

Large-scale synthesis and structure of boron nitride sub-micron spherical particles

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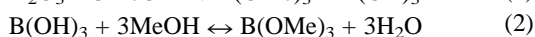
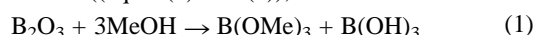
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A novel method, combining chemical vapor deposition and pyrolysis of trimethoxyborane under ammonia atmosphere, has been developed to synthesize spherical boron nitride particles with a uniform diameter distribution from 50 to 400 nm; chemical composition and high-resolution transmission electron microscopy analyses indicate that the sub-micron boron nitride particles exhibit a slightly distorted arrangement of the shell layers.

Boron nitride (BN) has received considerable attention due to its advantageous properties such as extreme hardness, high thermal conductivity, chemical inertness, transparency and electrically insulating performance. These properties make BN an interesting material for many applications such as lubricants, protective and optical coatings, advanced ceramic composites, and mold release liners.^{1–5} Considering the low filler loading of plate-like BN particles, it has been suggested to synthesize the spherical BN particles with very small diameters because this morphology could permit higher loading. Classical synthetic methods, such as high-temperature metallurgical syntheses,^{6,7} chemical vapor deposition (CVD)⁸ and polymer pyrolysis,⁹ usually result in platelet-like BN particles. Although boron halides reacting with ammonia has been the most popular system used in the CVD of BN,¹⁰ the formation of the spherical BN particles has still been performed using the reaction of boron trichloride and ammonia at low temperature.¹¹ The spray pyrolysis of poly(borazinylamine) precursor dissolved in liquid ammonia could also form spherical BN particles.¹² Recently, an inexpensive and easy method of aerosol assisted vapor deposition has been proposed for the formation of BN with the particles of spherical morphology.¹³ Therein, the BN particles with an average diameter of 1–2 μm were synthesized through the reaction between aerosol droplets containing water-soluble boric acid and ammonia at an elevated temperature.

In this communication, we describe an alternative route to synthesize spherical BN particles with uniform diameters ranging from 50 to 400 nm, by using a two-step synthetic process. The spherical B–N–O precursor was first synthesized at 700 °C by a CVD reaction of trimethoxyborane dissolved in methanol solution and ammonia, and then the oxygen was removed from the pyrolysis precursor *via* heating under ammonia atmosphere at 1100 °C. The technique described here, which is a continuous process, and produces low-cost, high-purity and high yield of the resultant material, is particularly useful for future commercial applications.

The CVD precursor, trimethoxyborane (B(OMe)₃) dissolved in methanol (MeOH), was prepared by direct esterification of boron oxide (B₂O₃) *via* the reactions between 1 mol of B₂O₃ and 7.5 mol of MeOH (eqns. (1) and (2)),¹⁴



The excess methanol is necessary for fully converting B₂O₃ to B(OMe)₃. The synthesized B(OMe)₃ is a colorless volatile liquid with a slightly lower density than water,¹⁴ and therefore, it is easy to transport the B(OMe)₃ by a nitrogen flow to a quartz tube mounted in a tube furnace, which was heated to 700 °C under an argon flow. Gaseous ammonia was fed simultaneously

into the tube and initialized the CVD reaction. After the reaction, a white powder was collected from the inner wall of the quartz tube. The powder was subsequently annealed at 1100 °C for 4 h under ammonia flow.

The phase purity and chemical composition of the powders were thoroughly examined by X-ray diffraction (XRD) using Cu-Kα radiation, Fourier-transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), high-resolution transmission electron microscopy (TEM), energy-dispersive X-ray (EDX) spectroscopy, and electron energy loss (EEL) spectroscopy.

The XRD pattern of the CVD product is shown in the bottom of Fig. 1. It contains two broad diffraction peaks located at the (002) and (100) reflection positions of hexagonal BN (h-BN) and/or at the (003) and (101) reflection positions of rhombohedral BN (r-BN),¹⁵ verifying the occurrence of the BN phase in the low-temperature CVD product. Chemical composition analysis indicates that the product contains B, N, O and small amount of carbon and hydrogen. The atomic ratio of B:N:O is varied dependent on the different measurement techniques. The average ratio is approximately 1.5:1:0.3, which corresponds to the stoichiometric composition of BN containing some boron-oxygen compounds.

The oxygen content could be effectively reduced and the low degree of crystallization could also be improved by further pyrolysis under ammonia at 1100 °C, as indicated by the XRD pattern of the powder sample after pyrolysis (top, Fig. 1). The pattern could be well indexed based on a mixed phase structure of h-BN and r-BN, although it exhibits broad reflections especially for the strongest (002) diffraction peak of h-BN and (003) of r-BN. The broad diffraction peaks might result from the poor crystallization or from the very small crystallite size.

SEM examination indicates that both products consist of spherical particles of a fairly uniform diameter. Fig. 2(a) shows a typical SEM image of the CVD sample. Although some particles with diameter larger than 100 nm could be observed

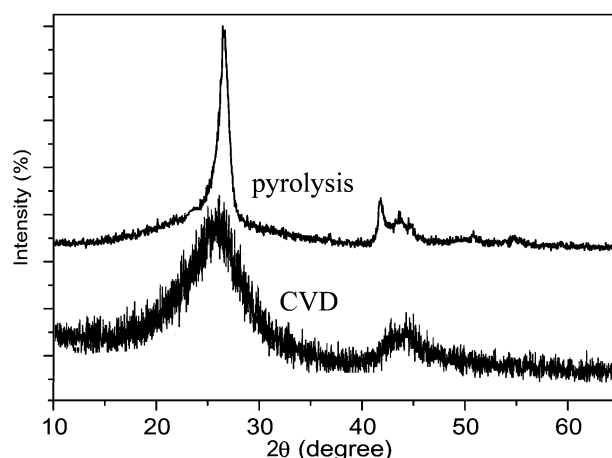


Fig. 1 XRD patterns of spherical BN particles synthesized by CVD reaction (bottom) of B(OMe)₃ and ammonia, and subsequent pyrolysis at 1100 °C for 4 h (top).

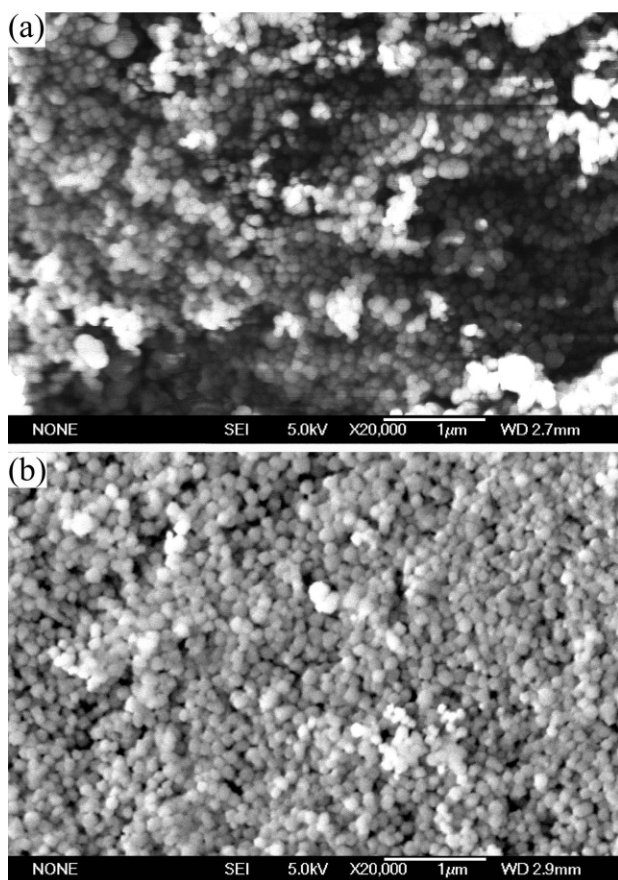


Fig. 2 SEM images of spherical BN particles synthesized by (a) CVD and (b) subsequent annealing at 1100 °C.

most of the BN particles are of 50–100 nm diameter with an average size of approximately 70 nm. The further pyrolysis under ammonia has less influence on the morphology of the BN particles; however, the size was found to be slightly increased. Fig. 2(b) shows the SEM morphology after annealing. The diameters increase to 50–400 nm.

EEL spectroscopy composition analysis and a high-resolution TEM image of the sample after pyrolysis are shown in Fig. 3. Only B and N characteristic K-edges can be clearly observed in the EELS spectrum. The N/B ratio calculated from this spectrum is 1.05. In fact, the N/B ratio obtained from many EEL spectra taken from the particles ranges from 1.15 to 0.85. No detectable C and O contents were observed in the product. Considering the EELS measurement experimental error, the synthesized particles exhibit a stoichiometric composition of

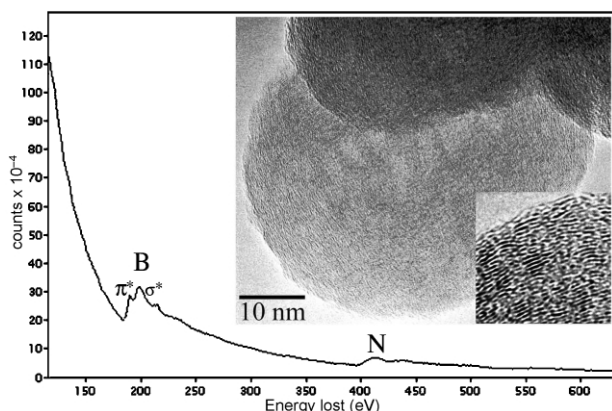


Fig. 3 EEL spectrum obtained from a spherical BN particle (inset) synthesized by CVD and subsequent pyrolysis under ammonia at 1100 °C. (Inset) high-resolution TEM image with an enlarged surface area is shown.

BN. FTIR measurement also indicates that there are only two characteristic peaks at about 1400 and 800 cm^{-1} in the spectrum, which are attributed to the in-plane B–N stretching and out-of-plane B–N–B vibrations of h-BN or r-BN.¹⁶ No vibration peaks associated with C and O are observed.

It is also worth noting that the fine structure of the B K-edge displays a weaker π^* peak than σ^* , while well-crystallized h-BN and BN nanotubes possess stronger π^* -bonding peaks.^{17,18} This implies a weakened interlayered bonding and/or a partially disordered arrangement of the BN layers. In fact, the high-resolution TEM image shown in Fig. 3 clearly confirms that, although the basic layered structure is retained, the stacking of the spherical BN particle exhibits considerably strong distortion normal to the BN shell direction.

Sato and coworkers⁶ carried out a microstructural study to evaluate the relationship between BN crystalline structure and its morphology. Columnar BN particles possessing no three-dimensional order (turbostractic) were first synthesized at 900 °C by using melamine diborate as a pyrolysis precursor. Under heat treatment at a temperature higher than 1700 °C, turbostractic BN (t-BN) could be converted to the well-crystallized h-BN or r-BN having a three-dimensional ordering; this exhibits plate-like morphology particles. However, during the crystallographic transformation, a spherical morphology was unexpectedly observed at the intermediate heat-treatment temperature of 1600 °C. The authors thus speculated that a partially ordered structure is responsible for the formation of a BN powder with spherical particles. Our TEM and XRD observations discussed here are in accord with the assumption of partial disorderings in spherical BN particles.

Spherical morphology of a BN layered crystal is a metastable intermediate phase, and its occurrence strongly depends on the morphology of the pyrolysis precursors and temperature. Therefore, spherical BN precursor particles, B–N–O–H, from aerosol-assisted vapor synthesis¹³ and B_2O_3 –BN from the reaction of ammonia with urea–boric acid⁶ mentioned above, and the B–N–O discussed here, are required for the formation of spherical BN crystals. Further research on the detailed morphological transformation under different heat treatments, and the potential application of BN spherical particles in lubricants and composite materials are under way.

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