Research Article

A Novel Technique for the Synthesis of Nanodiamond Powder

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We developed a novel technique to synthesize nanodiamond powder through the decomposition of graphitic C_3N_4 under high pressure and high temperature. The nanodiamond obtained by the present method is in an extremely pure form with no sp^2 carbon contaminations. Individual nanodiamond grains are very uniform in size and virtually monodispersed single crystals. The grain size can be controlled from less than 1 nm to several hundred nanometers by adjusting the heating temperature (and also potentially by controlling pressure) used for the synthesis. The present product requires neither post-surface treatment to remove outer shell made of sp^2 carbons nor degglomeration and size classification unlike the case for nanodiamond obtained by the conventional TNT detonation method.

1. Introduction

Nanodiamond powder has been adopted for many industrial uses such as for polishing, coating, lubricant additives, and catalysts due to its excellent thermal and chemical stability combined with the superhard nature [1]. Due to the properties of nontoxicity and high biocompatibility, it has also attracted considerable attention on some new applications, especially in the biomedical field (i.e., imaging, diagnostics, and drug or gene delivery) [2, 3]. To date, the major commercially available technique for nanodiamond powder synthesis is the trinitrotoluene (TNT) detonation method. In this technique, nanodiamond crystals with grain sizes in nanometric ranges were obtained as a result of incomplete combustion of the explosive (TNT) in a closed container. The detonation process is so complex and instantaneous that the indisputable mechanism of nanodiamond formation during detonation has not been put forward so far, although several models have been suggested [4, 5]. The detonation nanodiamond usually consists of a diamond core of 2–4 nm in diameter and an outer surface composed of a graphitic shell or amorphous carbon, which is dominated by dangling bonds. Although the presence of such disordered sp^2 carbon and surface dangling bonds can be utilized from the viewpoint of functionalization, it is rather unfavorable because it causes

strong agglomeration of primary nanodiamond particles (<10 nm), forming secondary clusters up to 100 nm or even larger [3]. In order to fully utilize the intrinsic feature of nanodiamond itself, deaggregation into individual primary particles is often needed. Ozawa et al. [6], for example, demonstrated that mechanical milling using ceramic micro-beads combined with ultrasonic vibration is effective for the degglomeration. However, such mechanical milling may result in chemical/physical contamination by the milling media, and therefore degglomeration of detonation nanodiamond particles is still a challenging task [7].

Here we report a novel technique to produce nanodiamond powders based on a static high pressure and high temperature method. The nanodiamonds obtained by this technique are extremely pure with no contamination of sp^2 carbon phases and equigranular single crystal particles in a virtually monodispersed state.

2. Experimental Method

Nanodiamond powder synthesis was conducted by high-pressure experiments using a 2000t multianvil apparatus (ORANGE-2000) at Ehime University. WC anvils of 4 mm truncation edge-length and MgO pressure medium (octahedron) of 10 mm edge-length were used. Platinum capsule

FIGURE 1: The variation of XRD (a) and Raman (b) patterns collected from the samples heated to different temperatures at 22 GPa, respectively. Inset in (a) is a microscopic image of diamond nanopowder enclosed in a Pt capsule (recovered from 1600°C).

was used to seal the samples thoroughly during high P-T experiments. The details of the cell assembly used were described in our earlier report [8]. The starting material used was graphitic C_3N_4 (g- C_3N_4) prepared by a benzene-thermal reaction between $\text{C}_3\text{N}_3\text{Cl}_3$ and NaNH_2 at 220°C for 12 hours by following the method described in [9]. The g- C_3N_4 obtained in such a way is a light yellowish-brown powder of amorphous-like, poorly crystalline particles [8]. The sample was compressed to a desired pressure at room temperature, heated to 800–2000°C for 5–30 min, and then quenched and decompressed to ambient condition. The recovered samples were first analyzed by microfocus X-ray diffraction (Bruker AXS, M21X) and Raman (Renishaw, RS-SYS1000) for phase identification and then examined by field-emission scanning electron microscopy (FE-SEM: JEOL, JSM-7000F) and transmission electron microscopy (TEM: JEOL JEM-2010) for microtexture observation.

3. Results and Discussion

In the present study, all the nanodiamond samples were obtained through the decomposition of g- C_3N_4 at high P-T conditions. After pressure release, a sample container made of platinum was taken out from the cell, and one of the capsule ends was carefully cut open by using a sharp razor. Note that there is clearly a space (gap) between the white diamond powders compacted in a cylindrical form and the surrounding platinum capsule (Figure 1(a) inset). This opening space is probably derived from the liquid nitrogen that had been formed through the decomposition of g- C_3N_4 at high temperature but was vaporized and released to the air

during decompression. In fact, the phase stability diagram for pure nitrogen obtained through experimental studies [10] shows that nitrogen melts to form N_2 above 700–1000 K in the studied pressure range (15–25 GPa). Therefore, the diamond powders produced in the present study are considered to crystallize in liquid nitrogen regime.

Figure 1 shows X-ray diffraction patterns and micro-Raman spectra collected from the samples synthesized at 1000, 1400, and 1600°C at 22 GPa. The XRD result shows that diamond is the only phase found in the sample containers, although a few peaks forming the surrounding platinum capsule were also detected. The observed diamond 111 and 220 peaks are considerably broad and weak at 1000°C but become sharper and more intense with increase in heating temperature, suggesting a remarkable grain growth of the diamond crystals formed. It is also seen that the nanodiamonds obtained from 22 GPa apparently show broader peaks than those at 15 GPa, suggesting that the higher the synthesis pressure, the smaller the grain sizes of the diamond crystals formed.

The Raman spectrum of the sample quenched from 1000°C at 22 GPa shows continuous broad bands ranging from 1400 to 1600 cm^{-1} , which implies the presence of minor amounts of disordered (amorphous) carbon species such as diamond-like carbon [11] in addition to poorly crystalline diamond, while those of the samples recovered from 1400 to 1600°C are characterized by the diamond vibration mode centered at 1331 cm^{-1} (Figure 1(b)). The diamond Raman peak becomes sharper and more intense as the heating temperature increases, again suggesting significant grain growth of the crystals with temperature increase.

FIGURE 2: TEM images of nanodiamond samples recovered from different temperatures at 22 GPa: (a) 1000°C, (b) high-resolution image of (a), (c) 1400°C, and (d) 1600°C.

We also examined the nanodiamond products by transmission electron microscopy. Figure 2 shows TEM images of the nanodiamond samples synthesized at 1000–1600°C and 22 GPa. The product obtained from 1000°C was found to be so fine and poorly crystalline (Figure 2(a)) that individual crystals cannot be recognized even at the high magnification (Figure 2(b)). The selected area electron diffraction (SAED) pattern collected from a local area of 1.2 μm diameter shows two faint but continuous diffraction rings which can be indexed as 111 and 220 reflections of diamond, indicating a randomly oriented, amorphous-like feature of the product. On the other hand, the diamond crystals synthesized at temperatures above 1400°C show well-developed euhedral morphology with grain sizes ranging from several tens of nanometers to a half of micrometer as the heating temperature increases from 1400 to 1600°C (Figures 2(c) and 2(d)). SAED pattern analysis and high-resolution imaging also showed that these individual grains are purely single crystals of diamond with no graphite/amorphous carbon phases. It is also important to note that the nanodiamond crystals synthesized at a given pressure and temperature are remarkably uniform and all discrete unlike those produced from the TNT detonation methods.

Figure 3 shows the relationship between heating temperature and grain size of diamond produced at different pressures. It is clearly seen that the grain size of diamond crystals increases drastically (i.e., almost linearly in a log scale) from ~ 1 nm to $1 \mu\text{m}$ with increasing heating temperature. There also seems to be a pressure effect that the higher the pressure

FIGURE 3: The relationship between grain size and heating temperature of diamond produced at different pressures.

the larger the grain size of the diamond synthesized. Such a pressure effect can be interpreted in terms of the difference in activation energy required for the diamond nucleation at different pressures. In the theory of crystallization (e.g., [12]), the critical nucleus size (i.e., minimum size required to energetically stabilize the initial nuclei) generally decreases

with increase in pressure. In other words, at higher pressure the rate of nucleation tends to become predominant over the rate of the subsequent crystal growth, resulting in the formation of smaller crystals than the case at lower pressure.

Nanodiamond powders synthesized by the present high pressure and high temperature (HPHT) technique have some advantages over those obtained by the conventional TNT detonation method: nanodiamond by HPHT technique is a purely single phase of diamond with virtually no sp^2 carbon contamination (although the product synthesized at 1000°C and 22 GPa likely contains a minor amount of sp^2 carbon species as shown by its Raman spectrum), while detonation diamond occurs in the form of aggregated particles whose outermost layer is usually covered by sp^2 (graphitic/amorphous) carbons. This means that the nanodiamond prepared by the present technique does not require post-surface treatment unlike the latter case and can be used for various applications in the as-synthesized form. In addition, in the former case individual grains are dispersed single crystals of a uniform size range, which can be readily controlled by changing the heating temperature for synthesis; that is, degglomeration processing and particle size classification are also not necessary. Taking into account these superior features, nanodiamond synthesized by the present method is expected to expand the range of potential applications in various fields.

4. Conclusions

We found a new technique to synthesize diamond nanopowders through the decomposition of graphitic C_3N_4 under HPHT. Compared with nanodiamond obtained by the conventional TNT detonation method, the present product exhibits some outstanding features and advantages; it is purely a single phase of diamond with no sp^2 carbon contamination, it occurs substantially as monodispersive crystals of a uniform size range, and the grain size can be controlled by adjusting heating temperature for the synthesis. This means that the nanodiamond obtained by the present method requires neither post-surface treatment to remove sp^2 carbon outer shell nor degglomeration and size classification, which should be routinely performed for detonation nanodiamond. This novel method is important and helpful for producing high-purity nanodiamond powder and its potential applications in various fields.

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