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Growth of spherical boron oxynitride nanoparticles with smooth and petalled surfaces during chemical vapour deposition process

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ABSTRACT

A rich variety of hollow and solid (without internal hollow spaces) spherical boron oxynitride nanoparticles (BNO-NPs) with smooth or petalled surfaces were synthesized during a boron oxide-assisted chemical vapour deposition (BOCVD) process. Diverse BNO-NPs were obtained while utilizing different precursors, gas flow rates and synthesis temperatures in the range of 1200-1430°C. The BNO-NP morphologies, atomic structures and spatially-resolved chemical compositions were studied by scanning (SEM) and transmission electron microscopies (TEM), X-ray diffraction (XRD), energy-dispersive X-ray, Fourier-transform infrared and confocal Raman spectroscopies. Particle size distributions were measured using dynamic light
scattering under visual microscopic control. The growth model of different spherical BNO-NPs types based on the detailed analysis of physical-chemical processes at different BOCVD stages was proposed. The new type of spherical BNO-NPs of “hedgehog” morphologies with BN nanowires on their surfaces was first predicted in accordance with the designed model and then experimentally verified.

**Keywords:** boron oxynitride, spherical nanoparticles, CVD, morphology, structure, formation mechanism

**INTRODUCTION**

Hexagonal boron nitride (h-BN) is a layered material exhibiting superb resistance to oxidation, profound chemical inertness and high thermal stability. Over the last decade, there has been a great interest in h-BN nanostructures because of their high thermal conductivity, excellent lubricating properties, low density (2.27 g·cm⁻³), and good biocompatibility.¹⁻⁶

All the mentioned properties presume different potential applications of BN nanostructures in lubricants and heat resisting materials, functional and superhydrophobic coatings, advanced ceramics and light metal composites, drug delivery systems, catalysts, and hydrogen accumulators.⁵⁻¹²

BN nanostructures of various morphologies (nanotubes, nanowires, nanoribbons, nanofibers, nanospheres, nanocages, nano-polyhedrons, nanosheets) can be fabricated through high temperature syntheses (> 2000°C), i.e. by plasma-chemical methods, arc discharge, and laser ablation; and lower temperature syntheses (< 2000°C), i.e. carbothermal reaction, ball milling, and chemical vapour deposition (CVD).¹³⁻¹⁹ Nowadays, the high-yield methods for obtaining BN nanotubes are plasma-chemical route in N₂-containing atmosphere and annealing of porous boron-containing precursors.²⁰⁻²² However, for synthesis of BN nanoparticles of spherical morphology such methods are not widespread and the most developed approach is a CVD method. These days, spherical BN nanoparticles are in a demand in many
high-end applications in biology, medicine and ecology fields and one may expect that the areas of spherical BN nanoparticles utilization will further be rapidly expanded due to their excellent physical and chemical properties.

Some synthetic methods of spherical BNNPs production were already presented. For example, Tang et al.\textsuperscript{17} reported high yield synthesis and detailed characterization of solid spherical BN nanoparticles with diameters of 50-400 nm, produced by a CVD reaction between B(OMe)\textsubscript{3} and ammonia at 980°C followed by high-temperature annealing at 1400°C. The authors proposed the relevant formation mechanism and discussed on the origin of oxygen impurities in BN nanoparticles and their influence on the morphology.

A two-step synthesis method of solid spherical BN particles with a size distribution from 50 to 400 nm was described by Tang et al.\textsuperscript{18} The method combines processes of chemical vapour deposition (T=700°C) and pyrolysis (T=1100°C) of trimethoxyborane under ammonia atmosphere. According to chemical composition and high-resolution TEM analyses it was shown that BN particles had exhibited a slightly distorted arrangement of the shells. In addition, TEM and XRD observations suggested their partial disordering.

Spherical BN nanoparticles were also synthesized through a reaction of boric acid and ammonium chloride at T=950°C under N\textsubscript{2} atmosphere.\textsuperscript{23} A certain amount of copper oxide was crucial for the formation of uniform BNNPs with an average size of 30 nm. Hollow BN nanocages and BN-nanocage-encapsulated GaN nanocrystals were synthesized by using a B-N-O precursor at 1750°C in Ar and NH\textsubscript{3} flows.\textsuperscript{24} B-N-O precursors were also proved to be effective sources of boron for the preparation of BNNTs and BN nanocages. The high yield synthesis of solid BN\textsubscript{x}O\textsubscript{y}C\textsubscript{z} spherical particles with smooth and “crumpled aluminum foil ball” surfaces was reported.\textsuperscript{25, 26} The authors suggested that the reaction of gaseous ammonia with aerosol droplets of organoborate (MeO)\textsubscript{3}B suspended in nitrogen in a flight tube heated to 800-1600°C had produced non-agglomerated spheres with a size of 0.5-2 μm “dusted” with fine particles of 100-150 nm in diameter. Chen et al.\textsuperscript{27} developed an approach to prepare smooth
hollow BN nanospheres under reaction of NaNH$_2$ and BBr$_3$ at room temperature. These authors synthesized agglomerates of h-BN hollow spheres with a diameter between 80 and 300 nm and proposed that BBr$_3$ droplets had served as templates for the spheres growth. The synthesis of nanosheet-structured BN by a catalyzing thermal evaporation method from solid B powders was also illustrated in.\textsuperscript{28} The spheres of 700 nm to 4 μm in diameter formed only at a certain reaction temperature were made of radial-oriented ultrathin nanosheets with their edges protruded out of the sphere surfaces. The authors demonstrated a high potential of using such structures for water cleaning.

Hollow spherical BN nanoparticles of 100–200 nm in diameter with petal-like surfaces were fabricated by a CVD method using boron oxide vapour and flowing ammonia\textsuperscript{6}. The structural investigations demonstrated that the surface of particles was made of numerous nanosheet petals. The capability of utilization of such structures as antitumor cells was additionally shown.

Several models were proposed to explain the formation mechanism of spherical BN nanoparticles. It was considered\textsuperscript{18} that the presence of initial spherical particles in the precursors is essential for the creation of spherical morphology in BN nanoparticles independent on precursor chemical composition for the systems: B–N–O\textsuperscript{18}, B–N–O–H\textsuperscript{25} and B$_2$O$_3$–BN\textsuperscript{29}.

Zhong \textit{et al.}\textsuperscript{30} suggested a mechanism of hollow BN nanoparticle formation relying on decomposition of ammonia borane (NH$_3$BH$_3$) at 300°C and formation of gaseous phases containing B, N and H. These gases could flow into a high-temperature reaction zone where they react with each other and condense into the BNH liquid droplets. After the particle diameters had exceeded a certain critical size, the BNH droplets in the vapour phase deposited onto an Al$_2$O$_3$ substrate due to the gravitational effect. With an increase in temperature, the viscous BNH solid nanospheres undergo a dehydrogenation process which results in small bubbles appearance within the spheres. The bubbles tend to merge together under surface tension of the viscous matrix, leading to the formation of final BN hollow nanospheres.
The model of solid spherical BN nanoparticles formation was proposed by Tang et al.\textsuperscript{17} Reaction of trimethoxyborane $\text{B(OMe)}_3$ and ammonium led to the creation of spherical $\text{B(OMe)}_{3-x}\text{H}_{3-x}\text{N}$ intermediates which then transform into solid BN particles through decomposition and diffusion processes of gaseous byproducts at high temperatures.

The current interest in spherical BN nanoparticles stems from a demand of obtaining homogenously structured discrete spherical nanoparticles in large amounts for multi-functional applications. However, the development of an effective synthetic technique is still a great challenge. Since it was shown that boron oxide-assisted CVD technique (BOCVD) is the most effective approach for preparation of various BN nanomaterials, we thoroughly studied this method for the controlled fabrication of versatile BN nanoparticles.

Thus, in the present work we analyzed the growth of spherical BN nanoparticles of various morphologies during the BOCVD process under varying experimental conditions, namely, precursor composition, temperature, carrying and reactant gas flow rates and synthesis time. The morphology, structure, chemical composition and nanoparticle size distribution were studied in details and peculiar growth mechanisms for each particle type were uncovered.

1. EXPERIMENTAL METHODS

1.1. Experimental Set-up

Synthesis of BN nanoparticles was carried out in a vertical CVD induction system operating at 41.4 kHz. The experimental set-up is shown in Fig. 1. The CVD system consists of a quartz cylindrical chamber, a cylindrical graphite heater (susceptor), a cylindrical reactor made of BN ceramics, a gas supply and exhaust system. Ammonia was introduced in the BN reactor from the top and argon was supplied from the bottom of the furnace. The heater was isolated from the quartz chamber by a low-dense material made of carbon fibers. The temperature gradient (the scale on the right hand-side of Fig. 1), was monitored by a W-Re thermocouple (A
type) introduced in-between the heater and the thermal insulation, and a pyrometer was focused on the bottom of a crucible with precursors through a hole in the BN reactor bottom. This gradient can be varied by adjusting relative positions of the inductor and the BN reactor.

The BN reactor consisted of three cylindrical parts with the external and internal diameters of 75 and 55 mm, respectively, and a total height of 340 mm. Its height was more than a height of the heater for approximately 30% to achieve a significant temperature gradient (Fig. 1). Initially, the temperature profile along the reactor was measured with an external thermocouple. The reactor (2) had a hole of 3 mm in diameter in its upper side wall part. A BN ceramic crucible (7) was placed in front of this hole for collecting nanoparticles transported from the BN reactor by a gas flow. Another BN crucible with a precursor (6) was placed in the bottom of the reactor, just above the argon inlet hole. The lower part of the reactor with the precursor was filled with argon and called hereafter as an “argon zone”. Above the “argon zone” was the zone where ammonia is present. This zone is called as the “ammonia zone”.

The furnace chamber was evacuated up to 10^{-2} mbar under slow heating to 360°C for outgassing of the low density graphitic thermal insulation. Then, an argon flow was introduced, the pressure of 1 bar was maintained, and heating to the synthesis temperature was started, this took about 15-18 min. At 1100°C, ammonia flow was introduced. The precursor temperature (synthesis temperature) was varied in the range of 1200-1430°C. An ammonia flow was set in the range of 30-150 cm³/min, and the Ar/NH₃ flow ratio was maintained from 2 to 6. The syntheses were carried out for 3-7 hrs. After the synthesis the reactor was naturally cooled to room temperature in argon.

1.2. Materials

Powder mixtures of B, MgO, H₃BO₃, FeO or SnO were used as the precursors. Three types of mixtures were tested as a source of boron oxide vapour, i.e. FeO+MgO+B,
SnO+MgO+B and H₃BO₃+MgO+B. The molar ratios of chemicals in the precursor powder mixtures are presented in Table 1.

Table 1. Chemical compositions of precursor powder mixtures for BOCVD syntheses.

<table>
<thead>
<tr>
<th>Mixture No.</th>
<th>B</th>
<th>MgO</th>
<th>FeO</th>
<th>SnO</th>
<th>H₃BO₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.5</td>
<td>1.25</td>
<td>1</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>3.5</td>
<td>0.1</td>
<td>1</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>3.5</td>
<td>0.2</td>
<td>1</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>1</td>
<td>1</td>
<td>-</td>
<td>1</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>3.5</td>
<td>0.1</td>
<td>-</td>
<td>1</td>
<td>-</td>
</tr>
<tr>
<td>6</td>
<td>3.5</td>
<td>0.2</td>
<td>-</td>
<td>-</td>
<td>2.6</td>
</tr>
</tbody>
</table>

The reagents of following grades were used: MgO - analytical grade, amorphous B - >99%, FeO - pure, SnO - 99%, H₃BO₃ - chemical grade. Magnesia was calcined at 450°C in air for 1 h for dehydration just before weighing.

Precursor mixtures were mechanically ground in a mechanical alumina mortar for 1 h with addition of isopropyl alcohol. Argon of 99.993% purity was used as a carrying gas and ammonia of 99.98% purity was used as the reactant gas.

1.3. Characterization

The synthesized product morphologies and their elemental compositions were analyzed using a scanning electron microscope JSM-7600F (JEOL) equipped with the energy-dispersive X-ray (EDX) detector.

Transmission electron microscopy (TEM) and electron diffraction (ED) studies were performed using a Tecnai G2 30 UT (LaB₆) microscope operated at 300 kV with a 0.17 nm
spatial resolution and equipped with an EDAX EDX detector. High-angle annular dark field (HAADF) scanning TEM (STEM) imaging and EDX elemental mapping were performed using a JEM ARM200F cold field emission gun (FEG) probe and image aberration corrected electron microscope operated at 200 kV, equipped with a large solid-angle CENTURIO EDX detector and a Quantum GIF. The powder samples for TEM were ground in methanol, and the resulting dispersion was transferred to a holey carbon film deposited on the Cu supported grid.

Chemical and phase compositions were investigated by EDX spectroscopy using a 80 mm² X-Max EDX detector (Oxford Instruments), confocal Raman spectroscopy using a NT-MDT NTEGRA Spectra instrument with an excitation wavelength of 473 nm, X-ray diffraction analysis using a DRON-3 diffractometer (Burevestnik) operated with Cu Kα radiation and Fourier-transform infrared spectroscopy (FTIR) with a Vertex 70v vacuum spectrometer (Bruker) in the range of 400–2000 cm⁻¹ using the partial internal reflection device. In order to separate the agglomerates into discrete individual BNO-NPs, they were ultrasonically treated in a distilled water solution (nanoparticles concentration 2 mg/ml) employing a Sonoplus HD2200 unit (Bandelin) at a power of 80 W for 30 min. To control spherical nanoparticle sizes and the homogeneity of size distribution, the parallel studies using dynamic light scattering method on a particles size analyzer Zetasizer Nano ZS (Malvern Instruments), while utilizing SEM method, were performed.

2. RESULTS

After each synthesis, a thin white-colored deposit was observed on the inner surface of the BN reactor and in the collecting crucible (Fig. S1(a) in the ESI). Typically, 250-400 mg of the white material was obtained in the BN crucible from 10 g of the precursor after a 7 h process. When the Ar/NH₃ flow ratio was less than 4, a white powder also covered the precursor surface, Fig. S1(b) in the ESI. In this case the traces of outgasing were seen in this newly formed material.
X-ray diffraction patterns of synthesized materials obtained from various precursors were very close to that of a hexagonal BN phase (Fig. S2 in ESI). The XRD pattern of h-BN (COD card No. 96-900-8998, cell parameters $a=2.5040\,\text{Å}$, $c=6.6612\,\text{Å}$) was used as a reference. Small shift of peaks’ positions is associated with the slightly larger unit cell parameters due to the presence of a small amount of oxygen in the structures, as was also detected by FTIR and EDX analyses.

SEM investigations proved that the synthesized material consisted of nanoparticles of a spherical shape. EDX analysis (not shown here) confirmed that the nanoparticles generally consisted of B, N species with the atomic ratio B:N close to 1:1 and also showed the presence of oxygen in this sample.

The Raman spectra of the materials synthesized from different precursors display a clear band at $1368\,\text{cm}^{-1}$, corresponding to $E_{2g}$ mode of a hexagonal BN. Typical Raman spectrum of a material obtained at $1300\,\text{°C}$ from the $\text{H}_3\text{BO}_3+\text{MgO+B}$ precursor present in Fig. S3 in ESI. The difference was found in full width at half maximum (FWHM) values of the Raman peak. The FWHM was about $25\,\text{cm}^{-1}$ for the samples synthesized from the $\text{H}_3\text{BO}_3+\text{MgO+B}$ precursor and about $40\,\text{cm}^{-1}$ for the samples synthesized from the $\text{FeO+MgO+B}$ and $\text{SnO+MgO+B}$ mixtures. Such narrowing of the bands corresponds to improving the overall sample crystallinity.

FTIR spectra from the samples synthesized from different precursors are shown in Fig. 2. The FTIR spectrum recorded from the sample prepared from $\text{FeO+MgO+B}$ precursor included two main features: a sharp peak at $769\,\text{cm}^{-1}$ and a broad band at $1359\,\text{cm}^{-1}$ corresponding to out-of-plane B-N-B bending and in-plane B-N stretching vibrations, respectively.31 These peaks are the fingerprints of the sp$^2$-bonded BN. The FTIR spectrum of the sample synthesized from $\text{H}_3\text{BO}_3+\text{MgO+B}$ precursor had some additional features - broad zones with a high absorbance in the ranges of $400$-$720\,\text{cm}^{-1}$, $850$-$1200\,\text{cm}^{-1}$, and $3000$-$3500\,\text{cm}^{-1}$. These features can be due to some amount of oxygen and/or O-H impurities;31,32 these are apparently related to the usage of
boric acid in this precursor and its evolution during the synthesis. Thus from comparison of Raman and FTIR data one may conclude that oxygen somehow improves crystallinity of BNO nanoparticles.

X-ray, FTIR, and EDX analyses evidenced that the synthesized materials are hexagonal boron nitrides with some oxygen contents; therefore hereafter we name the synthesized products as boron oxynitride nanoparticles (BNO-NPs). The experimental conditions affected the oxygen contents in the products at some extent and the BNO-NPs product yield. SEM analysis revealed that the BNO-NPs possess two major surface morphologies: smooth and petalled (Fig. 3(a, b)). The petals were made of numerous thin BNO nanosheets reminiscent of graphenes. Usually, spherical particles with smooth and petalled surfaces were found to coexist, whereas the latter morphology dominated. Some syntheses almost exclusively produced particles with the petalled surfaces (with a yield of more than 90%). The nearly sole smooth surface nanospheres were observed only in a few experiments at the certain synthesis conditions. The preferential fabrication of BNO-NPs with a distinct surface morphology could be controlled through selecting the precursor composition, gas atmosphere and flow rates of carrying and reactant gases.

Particle size distribution analysis showed that the BNO-NPs size was in the range of 80-350 nm for all types of particles synthesized from various precursors. Both SEM and particle size distribution revealed that BNO-NPs became perfectly separated after the ultrasonic treatment. The procedures of ultrasonic treatment and particle size measurements were similar to those described in our earlier publication. 6

Detailed TEM investigations allowed us to identify six major types of BNO-NPs structures (Fig. 4): hollow or solid, with thick or thin shells and with smooth or petalled surfaces. The first type of structures (type I) was the solid “onion”-like particles with a smooth surface (Fig. 4(a)). Second type (type II) was the solid particles consisting of BN nanosheets forming “pompon”-like structures (Fig. 4(b)).
Other types of BNO-NPs were hollow. These types of particles may have a thin, almost regular spherical shell, or thick shells of both spherical and irregular shapes. BNO-NPs of type III are hollow structures of a spherical shape with a thin shell (shell thickness of 10-20 nm) and a smooth surface (Fig. 4(c)). BNO-NPs of type IV are hollow spherical structures with a shell consisting of numerous large BNO nanosheets whose size is comparable with a diameter of the hollow core (Fig. 4(d)). BNO-NPs of type V are hollow structures with a smooth thick shell having a thickness comparable with the hollow core diameters (Fig. 4(e)). The hollow may be shifted from the center of the particle so that the particle walls become of a variable thickness. Sometimes this type of BNO-NPs contains two and more hollows. These nanoparticles often have an irregular shape. BNO-NPs of type VI are hollow structures with the petalled thick shells, whose thickness is comparable with the hollow diameters (Fig. 4(f)). The shells of these nanoparticles consist of two segments, i.e. the smooth inner domain and the outer petalled shield. The petals are less spacious in size but are more densely populated than in the case of type IV particles. In these particles the hollows may also be out of particle centers, like in type V particles.

The detailed HRTEM study was carried out for the BNO-NPs with two selective types of surface morphologies, namely with the smooth surfaces (types III, V) produced at 1310°C from the FeO+MgO+B precursors and with the petalled surfaces (type IV) synthesized at 1245°C from the SnO+MgO+B precursor. TEM images (Fig. 5(a, b, c)) illustrate spherical BNO nanoparticles with layered structure. The internal structure of particles presented in Fig. 5(c) corresponds to hexagonal BN with the interlayer spacing of 0.33 nm.

The results of TEM studies of BNO-NPs with the smooth surface are shown in Fig. 6(a, b). Bright-field image of nanoparticles with a size of around 80-100 nm and smooth surface is presented in Fig. 6(a). The wall thickness is quite irregular being in the range of 20-35 nm. The light grey contrasts inside the particles suggest the lack of any solid fillings and existence of
hollow cores. The wall thickness remains the same (20-35 nm) even in larger particles, ~200 nm in size, although their inner diameter is significantly larger. TEM images of the BNO-NPs of both types III and V are shown in Fig. 6(c). To verify the BNO-NPs local chemical compositions, the EDX elemental mapping was performed (Fig. 6(d-f)). HAADF-STEM image of BNO-NPs is depicted in Fig. 6(c). The contrast in a HAADF-STEM image is roughly proportional to the thickness of the specimen and to the square of the atomic number of the element (~Z^2). Thus HAADF-STEM imaging represents both chemically and thickness sensitive contrasts. In this respect, it is clear that the contrast in HAADF-STEM image (Fig. 6(c)) is due to the thickness difference, thus unambiguously supporting the hollow structure of the BNO-NPs. Non-homogeneous contrast inside the large BNO-NPs is most probably related to variable thickness of the particles shell. EDX mapping (Fig. 6(d-f)) confirms that the particles consist of B, N, O.

TEM observations of a sample with the petalled surface revealed more complex structures (Fig. 7(a)). The surface of BNO-NPs consists of numerous BN petals. Such petals were previously observed in porous BN nanospheres. SAED analysis confirmed that the petals are made of hexagonal BN (the inset in Fig. 7(a)). Elemental mapping (Fig. 7(b)) showed that they consist of B, N, and O. HRTEM images (Fig. 7(c, d)) revealed the presence of stacked heavily curled and bent BNO nanosheets with a thickness of 3-4 nm. The similar BN nanosheets with thickness from 3.1 to 9.1 (depending on precursor composition) were observed on the spherical BN particles. The lattice fringes corresponding to the typical d-spacing of h-BN viewing along two orthogonal ([1010] and [0001]) projections are clearly seen on the HRTEM images. EEL spectra of this sample are presented in Fig. S4 in ESI. The spectra from the central region and from the near-surface region (shell) of nanoparticle were similar and basically exhibited h-BN structure.

To sum up, in accordance with our thorough structural and morphological analyses, six different types of BNO-NPs with smooth or petalled surfaces were identified: four types having...
hollow morphologies and two types with empty cores, *e.g.* “onion”-like and “pompon”-like particles (Fig. 8).

### 3. ANALYSIS AND DISCUSSION

According to the existing literature, various spherical BN nanoparticles, *i.e.* hollow and solid, with smooth or petalled surfaces can be synthesized by means of different methods. Generally, one method produces one (or rarely) a few types of BN nanospheres. Only the applied BOCVD method based on reaction of ammonia with boron oxide vapour generated during thermal decomposition of boron-oxide precursor has an advantage of producing a variety of spherical BN-based nanoparticles. Our systematic investigation of the presently utilized BOCVD process allowed us to propose a more general model of spherical BN-based particle formation. Below we consecutively analyze different stages of the physical-chemical processes.

#### 3.1. Processes in Precursor

Two types of B sources in the precursors were tested, *i.e.* boron oxide-based (B$_2$O$_3$+BN), (MgO+$n$·B$_2$O$_3$) and elemental boron-based - (B+$B_2$O$_3$), (B+MgO+FeO), (B+MgO+SnO). Under heating of the first precursor type boron oxide is melted with the formation of borates, for example Mg borate in case of using MgO. The volatile fractions of boron oxide compounds (BOC) are vaporized. The kinetics of this process depends on temperature and precursor composition (Fig. 8, stage a). In case of using heterogeneous precursors consisting of liquid and solid phases at high temperature, in addition to the surface vaporization, vaporization also occurs from the liquid-solid interfaces enhancing the overall vaporization kinetics. In addition to vaporization, the bubbling is also possible, if the liquid surface tension is high enough. This also depends on melt composition and temperature. The essential condition for bubble formation is the presence of a solid phase particles in the melt. The latter plays a role of the frame for liquid film formation similar to soap bubbling. It is known that boron oxide-based melts have a high ability to form films and foams due to a polymeric nature of (-B-O-) bonds. Increasing melt
temperature leads to a decrease in its viscosity resulting in the bubble wall thinning (Fig. 8, stage b). By contrast, if the temperature is not high enough, thick-walled bubbles appear (Fig. 8, stage c). Increasing the MgO content in the precursor (more than 50% mol) favors thick-walled bubbles due to the formation of refractory Mg borates. The more Ar flow rate over the precursor the faster vaporization and bubbling took place due to a decrease of partial vapour pressure above the melt and the overall pressure according to the Bernoulli law.

Under heating of the B-containing precursor its oxidation occurs along the following chemical reactions:

\[
2B + MeO_x \rightarrow B_2O_3 + MeO_y \tag{1}
\]

\[
2B + MeO_x \rightarrow B_2O_2 + MeO_z, \text{ where Me = metal} \tag{2}
\]

In this case the above-mentioned arguments remain valid because boron and metal oxides are still present in the melts.

In addition to boron oxide and borate vapours, the volatile B\(_2\)O\(_2\) oxide forms along with the redox reactions: \(^{34}\)

\[
2B (s) + 2MgO (s) \rightarrow B_2O_2 (g) + 2Mg (v) \tag{3}
\]

\[
2B (s) + 2FeO (s) \rightarrow B_2O_2 (g) + 2Fe (s) \tag{4}
\]

\[
2B (s) + 2SnO (s) \rightarrow B_2O_2 (g) + 2Sn (l) \tag{5}
\]

Briefly, vapours of BOC and thin or thick shell BOC bubbles form in this zone depending on temperature and precursor composition.

3.2. Processes above Precursor (Zone of Argon)
This zone is marked as Ar in Fig. 8. Its size depends on the Ar/NH₃ flow rate ratios and increases with an increase in Ar flow rate. In this zone, BOC vapours start to cool down and their condensation takes place if vapours concentration is high enough. At sufficient low pressure BOC vapour condensation does not occur (Fig. 8, stage e). Under high concentration of vapours condensation leads to the formation of a tiny liquid BOC droplets mist (yellow circles in Fig. 8). These droplet collisions lead to their enlargement and formation of BOC solid nanoparticles (Fig. 8, stage d), whereas impacts of droplets with bubbles results in increasing in bubble wall thicknesses (Fig. 8, stage f). Probability of such collisions is proportional to the Ar flow speed, the faster the speed the more is the flow turbulence. Under a large vertical temperature gradient, the viscosity of a boron-oxide melt within bubbles and droplets quickly increases under its upward propagation. This hinders the droplets and bubbles coalescence and leads to the formation of irregularly-shaped particles (Fig. 8, stage f).

Briefly, the condensation of vapour, tiny BOC droplets formation and coalescence of those occur in this zone.

3.3. Processes in Ammonia Zone

This zone is marked as NH₃ in Fig. 8. In this zone, the BOC vapour, ammonia and either hollow or solid nanoparticles pre-formed in the lower Ar zone are all present. Here, the temperature is continued to decrease and the BN-based phase is formed as a result of B-oxide reactions with ammonia under release of water vapour along with the following reaction:

\[ \text{B}_2\text{O}_3 + 2\text{NH}_3 \rightarrow 2\text{BN} + 3\text{H}_2\text{O} \]  

(6)

The kinetics of this reaction depends on temperature and ammonia concentration and influences the morphology of the final BNO products. If ammonia concentration is low, while the temperature is high, the volume of forming BN (and water) is not large, whereas the diffusion rate is fast. Under such condition, a water vapour easily diffuses outward of the particles without their breakage and the “onion”-like structures with smooth surfaces, or thin-
and thick-walled smooth particles are formed (types I, III and V). The analogous mechanism was considered by Tang et al. 17 during a reaction of trimethoxyborane with ammonia, elimination of gaseous MeOH и Me2O without losing the particle integrity, and the formation of solid spheres.

Under the opposite conditions, i.e. high ammonia concentration and a relatively low temperature, the volume of the releasing water vapour is increasing, while its diffusion rate within the particle volume is decreased. Thus the water vapour does not succeed to entirely penetrate through the growing BN layers leading to the inner pressure growth and resultant BNO shells breakage. As a result, BNO nanoparticles with the highly developed surfaces covered with numerous graphenelike BN petals appear. The size of petals and their amount depend of the defectiveness of BOC particles. Surface defects and inhomogeneities within these particles lead to a decreased petal size and an increase in their density on surfaces. Nanostructures of type VI (Fig. 8) are formed along with this scenario from the hollow irregularly-shaped BOC. Hollow smooth BOC particles of right spherical form exhibit the lesser defects, meaning that a small amount but spacious petals emerge on their surface. In case of thin-walled spheres these processes sometimes result in complete vanishing of shells leaving the particles with a crown-like appearance of the petals. Under further development of these structures, the type IV particles are crystallized; these have the petals with a size comparable with their overall diameters. In case of solid (without hollow) BOC nanoparticles, the processes of formation and breakage of BNO layers propagate inward forming the spherical particles made of numerous packed petals. Under the further growth these transform to the “pompon”-like particles, type II structure.

At the same time a CVD process based on the reaction of ammonia with BOC vapours, adsorbed on newly formed BNO surface, takes place. As a result, graphenelike BNO petals substantially grow in linear dimensions creating large surface flakes, like in case of type IV morphology. They are easily bent making numerous folds. These stimulate intense condensation of BOC vapours. The condensate readily reacts with ammonia leading to the nucleation and
growth of new BNO sheets and so producing dense and thick BNO coats, as in case of II, IV, and VI morphologies.

To summarize, in this zone adsorption, condensation, and reaction of BOC with ammonia occur leading to formation of BNO nanosheets and growth of both their size and amount.

3.4. Formation of Specific Morphology Nanoparticles

It worth noting that obtaining particles of totally identical morphology in a given synthetic run is not always possible, as the conditions for synthesis of some nanoparticles are rather close. As a result, occasionally, a mixture of various morphologies may be found in a product, as depicted in Fig. 9(a). The general condition for all structure formations is an intense vaporization of BOCs. B₂O₃ does satisfy this criterion, since it has a low vapour pressure under 1200°C. In addition, we note that boron anhydride has substantially slower kinetics of interaction with ammonia than borates of rare and rare-earth metals containing some amount of oxide-forming borate. From all precursors studied in the present work, a mixture of (B+B₂O₃), forming a volatile B₂O₂, and precursors in which Mg borates with a relatively low MgO concentration (<50 % mol.) are present, satisfy the regarded criteria. For the synthesis of “onion”-like structures (type I) a high temperature, fast Ar flow and low concentration of ammonia are advantageous. Under similar conditions, but at a higher ammonia concentration, “pompon”-like morphologies (type II) would form. For production of hollow particles, (B+B₂O₃), (B+MgO+FeO), (B+MgO+SnO) and (MgO+n·B₂O₃) precursors, which at high temperature consist of liquid and solid phases (B, Fe, MgO, Mg₂B₂O₅), are required. High temperature in the precursor zone, and in the ammonia zone, but low ammonia concentration, promotes the formation of thin-walled particles (type III). Increasing ammonia concentration and a larger temperature gradient along the reactor leads to the formation of surface BNO petals on hollow particles (type IV and VI) or “pompon”-like morphologies (type II). Decreasing temperature in the precursor zone and ammonia concentration, while increasing the Ar flow,
stimulates the formation of hollow particles with smooth thick shells (regular and irregular shapes) (type V). Table 2 qualitatively summarizes the reaction conditions favouring the formation of different particle morphologies.

Table 2. Experimental parameters favouring the formation of different particle morphology types.

<table>
<thead>
<tr>
<th>Type of BNO-NPs</th>
<th>Precursor composition enabling BOC bubbles formation</th>
<th>Temperature in the precursor zone ¹</th>
<th>Temperature in the ammonia zone ²</th>
<th>Ar flow rate ³</th>
<th>NH₃ flow rate ⁴</th>
</tr>
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<tbody>
<tr>
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<td>low</td>
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<tr>
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</tbody>
</table>

¹) in a range of 1200-1430°C;
²) in a range of 650-750°C;
³) in a range of 180-500 cm³/min;
⁴) in a range of 30-150 cm³/min.

The regarded analysis implies that the formation of BOC bubbles from a precursor melt and developing of their surface through condensation or adsorption of BOC vapours under reaction with ammonia is the crucial stage of specific morphology crystallization. To prove the validity of this claim an additional test experiment was undertaken. An 0.5 wt.% of Li₂O was added to the (B+MgO+FeO) precursor and the synthesis was carried out at the conditions when hollow smooth BNO thick-walled particles were formed without such addition. Under heating of the new precursor, lithium borate having both low melting point and high volatility should form, thus in the frame of the proposed model Li borate should crystallize on the BOC surfaces in the ammonia zone. This should change the resultant morphology. In fact, Fig. 9(b) illustrates the
formation of new “hedgehog”-like particles covered with BN nanowires. Importantly enough, in our recent work\textsuperscript{36} we have concluded that BN nanotubes and nanowires preferentially nucleate and grow from a Li borate-based melt. Therefore, the formation of surface-attached BN nanowires on smooth spherical BNO-NPs indicates the predicted condensation of Li borate vapours followed by this condensate reaction with ammonia, right in accordance with the developed model.

4. CONCLUSIONS

Six types of spherical BNO nanoparticles with external dimensions of 80-350 nm and having hollow and solid cores, and smooth and petalled surfaces (with numerous thin-walled BN petals) were synthesized using three kinds of precursor compositions, \textit{i.e.} FeO+MgO+B, SnO+MgO+B and H\textsubscript{3}BO\textsubscript{3}+MgO+B at 1200-1430°C using a CVD approach. BNO-NPs were obtained as homogeneously structured agglomerates. Changing the experimental conditions affects the particle morphology, oxygen content and the product yield. The structures and morphologies of various BNO-NPs were analyzed in detail and the particular mechanism for each particle morphology appearance was uncovered. BNO-NPs of new “hedgehog” morphology with surface-attached BN nanowires were first predicted and then synthesized in the test experiment along with the model. We envisaged that the present research would be highly valuable in the field of BN nanomaterials fabrication and their utilization in diverse industrial fields.

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