High-Pressure Synthesis of cBN Nanoparticles with High-Density Nanotwin Substructures

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ABSTRACT: Cubic boron nitride (cBN) exhibits superior hardness and strength as compared with other ceramics that are commonly used as abrasives and cutting tools. The recently synthesized polycrystalline cBN bulk material with ultrafine nanotwin substructures possesses a remarkable combination of high hardness, fracture toughness, and thermal stability. The twin substructure has been demonstrated to exert dislocation-blocking effect similar to grain boundary, leading to strengthening of materials. So far, the synthesis of cBN nanoparticles with ultrafine nanotwin substructures has not yet been realized. Herein, we report on the synthesis of cBN nanoparticles from onion-like boron nitride (oBN) under high pressure and high temperature. Multiple characterization methods, including X-ray diffraction, Raman spectroscopy, and high-resolution transmission electron microscopy, revealed that the as-prepared cBN nanoparticles contained high-density nanotwin substructures. The use of the highly wrinkled oBN precursor and well-designed synthetic method were the key to obtain these unique ultrafine nanotwinned cBN nanoparticles.

INTRODUCTION

The most important superhard materials, diamond and cubic boron nitride (cBN) are extensively applied in turning, cutting, grinding, drilling, and other modern processing operations.1 Despite its inferior hardness compared with diamond, cBN outcompetes diamond in many applications owing to its superior thermal and chemical stability. For instance, cBN has less affinity for iron than diamond and is therefore very suitable for cutting and processing of iron-based alloys. Tools based on superhard cBN materials, such as polycrystalline cBN cutters, cBN grinding wheels, and cBN-coated drill bits, are widely used in the modern machining industry.

Crystals of cBN were first synthesized in 1957 by Wentorf using a high-pressure and high-temperature (HPHT) method in the presence of metal nitriles as catalysts.2 Over the following decades, cBN has been prepared via numerous methods, such as vapor phase deposition,3 solvothermal reaction,4 laser ablation,5 and plasma spraying.6 However, to the best of our knowledge, domains with nanotwin substructures have only occasionally been observed in synthetic cBN nanocrystals;7–10 and few studies have reported the synthesis of cBN with ubiquitous ultrafine nanotwin substructures. Recently, significant breakthroughs in the synthesis of cBN and diamond polycrystalline bulk materials with pervasively ultrafine nanotwin substructures have been achieved by directly transforming onion-like precursors under HPHT conditions.11,12 These unique onion-like precursors possess a highly wrinkled and curved structure that favors the evolution of high-density nanotwin substructures during the phase transition process. Although ultrafine nanotwinned cBN and diamond polycrystalline bulk materials have been synthesized, cBN and diamond nanopowders possessing high-density ultrafine nanotwin substructures have not been reported to date.

In this study, nanoscaled cBN particles containing ubiquitous ultrafine nanotwin substructures were successfully synthesized using the onion-like boron nitride (oBN) precursor in conjunction with a well-designed synthetic method. Potassium chloride (KCl) was used as a medium to effectively separate the precursor nanoparticles, so that each oBN nanoparticle would transform into a cBN nanoparticle with high-density nanotwin substructures individually. Microstructures of the oBN precursor and the obtained ultrafine nanotwinned cBN nanoparticles were examined in detail using high-resolution transmission electron microscopy (HRTEM) to elucidate the structural evolution.

RESULTS AND DISCUSSIONS

The precursor oBN nanoparticles (Figure 1a) were prepared according to a previously reported method.13 Statistical analysis of more than 600 nanoparticles revealed that the oBN nanoparticles had diameters ranging from approximately 10–40 nm with an average diameter of 130 nm, as shown in Figure 1b. Figure 1c presents an HRTEM image of an oBN
nanoparticle, revealing concentric graphite-like shells with a high degree of structural disorder due to numerous defects such as lattice puckering and bending as well as stacking faults. As shown in Figure 1d, the reflection peaks in the X-ray diffraction (XRD) pattern for oBN shifted toward a lower angle compared with hexagonal BN (hBN); the intershell spacing of oBN calculated from the diffraction peak at 2θ ≈ 25.3° was 0.352 nm, which is larger than the corresponding values of 0.3328 nm for the (002) reflection of hBN and 0.334 nm for the (003) reflection of rhombohedral BN (rBN). This lattice expansion likely originated from internal stress caused by the highly curved shell and stacking faults. Figure 1e shows the Raman spectrum of oBN, which contained a weak excitation peak at 1370 cm$^{-1}$ and a broaden peak centered at 2651 cm$^{-1}$ and a broaden peak centered at 343.9°, 50.28°, 74.33°, and 90.22°, which correspond to the (111), (200), (220), and (311) crystalline planes of cBN, respectively, indexed to the (111), (200), (220), and (311) crystalline planes of cBN. The weak intensity of E$_{2g}$ mode and the broaden peak indicate that oBN nanoparticles had a high degree of structural disorder, which is consistent with the HRTEM observations.

Figure 2a presents the XRD pattern of the synthesized cBN nanoparticles. Four characteristic peaks were observed at 43.39°, 50.28°, 74.33°, and 90.22°, which correspond to the (111), (200), (220), and (311) crystalline planes of cBN, respectively. To further examine the intrinsic structure, the Raman spectrum was measured as shown in Figure 2b. On the basis of previously calculated and experimental results, both of the excitation peaks could be assigned to cBN. The specific peaks at 1055 and 1303 cm$^{-1}$ can be attributed to scattering by the transverse optical and longitudinal optical phonon modes of cBN, respectively. It is worth noting that the peak shapes displayed low-frequency asymmetric broadening owing to the presence of numerous defects in the crystal. The presence of numerous defects in the crystal will break the translation symmetry, relax the conservation law of wave vector, and lead to the low-frequency asymmetry profile of the Raman peak.

Figure 3a presents a low-magnification bright-field TEM image of the synthesized cBN nanoparticles, which possessed diameters on the order of tens to hundreds of nanometers. The cBN nanocrystals were quasispherical, as previously reported for diamond nanoparticles. Such a morphology in nanoparticles results from a tendency to achieve lower surface energy. Statistical analysis of 485 as-prepared c-BN nanoparticles observed in TEM images revealed that the diameter ranged from 10 to 300 nm with an average diameter of approximately 85 nm, as shown in Figure 3c. Figure 3b shows a selected area electron diffraction (SAED) pattern taken from a wide area, revealing the presence of the cBN structure in accordance with the XRD results. The diffraction rings were, respectively, indexed to the (111), (200), (220), (311), (400), and (331) planes of cBN.

The substructure of the synthesized cBN nanoparticles was further examined via scanning TEM (STEM) images. Figure 4a–c displays a series of annular dark-field (ADF)-STEM images of the same region of the prepared cBN crystals at different tilt angles. Under ADF imaging, the lattice direction changes across the twin boundary, resulting in a change in diffraction contrast. Twin substructures can be observed in each nanoparticle as the specimen was tilted along the x- and y-axes. Figure 4d presents a typical ADF-STEM image of an individual nanoparticle viewed along the [101] zone axis, in which the twinning-induced diffraction contrast is clearly visible. It is readily apparent that the interior of the cBN nanoparticle contained abundant twin substructures.

The twin substructures in cBN nanoparticles of various sizes were further examined in detail via HRTEM. Figure 5a presents a TEM image of a cBN nanoparticle and its corresponding SAED pattern. The two-fold pattern indicates a successive twin substructure in the nanoparticle.
shows HRTEM images of cBN nanoparticles with diameters of approximately 70, 110, 210, and 270 nm, respectively. Notably, high-density of nanotwin substructures were consistently observed in the synthesized cBN nanoparticles with different sizes. In the phase transition process, the existence of plentiful defects in oBN nanoparticles greatly promoted the formation of phase-transition twins. Hence, the naturally puckered BN layers and the high concentration of stacking faults in the precursor nanoparticles were the main reasons for the formation of high-density phase-transition twins in the resulting cBN nanoparticles. In comparison, flawlessly graphite-like BN precursors commonly generate cBN nanoparticles with negligible nanotwins. 7,8,10 As shown in the HRTEM images, some stacking faults were also observed in the synthesized cBN nanoparticles.

Figure 5f shows the twin thickness distribution measured from the 316 nanotwins observed in the HRTEM images. The most of twins in the synthesized cBN nanoparticles have the thickness less than 5 nm, but twin thickness ranges from approximately 1 to 50 nm. In comparison, the reported nanotwinned cBN polycrystalline bulk material did not exhibit relatively wide twins (>15 nm). 11 This difference is mainly attributable to the further extrusion and plastic deformation of adjacent grains in polycrystalline bulk during densification. The formation of deformation twins relies on the motion of \{111\}(\{112\) partial dislocations during plastic deformation. 21 Thus, numerous deformation twins were generated inside the nanograins of cBN bulk material during the densification process. In this work, as the oBN nanoprecursors were uniformly separated by the KCl medium, the cBN nanoparticles did not undergo severe plastic deformation during the
densification. Consequently, the number of deformation twins in the cBN nanoparticles was largely reduced compared with that in polycrystalline bulk material, resulting in a wide range in twin thicknesses. As is well-known, nanotwinning reinforcement has been proved in polycrystalline bulk materials of both metals and covalent materials. Therefore, the synthesized cBN nanoparticles with high-density nanotwin substructures may also have an enhancement on its properties, which is worthy anticipated.

■ CONCLUSIONS

Ultrafine nanotwinned cBN nanoparticles were synthesized using the unique oBN nanoparticles as the starting material and an elaborate synthetic method. The highly wrinkled and defective oBN prefer to phase transition into nanotwinned cBN under HPHT conditions, and the additive KCl medium can effectively separate the precursor nanoparticles, thus leading to the direct transformation of each oBN nanoparticle into individual cBN nanoparticles with high-density nanotwin substructures inside. Further microstructural observations reveal that the average diameter of the synthetic cBN nanoparticles is about 85 nm, and the interior of cBN nanoparticles contains pervasively ultrafine nanotwin substructures with thickness mostly less than 5 nm. Our findings demonstrate a new strategy for fabricating nanosized cBN particles with nanotwinned morphologies by view of suitable precursor selection and synthesis process adjustment.

■ EXPERIMENTAL METHODS

Unlike the previous synthesis process of nanotwinned cBN polycrystalline bulk material, the prefabricated blocks used for the HPHT experiments in the present work were composed of a mixture of oBN nanopowders and KCl. The detailed manufacturing process of the prefabricated blocks was as follows. The oBN nanopowders and KCl were initially added to methanol, and after the KCl had fully dissolved, the oBN nanopowders were further dispersed via ultrasonication. To remove the methanol solvent and avoid agglomeration of the oBN nanopowders, the magnetic stirring was continued overnight at 50 °C to afford a solid powder consisting of uniformly distributed oBN and KCl. This powder was pressed into blocks for the HPHT experiments. The synthesis experiments were performed using a double-stage T2S multi-anvil system (Rockland Research Corporation). A standard compress 10/5 sample assembly, consisting of a 10 mm Al₂O₃ doped MgO octahedron with a Re heater and a LaCrO₃ thermal insulator, was used. The temperature was directly measured using C-type W5%Re–W26%Re thermocouples, and the pressure was estimated from previously determined calibration curves. The sample was compressed to 15 GPa at room temperature and then heated to a final temperature of 1800 °C at a rate of 20 °C/min. The final temperature was maintained for 5–30 min. The melting point of KCl is more than 2000 °C at 15 GPa, which is far above the temperature used in this experiment. Therefore, KCl only acts as a pressure medium to isolate the precursors. After the pressure and temperature had completely released to ambient conditions, the cBN nanoparticles were washed with deionized water to remove the KCl.

XRD patterns were acquired using an X-ray diffractometer (D8 ADVANCE, Bruker) with Cu Kα radiation. Raman spectra were collected using a LabRAM-HR spectrometer (HORIBA Jobin-Yvon) with 532 nm excitation (20 mW YAG laser) at ambient conditions. TEM images were recorded using a Talos F200X TEM/STEM (FEI) instrument operating at an accelerating voltage of 200 kV. The TEM specimens were prepared by evaporating a few droplets of an ethanolic solution of cBN nanoparticles treated with ultrasonic onto ultrasonicated copper grids.

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Notes
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■ ABBREVIATIONS

cBN, cubic boron nitride; oBN, onion-like boron nitride; hBN, hexagonal boron nitride; rBN, rhombohedral boron nitride; HPHT, high-pressure and high-temperature; KCl, potassium chloride; XRD, X-ray diffraction; TEM, transmission electron microscopy; HRTEM, high-resolution transmission electron microscopy; STEM, scanning transmission electron microscopy; ADF, annular dark-field; SAED, selected area electron diffraction; SFs, stacking faults; TBs, twin boundaries

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