

Hollow Boron Nitride (BN) Nanocages and BN-Nanocage-Encapsulated Nanocrystals

Ying-Chun Zhu,* Yoshio Bando, Long-Wei Yin, and Dmitri Golberg^[a]

Abstract: Hollow boron nitride (BN) nanocages (nanospheres, image on the left) and BN-nanocage-encapsulated GaN nanocrystals (right) have been synthesized by using a homemade B–N–O precursors. The as-prepared BN hollow nanocages have typically spherical morphologies with diameters rang-

ing from 30 to 200 nm. The nanocages have crystalline structures. Peanutlike nanocages with double walls have also been observed; their internal space is

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divided into separated compartments by the internal walls. The method is extended to sheathe nanocrystals with BN nanocages; BN-shell/GaN-core nanostructures have been successfully fabricated. The method may be generally applicable to the fabrication BN-sheathed nanocrystals.

Introduction

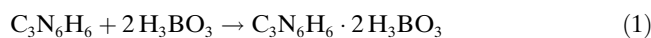
Much attention has been focused on boron nitride (BN) nanotubes and other fullerene-like nanostructures following the discovery of carbon nanotubes. Besides BN nanotubes, various fullerene-like structures have recently been fabricated and studied, such as nanocones, nanobamboos, nanocables, and nanocages.^[1–8] Graphite-like boron nitride has similar structure to graphite, but has distinguishing properties including significant electrical-insulating performance, high thermal stability and conductivity, and high chemical inertness.^[9] All these characteristics make it an important material in some specific application fields of nanoscience and nanotechnology. An important application of BN is as an insulating and protecting shell to enhance the stability of various nanostructures.^[10–13]

Nanocages are an important category of fullerene-like structures, to which particular attention should be addressed. Substances may show novel physical and chemical properties within these hollow cages. For instance, diamond single crystals can be produced in situ inside C-nested fullerenes under electron beam irradiation at high temperatures.^[14] BN fullerene-like nanocages have a high nitrogen content.^[15] Nanocages may effectively serve as nanocontainers for gas storage.^[16–18] Insulating BN nanocages may prevent encapsulated particles from oxidization and contamina-

tion.^[19] Many methods have been developed to prepare BN nanotubes, but there is no effective method for the bulk production of BN nanocages. BN nanocages have often been obtained on small scales as byproducts during the production of BN nanotubes.^[1,15] In our previous work, we are successful in coating semiconducting nanowires with BN sheathes by using B–N–O precursors, and found some nanocages as byproducts.^[20] This motivated us to prepare BN nanocages as the main products. We developed the experimental process and adjusted the experimental parameters to prepare BN nanocages. We report herein the successful fabrication of BN nanocages on a large scale by using a homemade B–N–O precursor. Moreover, this method is applicable to encapsulate nanocrystals into BN nanocages, and BN-nanocage-encapsulated GaN nanocrystals have been fabricated.

Experiment Section

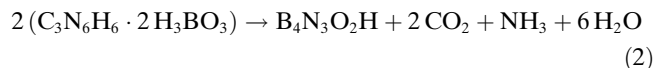
A B–N–O precursor was first synthesized for the preparation of BN nanocages. Melamine diborate ($C_3N_6H_6 \cdot 2H_3BO_3$) was synthesized through dissolving boric acid (H_3BO_3 ; 0.4 mol) in of water (1000 mL) at 100 °C. Melamine ($C_3N_6H_6$; 0.2 mol) was then slowly added into the solution. When the solution was cooled down and left for 48 h, white melamine diborate ($C_3N_6H_6 \cdot 2H_3BO_3$) precipitated. The reaction may be represented as that given in Equation (1):



The white precipitate was filtered and dried in a desiccator at 95 °C for 24 h. The precipitate was calcined at 500 °C

[a] Dr. Y.-C. Zhu, Prof. Y. Bando, Dr. L.-W. Yin, Dr. D. Golberg
Advanced Materials Laboratory
National Institute for Materials Science (NIMS)
Namiki 1-1, Tsukuba, Ibaraki 305-0044 (Japan)
Fax: (+81) 298-51-6280
E-mail: yingchunzhu@yahoo.com

in air for two hours for dehydration and decarbonization, and then calcined at 800 °C in nitrogen atmosphere for another 1 hour for further dehydration; the resultant yellow product was a B–N–O intermediate which might have the formula $B_4N_3O_2H$ and contains a BN skeleton and approximately 27% of oxygen.^[21] The reaction is formulated in Equation (2).



The products ($B_4N_3O_2H$) were heated at 600 °C in air for two hours to remove the remainder of water and carbon, yielding a white B–N–O product. The product may have the formula $B_4N_2O_3$ containing about 40% of oxygen.

The as-prepared precursor was put into a graphite crucible, which is enclosed within a graphite susceptor and heated in an induction furnace. The position of the crucible was adjusted to ensure that the B–N–O precursor was heated at 1750 °C. An argon flow (1.5 L min^{-1}) was passed through the B–N–O precursor from the bottom of the susceptor to carry in situ evaporated B–N–O vapors. NH_3 flow (0.1 L min^{-1}) was introduced into the susceptor from the top; this reacted with the B–N–O vapors to form hollow BN nanocages inside the susceptor. The schematic diagram of the apparatus for the synthesis of BN nanocages is illustrated in Figure 1.

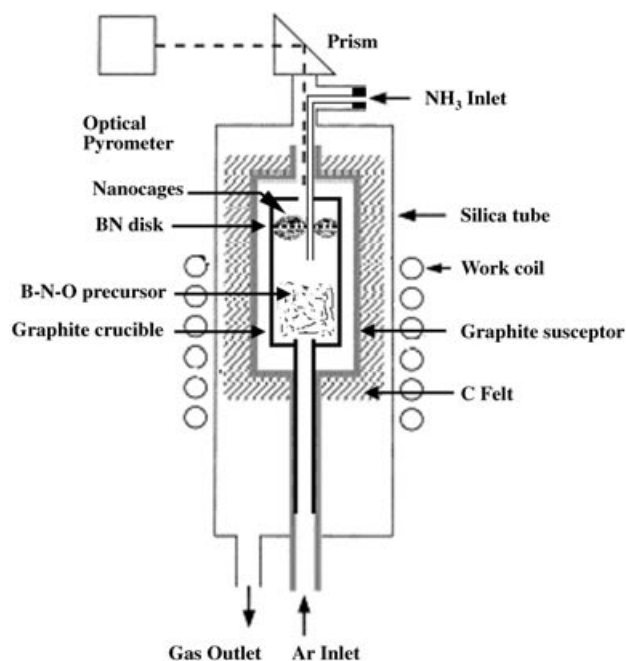


Figure 1. Schematic illustration of the reaction system.

For the preparation of BN-nanocage-sheathed GaN nanocrystals, a crucible containing Ga_2O_3 powder was placed above a crucible containing the B–N–O precursor. The crucible containing the Ga_2O_3 powder was heated to 1200 °C for 1 hour in argon and ammonia atmospheres to synthesize GaN nanocrystals. GaN nanocrystals were deposited in the

temperature region of 600–800 °C. In order to coat GaN nanocrystals with BN nanocages, the crucible containing the B–N–O precursor was heated to 1700 °C, while the temperature of the GaN nanocrystals was increased to 700–900 °C. After the coating process was carried out for another hour, GaN nanocrystals were sheathed with BN nanocages.

The as-prepared sample was characterized by scanning electron microscopy (SEM) and high-resolution transmission field emission electron microscopy (HRTEM), by using a JEM-3000F (JEOL) microscope operated at 300 kV, in tandem with electron energy-loss spectroscopy (EELS) and energy-dispersive X-ray spectroscopy (EDX).

Results

Figure 2a shows the morphology of the products, revealing a typically spherical appearance. High magnification SEM observation reveals that BN nanocages have uniform spherical morphologies with diameters ranging from 30 to 200 nm, as shown in Figure 2b. A depressed and a cracked BN nano-

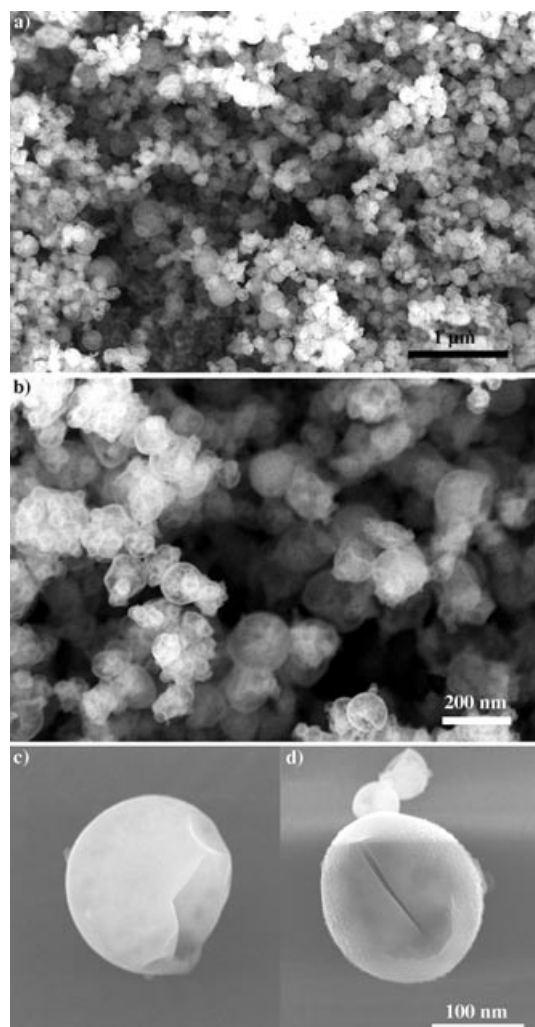


Figure 2. SEM images of BN nanocages. a) Low magnification SEM morphology of BN nanocages. b) High magnification SEM morphology of BN nanocages. c) A depressed BN nanocage. d) A cracked BN nanocage.

cage are displayed in Figure 2c,d, in which the hollow structure of the nanocage is clearly revealed.

The structures of the BN nanocages were further analyzed by TEM, as shown in Figure 3a,b. The results show

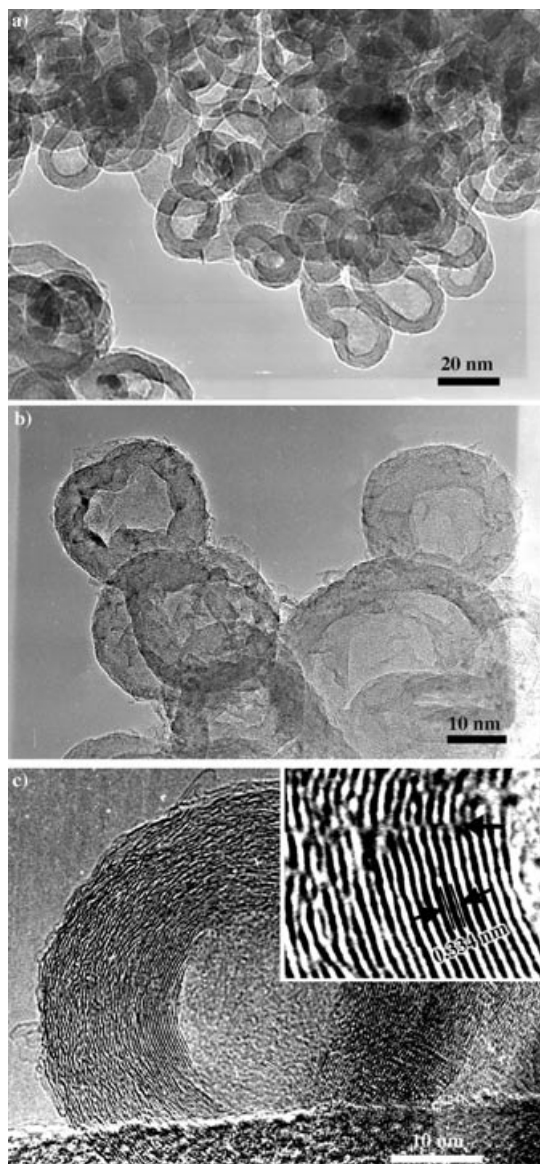


Figure 3. TEM images of the BN nanocages. a) Low magnification TEM image of BN nanocages. b) High magnification TEM image of BN nanocages. c) HRTEM image of BN nanocages. Inset is the high magnification image of (c).

that all of the nanoscale spheres have a hollow structure. The HRTEM image in Figure 3c shows that the nanocages have a crystalline onion structure with curved lattice planes. The lattices of the BN nanocages have an interlayer spacing of 0.334 nm, which corresponds well to an interplanar distance of the (002) planes of hexagonal BN. Dislocations are observed in the lattice planes, as indicated by letter “D” in the inset of Figure 3c. EEL spectroscopy composition analysis of the nanocages presents B and N characteristic K-edges at 188 and 401 eV, as shown in Figure 4. The N/B ratio cal-

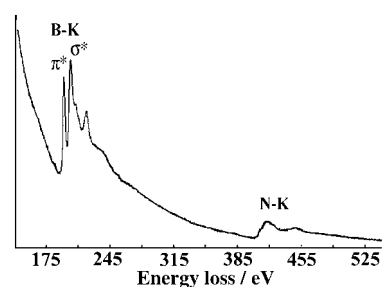


Figure 4. EELS spectrum of BN nanocages.

culated from this spectrum is approximately 1:1, consistent with the stoichiometric composition of BN.

Figure 5 represents special nanocages composed of B and N, as confirmed by EELS analysis. First, it is noted that the nanocages are connected together, showing a peanutlike ap-

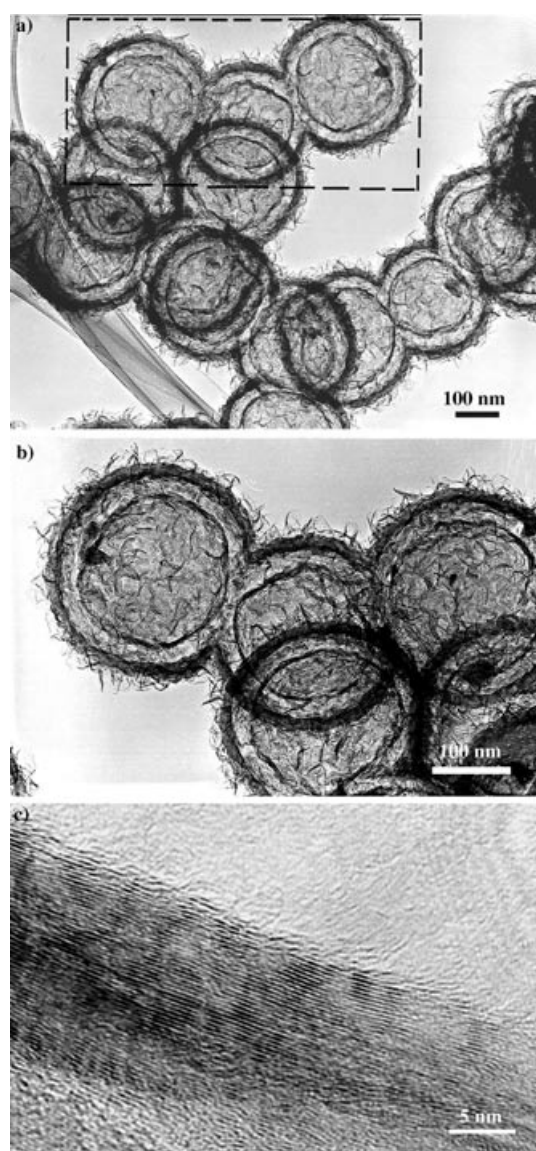


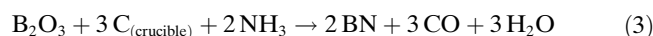
Figure 5. TEM images of double-walled peanut-like BN nanocages. a) Low magnification TEM image. The dashed square encloses a three-compartment peanutlike BN nanocage. b) High magnification TEM image. c) HRTEM image of BN nanofibers.

pearance. The peanutlike nanocages have double walls, that is, an external and an internal wall between which there is a space. The nanocages are linked together with the external walls and separated by the internal walls. The dashed square in Figure 5a encloses a peanutlike cage, whose internal space is divided into three compartments by the internal walls. It should also be noted that the nanocages are composed of nanofibers. The HRTEM image of the cross-section of the nanocages is unavailable due to the insulating property of BN, which causes electron flashes. However, the HRTEM image of the BN nanofibers in the nanocage reveals a crystalline structure, as shown in Figure 5c.

BN-nanocage-encapsulated GaN nanocrystals are presented in Figure 6. It can be seen that all of the nanocrystals are encapsulated within BN nanocages, as shown in Figure 6a. The core-shell structure of the BN-nanocage-encapsulated nanocrystals can be clearly seen in Figure 6b. It is noted that three nanocrystals are enclosed into one nanocage, labeled "M" in Figure 6b. An HRTEM image of BN-nanocage-encapsulated GaN nanocrystals is displayed in Figure 6c, in which the cores are labeled as GaN and the shells as BN. The lattice fringes in the cores reveal crystalline structures. The nanocrystal in bottom of Figure 6c was analyzed by a 1 nm electron beam. The selected-area electron diffraction (SAED) pattern from this nanocrystal (Figure 6c inset) reveals the hexagonal phase of GaN, with lattice constants of $a=0.319$ nm and $c=0.518$ nm (powder diffraction files (PDFs): 50-0792). The eyebrowlike pattern in the SAED corresponds to the diffraction of the (002) planes (with a spacing of 0.334 nm) of the curved BN sheathe, labeled as 002* in inset in Figure 6c. EDX analysis confirms that the nanocrystals are composed of the Ga and N, as shown in Figure 7a. The N/Ga ratio calculated from this spectrum is approximately 1.1, which is a little higher than the stoichiometric composition of GaN owing to the contribution of the outer BN shell. The formation of the GaN nanocrystals is confirmed by the XRD patterns, as shown in Figure 7b. The absence of the reflection of BN in Figure 7b may be due to their small quantity and the relatively low crystallization.

Discussion

The formation of BN nanocages may be described using the following chemical reaction [Eq. (3)]:



The B_2O_3 and B–N–O vapors were first generated when the B–N–O precursor was heated to 1750 °C, and were then carried away by the argon flow. These vapors then met and reacted with NH_3 inside the graphite susceptor forming hollow BN nanocages. Control experiments show that the compositions of the precursors strongly influence the structure of the products. The B–N–O precursor with a formula of $\text{B}_4\text{N}_3\text{O}_2\text{H}$ results in BN nanotubes;^[22] the B–N–O precursor with a formula of $\text{B}_4\text{N}_2\text{O}_3$ results in BN nanocages (this work); while the B_2O_3 precursor produces amorphous BN bulks, as confirmed by control experiments. The main differ-

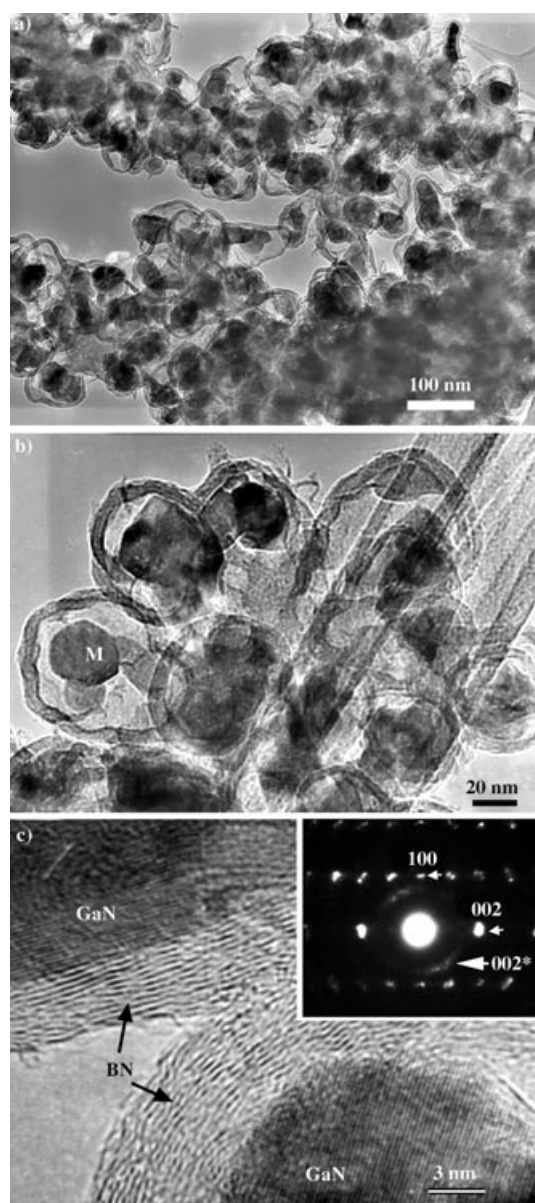


Figure 6. TEM images of BN nanocages filled with GaN nanocrystals. a) Low magnification TEM image of BN-nanocage-encapsulated GaN nanocrystals. b) High magnification TEM image of BN-nanocage-encapsulated GaN nanocrystals. c) HRTEM image of the nanocages. GaN nanocrystals and BN shells are labeled. Inset: SAED pattern of the GaN nanocrystal in the bottom of (c), taken by a 1 nm electron nano beam. The reflections of (100) and (002) correspond to the GaN nanocrystal; (002)* corresponds to the BN shell.

ence of the three precursors is the contents of oxygen. The oxygen contents of $\text{B}_4\text{N}_3\text{O}_2\text{H}$, $\text{B}_4\text{N}_2\text{O}_3$, and B_2O_3 precursors are 27%, 40%, and 67% respectively.

The evaporation rate of the boron source may influence the structure of BN. B_2O_3 is more easily evaporated than B–N–O precursors to provide source of boron for the formation of BN. The increase of oxygen content in the precursors implies the increase of B_2O_3 content. A greater source of boron is supplied with the increase of oxygen content in the precursors. It can be concluded that a high evaporation rate of B sources produces amorphous BN bulks, a mediate rate produces BN nanocages, and a low rate produces highly-

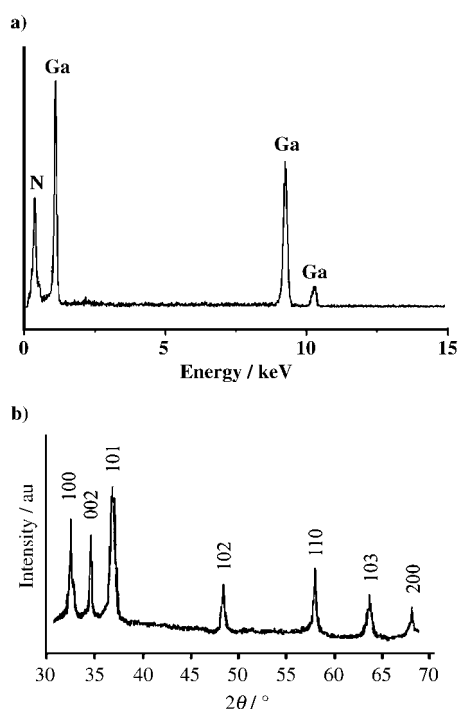


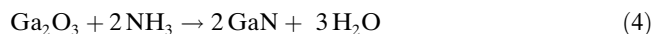
Figure 7. a) EDX spectrum of a GaN nanocrystal encapsulated in nanocages. b) XRD pattern of GaN nanocrystal encapsulated in nanocages.

crystalline BN nanotubes. The factors that influence the structures of BN are more complicated, of which the selection of precursors plays an important role. The category of the B–N–O precursors used in the present and previously related works^[22] have proved to be an applicable B source for the preparation of various BN nanostructures, such as nanotubes and nanocages. The structures of the products can be modulated by adjusting the composition of the B–N–O precursors.

In our previous work, we used the B–N–O precursor to sheath semiconducting nanowires with BN. In order to prepare BN nanocages, we changed the experimental procedures and the reaction atmosphere. An Ar flow was used as carrier gas to pass through the B–N–O precursor instead of an N₂ flow. The NH₃ flow was conducted into the reactor chamber from the top of the furnace instead of from the bottom by passing through the B–N–O precursor. The N₂/NH₃ flow reacts with the B–N–O precursor forming BN in the procedure of the previous work. This decreases the evaporation of B source, and thus influences the structure and output of the BN products. The two changes have improved the evaporation rate of B source by avoiding the reaction of the N₂/NH₃ flow and the B–N–O precursor. The factors influencing the structures of BN nanocages are complicated, such as the flow rates of the carrier gases and the temperature distribution of the furnace; a well-designed furnace is essential for the controllable study of the influencing factors.

The formation of nanocage encapsulated GaN nanocrystals is proposed in two basic steps: 1) GaN nanocrystals were initially fabricated and 2) BN nanocages were formed as outer shells on GaN nanocrystals. The Ga₂O₃ precursor was evaporated at 1200 °C and the vapors were carried by

the argon flow. The Ga₂O₃ vapors met and reacted with ammonia gas forming GaN nanocrystals through the reaction given in Equation (4):



The B₂O₃ and B–N–O vapors were generated at a higher temperature, and were carried by the argon flow and deposited on the surface of GaN nanocrystal in a lower temperature region. The B sources reacted with ammonia forming BN nanoshells on the surface of GaN nanocrystals. The absorption of B₂O₃ and B–N–O on the surface of nanocrystals may favor the formation of BN shells on the nanocrystals.

Conclusion

In summary, hollow BN nanocages and BN-nanocage-encapsulated GaN nanocrystals have been successfully synthesized by using a homemade B–N–O precursor through a thermochemical method. The category of the B–N–O precursors used in the present works proved to be a successful source of boron for the preparation of various BN nanostructures, such as nanotubes and nanocages. The structures of BN nanotubes and nanocages can be modulated by adjusting the composition of the B–N–O precursors. This approach may be generally applicable to fabrication of BN-nanocage-encapsulated nanocrystals; various nanocrystals may be encapsulated with BN nanocages by this route. Therefore, this method should be particularly important in the field of nanofabrication.

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