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Low-temperature Benzene-thermal Synthesis of Photoluminescent Turbostratic Boron Nitride Powders

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Photoluminescent turbostratic boron nitride (t-BN) powders can be easily synthesized from $NaBF_4$ and $NaNH_2$ via a facile benzene-thermal process at 260 °C. The prepared samples were characterized by XRD, XPS, FTIR, PL, TEM, and HRTEM. The possible active intermediates (BF_3 and Na_3N) are believed to be responsible for the growth of t-BN under mild conditions.

Boron nitride (BN) is of particular interest for the development of materials for high-performance applications.[1] Besides polymorphs with well-defined crystallographic structures (e.g., hexagonal BN: h-BN and cubic BN: c-BN), BN has partially disordered phases (e.g., turbostratic BN: t-BN).[2] The two-dimensional layers in the turbostratic phase are stacked roughly parallel to each other but show random rotation and translation about the layer normal.[3] High-temperature was usually the requisite for the synthesis of t-BN in traditional methods. Shore et al. synthesized tubular forms of t-BN by heating amorphous BN (a-BN) to 1100 °C.[4,5] Kaner et al. obtained t-BN powders via a rapid solid-state-precursor synthetic route at about 850 °C.[6]

In the past one decade, solvothermal synthetic routes are widely used for the synthesis of group 13 nitrides at low-temperature, including GaN,[7] InN,[8] and BN.[9,10] Hao et al. reported the benzene-thermal synthesis of h-BN nanocrystals by reacting Li_3N and BBr_3 at 250–550 °C for 2–3 days.[9] However, their XRD patterns do not possess the characteristic (100) and (101) peaks of h-BN, indicating that their products may be amorphous BN (a-BN). Recently, Chen et al. claimed the benzene-thermal synthesis of nanocrystalline h-BN by the reaction of BBr_3 and NaN_3 at 350 °C for >12 h.[10] In their XRD pattern, a long trail was found on the high diffraction angle side of the broad peak at $2\theta = 41.5$–$43.7°$, which is characteristic of the t-BN and the unresolved broad peak should be indexed as (10) of t-BN rather than (100) and (101) of h-BN.[3,6,7,11]

In the above reactions, energetical molecule BBr_3 was directly used as boron source, which is benefit for the synthesis of BN under relatively mild conditions. But BBr_3 is a very expensive and dangerous reagent, which is not a good choice for chemical synthesis of boron nitride in laboratory. Herein, we report a novel alternative chemical reaction for the synthesis of t-BN powders at 260 °C. The reaction scheme can be formulated as follows:

$$NaBF_4 + 3NaNH_2 \rightarrow \text{t-BN} + 4NaF + 2NH_3 \uparrow \qquad (1)$$

It was reported that ionic nitrides could be prepared by loss of ammonia from amide on heating[8,12] and $NaBF_4$ was thermally labile and decomposed to solid NaF and gaseous BF_3 under rapid heating in vacuum.[6,13] In the current reaction process, the following three chemical reactions are believed to play important roles according to the chemical dynamics and the chemical thermodynamics:

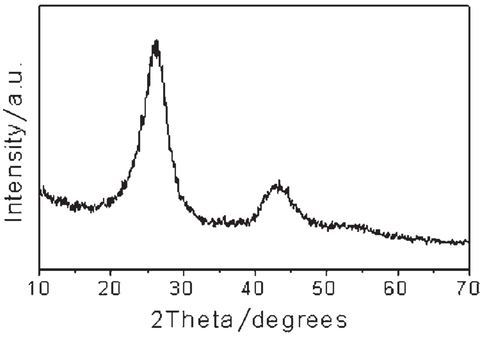

Figure 1. XRD patterns of the synthesized sample.

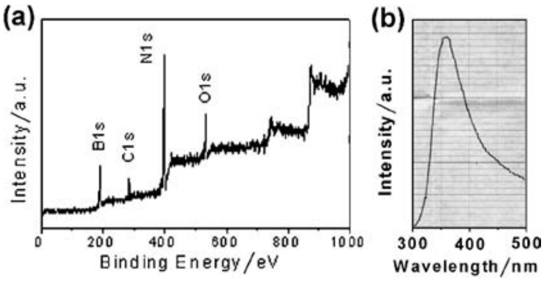

Figure 2. XPS survey spectrum (a), and PL spectrum (b) of the synthesized sample.

$$6NaNH_2 \rightarrow 3Na_2NH + 3NH_3 \rightarrow 2Na_3N + 4NH_3 \qquad (2)$$

$$NaBF_4 \rightarrow BF_3 + NaF \qquad (3)$$

$$Na_3N + BF_3 \rightarrow BN + 3NaF \qquad (4)$$

The reaction 2 and 3 are slow and reversible at 260 °C. The reaction 4 is fast but irreversible. Along with the progress of the reaction 4, chemical equilibrium 2 and 3 will move to the right continually, until the raw materials were used up. It is generally accepted that the formation of crystals with good crystallinity and homogeneous composition requires a fluid phase (such as vapor, solution, or melt) and a well controlled supplying rate of the reagents in the growth process.[14] Considering the low melting point (210 °C) of $NaNH_2$, there are at least two fluid phases in our reactions. In addition, the supplying rate of the possible energetic intermediates (BF_3 and Na_3N) is well controlled by the chemical equilibrium 2 and 3. The above two factors guarantee the formation of t-BN under mild conditions. In addi-

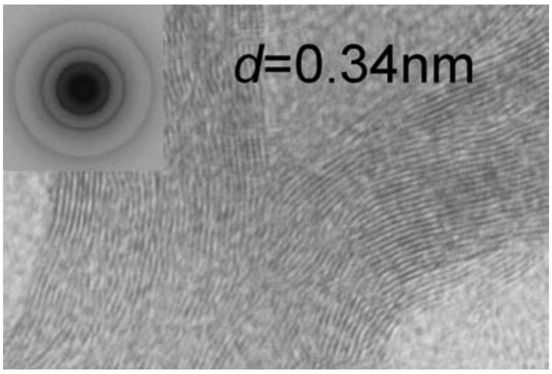

Figure 3. HRTEM image and SAED patterns (the inset) of the synthesized sample.

tion, benzene also plays important roles. First, it is used as a solvent. Second, the elevated benzene pressures will be beneficial for the formation of crystals under relatively low temperatures.

In a typical procedure, 60-mL stainless steel autoclave was loaded with 40 mL of benzene, 2.2 g of $NaBF_4$, and 2.7 g of $NaNH_2$. The autoclave was sealed and maintained at 260 °C for 15 h, then cooled to room temperature and opened carefully in a drafty place (Caution: the produced NH_3 gas is an eye and nose irritant, don't stare and smell closely!). The gray product was washed with ethanol and then distilled water. The obtained product was dried in vacuum at 60–70 °C for 2–3 h.

The XRD (Phillips X'Pert SUPER, Cu Kα radiation) patterns (Figure 1) are in good agreement with that described in the literatures for t-BN.[3,5,11] The intense 002 diffraction at $2\theta = 26.1^\circ$ ($d = 3.41$ Å) indicates the presence of layered structures. A less intense, broad peak at $2\theta = 43.0^\circ$ ($d = 2.10$ Å) correspondes to the (10) diffraction (unresolved (100) and (101) diffractions for h-BN).[5]

B, N, and minor C and O were observed on the XPS (ESCALab MKII) survey spectrum (Figure 2a). The carbon and oxygen contamination on the surface of the sample came from the adsorbed CO_2, H_2O, and O_2 during the post-treatment. Higher resolution spectra (not showing here) of B1s and N1s showed symmetry peaks at about 190.0 and 398.0 eV, respectively. The calculated atomic ratio of B to N on the surface of the sample was 1.057:1.

Two strong characteristic peaks of boron nitride were observed at the position 1410 and 780 cm^{-1} in the FTIR (Nicolet Model 759) spectrum (not shown here). In addition, a weak broad absorption at 3420 cm^{-1} was observed, which may mainly be attributed to the stretching vibration of residual N–H groups.[5]

The PL (HITACHI-850) spectrum (Figure 2b) showed one intense broad emission band at $\lambda em = 360$ nm (≈ 3.5 eV) in the range of 300–500 nm when the synthesized sample was excited by ultraviolet light with $\lambda ex = 257$ nm. This PL spectrum was very similar to the reported luminescence data of t-BN ($\lambda em = 340$ nm) in the literature,[11] which supported the conclusion that our synthesized boron nitride is t-BN. In addition, our synthesized t-BN has larger emission bandwidth than that of the reported t-BN.[11]

TEM (JEOL-2010) image (not shown here) of the sample indicated that the synthesized sample had an irregular morphology and did not appear porous. The diffraction rings in the SAED (JEOL-2010) patterns (the inset of Figure 3) can be indexed as the (002) and (10) reflections by reference to the XRD patterns of h-BN.[5] HRTEM (JEOL-2010) image (Figure 3) indicated that the microstructure of the synthesized sample was characterized by the curly layered structure, which again supported that the synthesized BN was t-BN. The lattice spacing in HRTEM image was measured to be ≈ 0.34 nm.

In summary, we reported the low-temperature benzene-thermal synthesis of photoluminescent t-BN powders from $NaBF_4$ and $NaNH_2$. The possible active intermediates (BF_3 and Na_3N) are believed to be responsible for the growth of t-BN under mild conditions.

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