Earth Sciences and the State Key Laboratory of Geological Processes and Mineral Resources, China University of Geosciences (Wuhan).

2.4. Synchrotron-Based X-ray Diffraction. Synchrotron-based XRD experiments at ambient pressure and high pressure were conducted at beamline 13-BM-C of the Advanced Photon Source, Argonne National Laboratory. A short symmetric DAC with 300 μm diameter Boehler-Almax diamonds was used to achieve high pressure in XRD experiments. A hole of ~150 μm diameter was drilled in an indented ~35 μm thick rhenium gasket as the sample chamber to load the sample. Neon was also loaded into the sample chamber as the pressure-transmitting medium along with a ruby as the pressure calibrant. The collected 2-D XRD patterns were integrated using the Dioptas software,³² and the lattice parameters were refined using the PDindexer software.³³ The obtained *P*–*V* relation was fitted by a Birch–Murnaghan equation of state (EoS) using Eosfit.³⁴

2.5. Transmission Electron Microscopy. The TEM analyses were performed by JEOL JEM-F200 at the Institute of Tibetan Plateau Research, Chinese Academy of Sciences, at an accelerating voltage of 200 kV with a double-tilt specimen holder. The TEM sample recovered from the MAP experiment was crushed between two glass slides before loading the powders onto the lacey-carbon thin film of a copper TEM grid.

3. RESULTS AND DISCUSSION

3.1. Raman Spectroscopy. Raman spectroscopy was employed to characterize the types of substances and the chemical bonds of the studied materials. Representative Raman spectra of the starting material (C₁₄H₁₂, *trans*-stilbene) and run products are shown in Figure 1. The Raman signals of hydrocarbon intermediates produced by experiments heated to 800 °C are dominated by a fluorescent background. The quenched samples from experiments at 1200 and 1600 °C and 15.5 GPa show characteristic diamond peaks at 1330 and 1333 cm^{−1}, respectively (Figure 1).

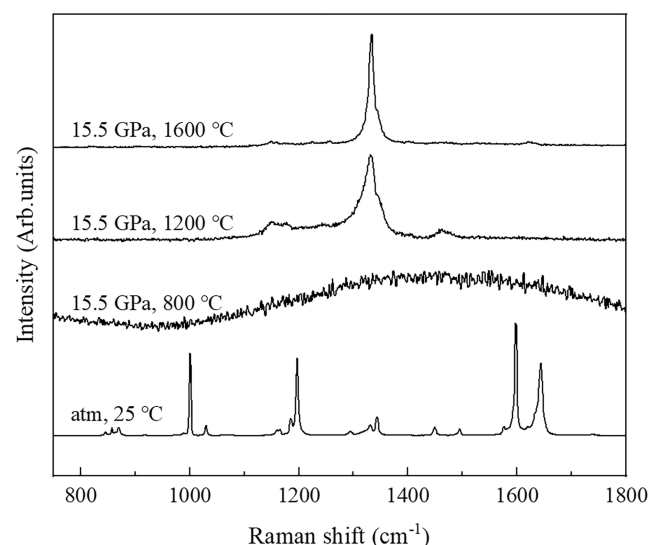


Figure 1. Representative Raman spectra of the starting material (C₁₄H₁₂, *trans*-stilbene) and quenched run products at 15.5 GPa and 800, 1200, and 1600 °C. Raman analysis revealed intense organic fluorescence at the 800 °C run, and characteristic diamond peaks (near 1332 cm^{−1}) emerged from 1200 and 1600 °C runs.

Synthetic diamonds at 1200 °C exhibit a slightly lower wavenumber (1330 cm⁻¹) compared to those synthesized at 1600 °C (1333 cm⁻¹). Previous studies have revealed that in ultrasmall nanodiamonds (<10 nm), the characteristic Raman peak of diamond displays a size-dependent red-shift, and the magnitude of the red-shift progressively increases as the nanoparticle's dimensions decrease. The phenomenon is attributed to the enhanced phonon confinement effects arising from quantum confinement-induced modifications in vibrational mode density.^{26,27} It indicates that when a diamond is reduced to the nanoscale, the spatial distribution of phonons becomes confined. In addition, the asymmetry of the Raman peak at around 1333 cm⁻¹ was observed, similar to the observations in previous studies.^{16,25–27,35} The starting material C₁₄H₁₂ in this study excluded the effect of halogens, and this peak asymmetry may be attributed to either the phonon confinement effect, or the overlapping between the diamond peak and the deformation vibrations of C–H bonds at 1340 cm⁻¹, or a combination of both factors^{36,37} (Figure 2).

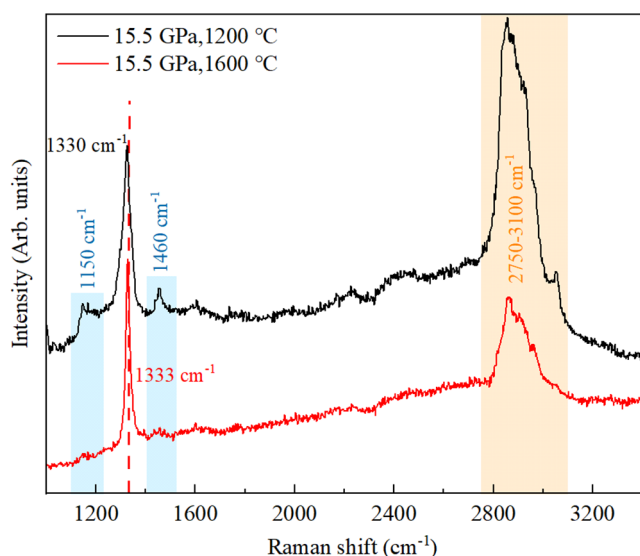


Figure 2. Raman spectra of nanodiamonds synthesized at 15.5 GPa and 1200 and 1600 °C. Nanodiamonds synthesized at 1200 °C show clear trans-polyacetylene peaks around 1150 cm⁻¹ and 1460 cm⁻¹ and strong CH_x peaks from 2750 cm⁻¹ to 3100 cm⁻¹, which reveal the high concentration of hydrogen on the surface of nanodiamonds.

In the Raman spectrum of diamond synthesized at 15.5 GPa and 1200 °C, two additional peaks, one around 1150 cm⁻¹ and the other around 1460 cm⁻¹, were observed. These two peaks shrank for the diamond synthesized at a higher temperature of 1600 °C. These peaks may have originated from trans-polyacetylene segments at grain boundaries and surfaces.³⁸

The diamond peaks were accompanied by a set of peaks around 2900 cm⁻¹, which was due to surface C–H termination at 15.5 GPa and 1200 and 1600 °C. This finding aligns with prior research on hydrogen-terminated nanodiamonds and hydrogenated diamond surfaces, while the demonstrated spectral features specifically confirm the characteristic surface chemistry of hydrogen-terminated nanodiamonds.^{24,39} Ekimov et al. also observed CH_x vibrations (2750–3100 cm⁻¹) in nanodiamonds synthesized at high temperature and pressure^{15,27,28} and suggested that the dehydrochlorination polymerization of halogenated hydrocarbons promotes the

formation of hydrogen-terminated nanodiamonds. Overall, the Raman peaks show no significant differences between those synthesized from hydrocarbons and halogenated hydrocarbons. As the temperature increases, the ratio of CH_x to diamond peaks decreases, which may be caused by the reduction of CH_x bonds and a decreased ratio of the surface area to the volume of the probed nanodiamond.

3.2. X-ray Diffraction and Transmission Electron Microscopy. X-ray diffraction was employed to analyze the crystal structure and particle size of the nanodiamonds (Figure 3). The observed XRD patterns can be well attributed to the diamond diffraction. The diamond peaks are broad, indicating the formation of nanodiamonds.⁴⁰ The unit-cell parameters were determined by fitting the XRD patterns collected under ambient conditions. The zero-pressure lattice parameter and volume of the sample synthesized at 15.5 GPa and 1200 °C with a higher hydrogen concentration are $a = 3.585(12)$ Å and $V = 46.1(7)$ Å³, respectively, and those of the sample synthesized at 15.5 GPa and 1600 °C with a lower hydrogen concentration are $a = 3.567(2)$ Å and $V = 45.4(1)$ Å³, respectively. In comparison, the zero-pressure volume of nonhydrogenated diamond is 45.38 Å³.⁴¹ These zero-pressure volumes, particularly of the two samples from this study, show a positive correlation with the extent of hydrogenation.

The characteristic full width at half-maximum (FWHM) and θ values of (111), (220), and (311) peaks were used to calculate the crystalline sizes and strain of the synthetic samples through the Williamson–Hall equation:

$$\beta = \frac{K\lambda}{d} + 4\epsilon \sin \theta \quad (1)$$

where β is the FWHM of the diffraction peak, K is the Scherrer constant (typically taken as 0.89), λ is the wavelength of the X-ray, d is the crystalline size, ϵ is the lattice strain, and θ is the Bragg angle. The crystalline sizes were calculated to be 3.02 and 7.23 nm for the nanodiamonds synthesized at 15.5 GPa and 1200 °C and 1600 °C, respectively. For comparison, the Scherrer method was also used to approximate the crystalline size of nanodiamonds, which obtained 2.6 and 6.4 nm for products from 15.5 GPa and 1200 and 1600 °C, respectively. The crystalline sizes determined using two methods are generally consistent with each other, while the slighter underestimation by the Scherrer method may originate from the ignorance regarding lattice strain. The strain was 0.45% and 0.1% for the nanodiamond synthesized at 1200 and 1600 °C, respectively, showing a similar trend to that by Ekimov et al.²⁷ such that the lattice strain decreases with increased grain size and synthetic temperature.

The average grain sizes of nanodiamonds synthesized are calculated to be 7.23 nm for those synthesized at 1600 °C and 3.02 nm for those synthesized at 1200 °C, which are smaller than those of the nanodiamonds synthesized before at similar temperature, lower pressure, and with a shorter heating duration^{26–28,35,42} (Figure S1). It is well established that an elevated temperature or extended heating duration significantly facilitates grain growth. On the other hand, higher pressure within the diamond stability field significantly enhances the nucleation density of diamond crystallites, facilitating the formation of nanodiamonds.¹⁸ Additionally, the Au capsule prevents the hydrogen or small hydrocarbon molecules to escape under high temperature and pressure. These molecules are then converted to hydrogen-terminated nanodiamonds or stored on the grain boundary of nanodiamonds, preventing the

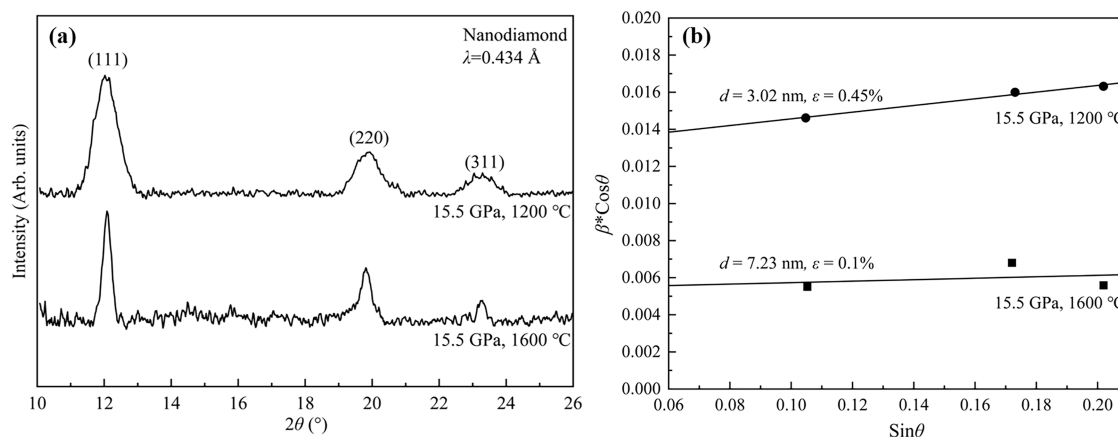


Figure 3. (a) X-ray diffraction patterns of the samples synthesized at 15.5 GPa and 1200 and 1600 °C. (b) Plot of $\beta^*\cos\theta$ vs $\sin\theta$ for the two synthesized samples and the fitted grain size and lattice strain from the Williamson–Hall equation.

further growth of nanodiamonds. Thus, we infer that the hydrogen/hydrocarbon molecules sealed in a closed environment may facilitate the formation of smaller-sized hydrogen-terminated nanodiamonds. Overall, the smaller grain sizes of nanodiamonds in this study compared to those synthesized at similar temperature and shorter duration (Figure S1) are likely due to the higher synthesis pressure and the H-species confined in the closed system in our experiments.

TEM analysis was carried out to identify the structure and morphology of hydrogen-terminated nanodiamonds synthesized at 15.5 GPa and 1600 °C (Figures 4 and S2). The

regions exposed to higher temperatures (promoting larger crystals). In addition, TEM directly images physical crystal dimensions, unaffected by lattice strain or diffraction artifacts. Thus, the size from the TEM image may better reflect the correct size range of the nanodiamond. The selected area electron diffraction (SAED) pattern shown in Figure 4b evidences a diamond crystal structure by the reflections of (111), (200), and (311) with the d spacing of $d(111) = 2.049$ Å, $d(220) = 1.252$ Å, and $d(311) = 1.073$ Å, respectively. High-resolution TEM (HRTEM) and fast Fourier transformation (FFT) techniques were used to show the microstructure of the nanodiamonds. The axis of the particle can be determined as $[-110]$ using HRTEM and the corresponding FFT from the distances of $d(111) = d(1\bar{1}1) = 0.204$ nm and the angle 70.6° between the two planes (Figure 4c,d). The spacings, as measured by HRTEM and its corresponding FFT, are consistent with the ones obtained by the XRD and SAED patterns with $\sim 1\%$ discrepancy, within the conventional error range by the HRTEM+FFT analysis.

3.3. Compressibility of Hydrogen-Terminated Nanodiamond. In previous studies, hydrogen-terminated nanodiamonds have been synthesized several times using different starting materials and P – T conditions. However, the compressibility of synthesized samples has never been investigated so far. High-pressure experiment using DAC combined with the synchrotron-based XRD was performed on hydrogen-terminated nanodiamond synthesized at 15.5 GPa and 1600 °C to investigate its compressibility (Figures 5 and S3). No phase transition or volume discontinuity was observed up to 33.6 GPa at room temperature (Figure 6 and Table S1). The P – V data were weighted by the uncertainties in both pressure and volume and then fitted by a second-order Birch–Murnaghan EoS, which obtained the bulk modulus $K_0 = 424(12)$ GPa, its first derivative, $K'_0 = 4$ (fixed), and zero-pressure volume $V_0 = 45.50(2)$ Å³. The V_0 obtained from the equation of state is within the error range compared to ambient volume directly determined by XRD and TEM. The zero-pressure volume of a hydrogen-terminated nanodiamond was 0.26% larger than that of a hydrogen-free diamond,⁴¹ but 0.17% smaller than that of a similar-sized nanodiamond synthesized from halogenated hydrocarbons.²⁷ The bulk modulus of a monocrystal diamond is about 440 GPa⁴³ (Table 1). Previous studies on the bulk modulus of nanodiamonds were conducted by synchrotron-based

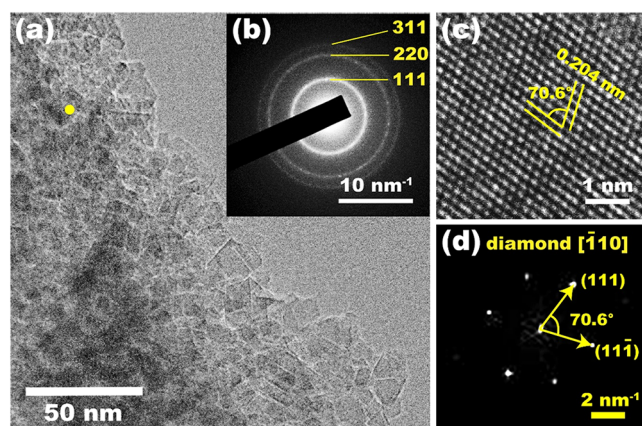


Figure 4. (a) Transmission electron microscopy micrograph of the nanodiamonds synthesized at 15.5 GPa and 1600 °C. (b) SAED pattern corresponds to the area of (a). (c) High-resolution TEM image obtained from the region marked by a yellow dot in (a). (d) FFT pattern of (c).

nanodiamonds are closely packed together. The grain sizes of nanodiamonds revealed by TEM are approximately 6–15 nm, while those inferred from XRD are 7.23 nm. The discrepancy between the TEM and XRD analyses was also observed in the previous study, which may be attributed to several factors.³⁵ First, TEM selectively visualizes localized regions of the sample, potentially highlighting larger crystals within the imaged area, whereas XRD provides volume-averaged crystallite sizes across the entire sample, inherently weighted toward smaller dimensions due to statistical averaging. Second, during the synthesis process, temperature gradients within the capsule may lead to nonuniform crystal growth. TEM may capture

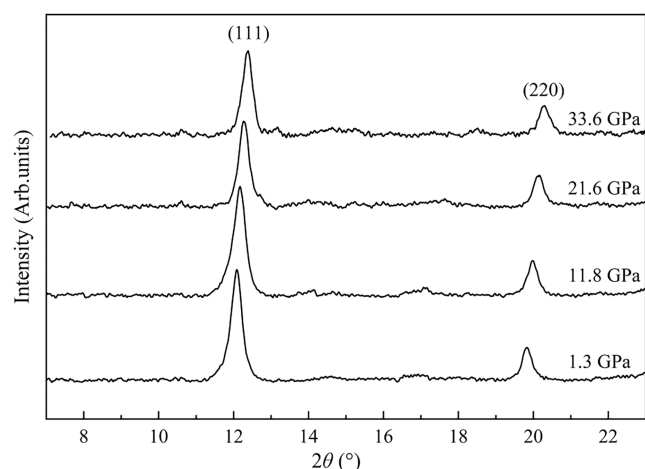


Figure 5. Representative XRD patterns of hydrogen-terminated nanodiamonds under high-pressure conditions. Peaks of Ne and diamond anvil were masked for clarity. XRD peaks shift to higher 2θ angles, owing to lattice contraction under high pressure.

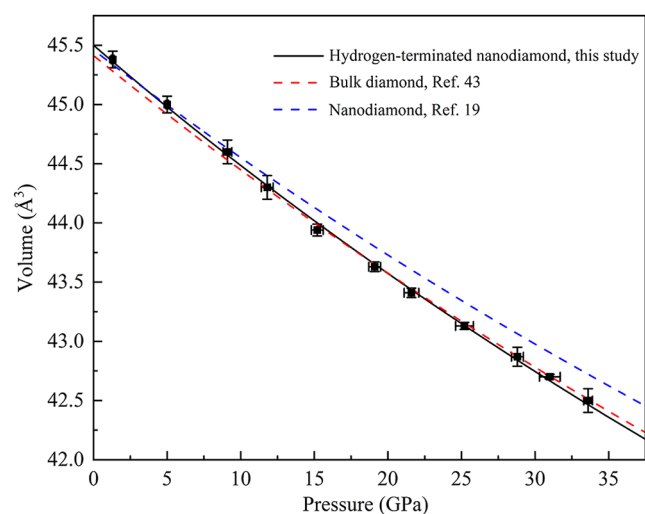


Figure 6. Unit-cell volume of the hydrogen-terminated nanodiamond as a function of pressure at room temperature compared with those of nanodiamond and bulk diamond.

XRD^{19,43,44} Raman spectroscopy,^{45,46} and calculations,^{29,47,48} which typically possess a higher bulk modulus than bulk diamond (Table 1). However, in this study, the bulk modulus of the hydrogen-terminated nanodiamond was determined to

be 424(12) GPa, which is lower than the bulk moduli of the bulk diamond and hydrogen-free nanodiamonds.

Similar to previous synthesis of nanodiamonds from halogenated organics,²⁷ we observed an increase in the nanodiamond lattice parameter compared to that of the bulk diamond. In addition, the bulk modulus of hydrogen-terminated nanodiamond in this study was found to be lower compared with that of the bulk diamond. The observed softening likely stems from lattice relaxation or defects induced by surface hydrogenation, weakening the overall bonding network. This feature allows hydrogen-terminated nanodiamonds to have a bulk modulus lower than that of bulk diamonds. However, a more definitive reason for the elastic softening will remain to be unveiled in the future.

4. CONCLUSIONS

Our study synthesized ultrasmall-sized hydrogen-terminated nanodiamonds by HPHT experiments using *trans*-stilbene as the starting material and a sealed gold capsule as the sample chamber. We found that high pressure and fluid sealing in the capsule can hinder the growth and recrystallization of nanodiamonds. Higher synthesis temperature leads to a larger grain size and a smaller lattice strain in the grain. Elevated temperature also results in a lower extent of hydrogenation and a smaller unit-cell volume at ambient conditions. We further investigated the compressibility of the newly synthesized hydrogen-terminated nanodiamonds and found that it has a lower bulk modulus of 424(12) GPa compared to bulk diamonds and the conventional nanodiamonds. This elastic softening likely stems from lattice relaxation or defects induced by surface hydrogenation. Overall, we presented the HPHT synthesis of hydrogen-terminated diamonds directly from the hydrocarbon system and showed the correlation between extent of hydrogenation, lattice parameters, lattice strain, elastic properties, and P – T conditions. It offers a method to regulate the properties of surface-functionalized nanodiamonds by HPHT synthesis.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.inorgchem.5c00974>.

Additional experimental details, data set, and data analysis (PDF)

Table 1. Equation of State (EoS) Parameters of Hydrogen-Terminated Diamond Compared with Those of Nanodiamonds and Bulk Diamond in Previous Studies

phase	size	P (GPa)	K_0 (GPa)	K_0'	V_0 (Å ³)	methods	references
nanodiamond	7.23 nm	0–33.6	424 (12)	4 (fixed)	45.50 (2)	XRD	this study
nanodiamond	<5 nm	0–85	~500	4 (fixed)		XRD	Pantea et al., 2006 ⁴⁴
nanodiamond	35–80 nm	0–29	474 (15)	4.18	45.46 (4)	XRD	Watkins et al., 2022 ¹⁹
nanodiamond	6–24 nm		480–670			DFT	Khabibrakhmanov et al., 2020 ²⁹
nanodiamond	2–5 nm	0–50	564			Raman	Popov et al., 2017 ⁴⁵
nanodiamond	~25 nm	0–50	443			Raman	Popov et al., 2017 ⁴⁵
nanodiamond	2–5 nm	26–66	607			Raman	Popov et al., 2019 ⁴⁶
diamond (¹³ C)	powder	0–8	438 (8)	4 (fixed)	45.383 (6)	XRD	Gillet et al., 1999 ⁴³
diamond	2–4 μm	0–21	446 (4)	4 (fixed)	45.413 (3)	XRD	Gillet et al., 1999 ⁴³

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Author Contributions

Y.Z.: writing, reviewing, editing, methodology, and data analysis. J.N.: writing and methodology. H.Z.: methodology and data analysis. F.Z.: writing, reviewing, editing, supervision, funding acquisition, and conceptualization. B.C.: methodology and funding acquisition. X.W.: methodology and funding acquisition. A.H.S.: methodology. D.Z.: methodology. X.L.: writing, reviewing, editing, supervision, methodology, funding acquisition, and conceptualization.

Notes

The authors declare no competing financial interest.

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