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Recent Progress on Fabrications and Applications of Boron Nitride Nanomaterials: A Review

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Boron nitride (BN) nanostructures with complementary functions to their carbon counterparts are one of the most intriguing nanomaterials. Here we devote a compact review on the syntheses of BN nanomaterials: typical zero-dimensional (0D) fullerenes and nanoparticles, one-dimensional (1D) nanotubes and nanoribbons, two-dimensional (2D) nanosheets as well as three-dimensional (3D) nanoporous BN. Combining low-dimensional quantum confinement and surface effects with unique physical and chemical properties of BN, *e.g.* excellent electric insulation, wide band gap, and high chemical and thermal stability, BN nanomaterials have drawn particular attention in a variety of potential applications, *e.g.* luminescence, functional composites, hydrogen accumulators, and advanced insulators, which are also reviewed.

1. Introduction

BN is a compound with alternatively linked boron and nitrogen atoms. There exist several crystalline varieties: cubic BN (*c*-BN) analogous to diamond, wurtzite BN (*w*-BN) similar to the lonsdaleite, and two sp^2-bonded layered configurations, *i.e.* hexagonal BN (*h*-BN) in AB stacking and rhombohedral BN (*r*-BN) in ABC stacking, corresponding to *h*-graphite and *r*-graphite, respectively. Among them, *h*-BN has been widely studied as an electrically-neutral model to understand low-dimensional layered materials. In history, *h*-BN nanomaterials were developing along with their carbon counterparts (Fig. 1): fullerenes/nanocages in 1990s[1,2], nanotubes in 1990s[3], nanosheets/white-graphenes in 2000s[4], and other morphologies, *e.g.* nanomeshes[5], nanoparticles[6], nanowires[7–10], nanoribbons[11], and nanoporous BN[12].

Analogous to isoelectronic *h*-graphite, *h*-BN is highly thermoconductive, mechanically strong, and lubricative owing to their similar intralayer strong σ bonds and interlayer weak *van der* Waals forces (Table 1). Nevertheless, because of heteroatom bonding nature, B–N bond is partially ionic in contrast to pure covalent C–C bond. In the σ bond, the electrons localize closer to nitrogen, while in the π bond involving empty *p*-orbital of boron and full-filled one of nitrogen, the electrons of nitrogen are much less delocalized comparing to the equivalent π electrons in C–C bond. Hence, *h*-BN is distinctively different from *h*-graphite in optical, electrical and chemical properties (Table 1). It is white or near transparent with a wide band gap, highly insulating, thermally and chemically stable. The unique physics and diverse functionalities enable *h*-BN nanomaterials to be applied as deep ultraviolet illuminants, dielectric gates, insulating thermal conductors, anti-oxidation lubricants, easily-dyed advanced materials, protective coatings, mold-release liners, and neutron capturers. In industry, BN has been widely used for cosmetics, insulation, lubrication, microwave-transparent objects *etc.*

Note that in Table 1 the data of Young's modulus[13–15] and thermal conductivity[16,17] come from experiments, and both intra-planar and inter-planar electron transports of graphitic layers behave as linear Ohmic characteristic at small voltages.

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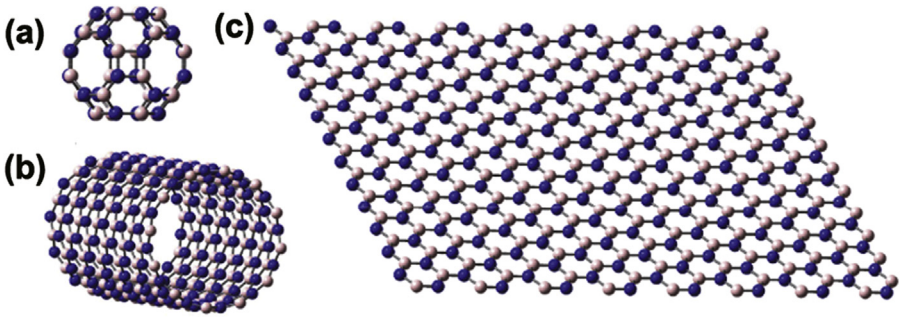

Fig. 1. Structural models of representative BN nanomaterials: (a) 0D $B_{24}N_{24}$ fullerene; (b) 1D BN single-walled nanotube; (c) 2D mono-layered BN nanosheet.

Table 1
Similar (first five items) and disparate characteristics of *h*-BN and *h*-graphite

Properties	*h*-BN	*h*-graphite
Bond length (nm)	0.144	0.142
Bond energy (eV)	4	3.7
Interlayer spacing, by diffraction (nm)	0.333	0.335
Young's modulus (TPa)	0.81–1.3	1.1
In-plane thermal conductivity (W/mK)	400	2600
Charge transferred between neighbors (e)	~0.4	~0
Band gap (eV)	5.5–6.0	~0
Breakdown voltage (MV/cm)	~7	Conductor
Oxidation resistance (°C)	~840	~600
Appearance color	White/near-transparent	Black

2. 0D BN Fullerenes and Nanoparticles

Nested BN fullerenes are structural analogs to C_{60} buckyballs. BN fullerenes were firstly found by electron irradiation in a transmission electron microscope (TEM) in 1998 (Fig. 2)[1,2,18]. The family of $(BN)_n$ nanosized cages ($n = 12, 20, 24$ or larger numbers) tends to utilize 4-, 6-, and 8-membered rings[19], which may demonstrate interesting properties in their assembled molecular solids. BN fullerenes demonstrated good lubrication[20], and high adsorption capacity of H_2 (4 wt.% at 298 K and 10 MPa) and organic pollutants[21,22]. They are still sparsely studied because of unavailable effective synthetic routes compared with C_{60}.

Nanoparticles with concentric BN layers were observed early in 1994[23,24]. Effective synthesis of BN microparticles with a diameter of 1–2 μm was conducted by aerosol-assistant vapor deposition under the reaction between boric acid droplets and NH_3[25,26]. BN nanoparticles with a diameter of 20 nm were synthesized analogously by a fast solid-state metathesis and explosive dispersion using NH_4BF_4 and NaN_3[27]. In 2002, high-throughput tens-of-gram production of BN nanoparticles was realized by a chemical vapor deposition (CVD) process over 1100 °C using trimethoxyborane and NH_3 (Fig. 3)[6,29,30]. The BN nanoparticles had uniform diameters varying from 10 to 400 nm. They were then applied to improve the heat transfer of nanofluid. With adding 6 vol.% BN nanoparticles, thermal conductivity of water matrix remarkably increased by 2.6 fold, while the viscosity was kept decently low[31]. Recently, the BN nanoparticles were used for making ultra-hard *c*-BN with Vickers hardness larger than 100 GPa (Fig. 3(d))[28]. BN nanoparticles also induced the apoptosis and inhibited the proliferation for prostate cancer cells, and thus served as boron-releasing preventative and therapeutic agent for prostate cancer[32].

3. 1D BN Nanotubes and Nanoribbons

Inspired by carbon nanotubes identification in 1991, BN nanotubes were also synthesized in 1995 (Fig. 4(a))[3,35]. Briefly, there are four mechanisms involved in the preparations for BN nanotubes: vapor-liquid-solid (VLS) growth, direct growth, substitution reaction, and template-directed synthesis.

Most of arc discharge and CVD methods to synthesize BN nanotubes were based on VLS growth. CVD typically utilized precursor vapors, *e.g.* borazine[36] or BO_x, and metal catalysts (usually in liquid forms under growth conditions) for growing solid-state BN nanotubes. The first breakthrough on large-scale synthesis of BN nanotubes was accomplished in 2002 by a CVD process using B and MgO (Figs. 4(b,c))[37,38]. The growth of BN nanotubes with diameters of 10–100 nm proceeded at the interface between BO_x–Mg flow and NH_3 flow. Other precursor

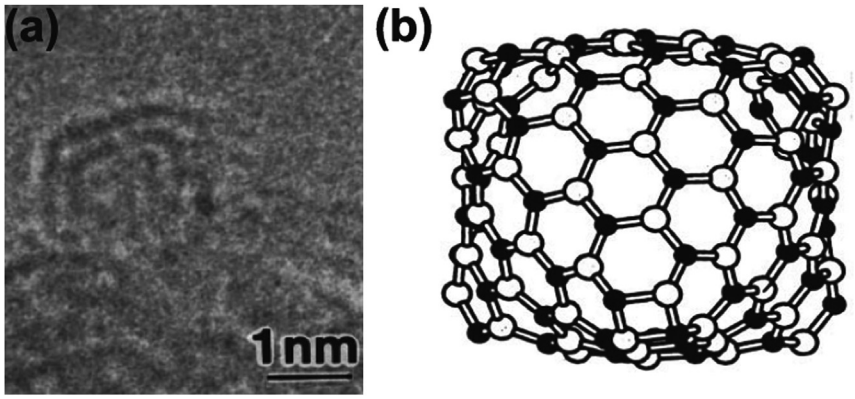

Fig. 2. BN fullerenes: (a,b) HRTEM image of an octahedral three-shelled BN fullerene and a proposed single-shelled model. They are reprinted from Ref. [2].