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Study of Two Temperatures on Lab-scale Synthesis and Characterization of Hexagonal Boron Nitride

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ABSTRACT

Hexagonal boron nitride (h-BN) is a potential 2D material due to its advantageous characteristics such as low specific density, resilience to high temperatures, increased interlayer shear force, broad bandgap, and resistance to oxidation. This study aimed to explore a cost-effective and lab-scale synthesis method of h-BN by optimizing two temperatures. For the synthesis of h-BN, sol-gel synthesis method has been used. The synthesized h-BN was characterized by FTIR, XRD, and Zeta potential. FTIR confirmed the formation of BN at 600°C for 4 M boric acid-based precursor solution. XRD analysis showed the crystal size 27.74 nm for h-BN. Zeta potential was measured -26.8 mV for h-BN. This study will help the scientific community to easily synthesize and further tune the properties of h-BN which will ultimately open a new door in many fields such as medicine, drug delivery, environmental remediation.

Keywords: h-BN, FTIR, XRD, Zeta Potential, Sol-Gel Synthesis

1. Introduction (Top heading should be in bold)

In modern era of science and technology hexagonal boron nitride contains specific properties like excellent heat conductivity, effective electrical insulation, strong neutron adsorption capabilities [1] . So, it has so many applications including shielding metals from corrosion and oxidation due to its exceptional oxidation resistance at high temperatures. BN nanosheets are perfect dielectric substrates for electronic devices based on 2D heterostructures and surface enhanced Raman spectroscopy (SERS) because they are flat insulators. Because of its significance in science and technology, BN nanosheets' light emission in the deep ultraviolet (DUV) and ultraviolet (UV) areas is also mentioned due to its excellent heat resistance, anti-oxidation behaviors, and neutron absorption capability, BN may be used in the aerospace and spacecraft sector for manufacturing space suits. Also used in corrosion protection, thermal management, adsorption, and separation, biomedical application, wastewater treatment etc. [2, 3]. The synthetic pathway of BN is divided into two categories: (1) top-down techniques and (2) bottom-up techniques. The top-down process is distinguished by its subtractive methodology, which divides a huge starting substance into smaller nano-sized components. In contrast, the bottom-up technique is defined by an incremental process that begins with precursor atoms or molecules, which eventually combine to generate nanostructured forms. The most utilized top-down methods are:

- Mechanical exfoliation
- Chemical or solvent exfoliation
- Laser Ablation
- Molecular beam epitaxy (MBE)

and the bottom-up approaches are:

- Atomic layer deposition (ALD)
- Physical vapor deposition (PVD)
- Chemical vapor deposition (CVD
- Chemical synthesis reaction [4]

CVD is still the method of choice for high-performance materials along with h-BN. It is perfect for several applications because it provides fine control over material composition and high-quality thin coatings. In 2023, Yamamoto, M., et al. used inductively coupled plasma-enhanced chemical vapor deposition (ICP-CVD) to create multilayer hexagonal boron nitride (h-BN) on substrates [5]. The precursor was liquid borazine that was kept at -10°C and supplied by N_2 bubbling at 0.2 sccm. The synthesis was carried out on Si, SiO_2/Si, and quartz substrates at low temperatures (400–500°C) during a growth period of 15 minutes. In addition to varying synthesis parameters including temperature, pressure, and RF plasma power (13.56 MHz), the procedure included carrier gases (Ar, N_2, and H_2). Prior to deposition, the base pressure was kept at around 5×10^{-4} Pa. However, CVD requires specialized equipment, expensive precursor materials, and considerable energy consumption, it is expensive. The complicated equipment needed for CVD, such as temperature control, vacuum systems, and reactors, raises the setup and maintenance expenses.

C Xiong et al. synthesized BN using direct chemical synthesis process [6]. The direct chemical production of

spherical requires boric acid, ammonium chloride, and copper oxide (CuO) as the primary ingredients. The reaction was conducted at a temperature of 950°C over a period of 4 hours in the presence of nitrogen gas, using varying molar ratios of copper oxide (CuO) to boric acid (H_3BO_3). Small-

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sized spherical BN nanoparticles were synthesized by adding a certain amount of CuO. The prolonged reaction time led to the consolidation of BN, causing the transformation from a state of finely distributed nanoparticles to bigger conglomerates. To get boron nitride nanoparticles of a reduced size and spherical morphology, the reaction time was fine-tuned to 4 hours. The average diameter of the BN nanoparticles in a spherical form was around 30 nm. However, high energy costs, exact temperature and nitrogen environment control, and possible contaminants in the finished product are some of the difficulties associated with the direct chemical synthesis of h-BN. The process is further complicated by the employment of expensive and dangerous chemicals.

Ghosh et al. used a liquid exfoliation method to synthesize hexagonal boron nitride (hBN) on a massive scale [7]. The initial procedure involved dispersing bulk hBN in a solution of gelatin, potassium chloride (KCl), and zinc chloride ($ZnCl_2$) using a probe sonicator. Zn^{2+} and K^+ ions intercalated between the hBN layers during a centrifugation process, which further improved the exfoliation. The centrifugation's supernatant was heated to 600°C for an hour in air to eliminate gelatin, and then it was heated to 800°C in an argon environment to enhance the hBN's crystallinity. However, the inability to achieve uniform exfoliation and scalability limits the use of liquid exfoliation of hBN, which frequently results in low yields of high-quality monolayers. The procedure may also require the employment of hazardous chemicals and drawn-out stages, which would increase its complexity and expense.

These methods of h-BN synthesis are very costly because of its high energy requirements, specialized reagents etc. Also, some of these methods needs heavy instruments in laboratory. For these challenges, there is a need for easier and low-cost method.

The Sol-gel method is a bottom-up approach. In the bottom-up approach, the particles are made from atoms or clusters. The sol-gel technique is a chemical process that transforms a solution (sol) into a solid (gel) phase by means of hydrolysis and polymerization processes, hence synthesizing materials [8].

Atoms → Cluster → Nano particles

The main steps of sol gel method are as follows:

$$\text{Sol} \xrightarrow[condensation]{hydrolysis} \text{Gel} \xrightarrow{evaporation} \text{Dried Gel} \xrightarrow{grinding} \text{Product}$$

Recently, h-BN was synthesized by sol gel method in a unique way by Kayani et al. [9]. The primary components required to produce BN thin film are boric acid (H_3BO_3), boron nitrate, ammonia (NH_3), and water. Ammonia (NH_3) is a substance used as a stabilizer. Solutions of boric acid with concentrations of 1 M and 0.5 M were produced. To create the solution, boric acid or boron nitrate

was dissolved in 20 ml of water by agitation for a duration of 2 hours. After adjusting the pH with a little amount of ammonia, the sol was stirred vigorously for a duration of 3 hours to achieve clarity and uniformity. A range of sols was produced by using different molar concentrations of Boric acid/boron nitrate. The solution was let to mature for a duration of 36 hours at ambient temperature [9]. However, this method includes dip coating method to produce thin films on glass substrates. Dip coating can provide inconsistent thickness, which limits its ability to produce uniform coatings on complicated geometries. Furthermore, it might be challenging to regulate the drying rate, which could result in flaws like poor adhesion or cracking.

The best approach for h-BN synthesis for lab-scale operation is chosen based on the materials and equipment that are available, the process's efficiency, and the overall cost of the procedure. The sol gel approach for the synthesis of BN was selected. Instead of dip coating, direct drying and heat treatment for precursor samples were used in this study. This novel project uses boric acid and a liquid ammonia mixture, along with the sol-gel method, direct drying, and heat treatment, to deposit h-BN. The reaction pathways were investigated, impact of two different temperatures with varying concentration were studied, and the synthesized h-BN was characterized by FTIR, XRD, and Zeta potential analysis. Structural properties were calculated from XRD. The dispersion stability of h-BN was measured by Zeta potential. This work provides valuable insights into synthesizing and modifying h-BN properties which have potential applications in drug delivery, environmental cleanup, and medicine [10].

2. Materials and Methodology

2.1 Materials

Boric acid (powder), liquid ammonia, ethanol, deionized water.

2.2 Methodology

By adding 1.25 g and 5 g of boric acid to 20 mL of deionized water, 4 samples (two 1 M and two 4 M) boric acid solutions were prepared. A magnetic bead was introduced into both boric acid solution and subsequently agitated at room temperature for 10 minutes on a heated plate, rotating at a speed of 800-1000 rpm. 1 M ammonia solution was slowly added dropwise to the acid solutions. After the solutions reached pH 7, ammonia droplets were not added anymore. The solutions were stirred for 2 hours at room temperature, rotating at a speed of 800-1000 rpm. Then the solutions were left for a duration of 24 hours to form gel. The solutions were thereafter subjected to sonication in a water-filled bath sonicator at a temperature of 50°C for a duration of 40 minutes. Afterwards, the samples were dried in a preheated oven at 100°C for 8 hours, followed by a 2-hour resting period, and then subjected to another 8 hours of drying, resulting in a total drying duration of 16 hours. The dried samples were milled using a mortar and pestle. Samples are then labelled as S (1 M, 400°C), S (4 M, 400°C), S (1 M, 600°C), and S (4 M, 600°C). S (1 M, 400°C), S (1 M, 600°C) stands for 1 M boric acid precursor-based sample and other two samples stand for 4 M boric acid precursor-based samples. S (1 M, 400°C), S (4 M, 400°C) subjected to

a temperature of 400°C for a duration of 3 hours while S (1 M, 600°C), S (4 M, 600°C) at 600°C for 4 hours in a furnace, with a gradual increase in temperature of 5°C per minute, requiring 2 hours to reach the desired temperature. After heat treatment, the samples were subjected to centrifugation using

DI water solvent at a speed of 3000 rpm for a duration of 10 minutes. The centrifugation procedure was iterated eight times until the nanoparticles achieved a pH of 7. The samples were dried in a high-temperature oven set at 80°C for a duration of 16 hours. Finally, the dried samples underwent milling again with mortar and pestle and then underwent characterization test: FTIR, XRD, Zeta Potential. Experimental setup is shown in Fig.1.

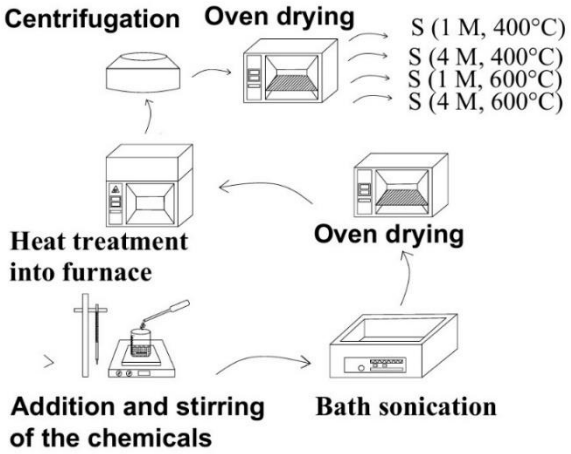

Fig.1 Experimental setup.

3. Results and Discussion

3.1 Graphs

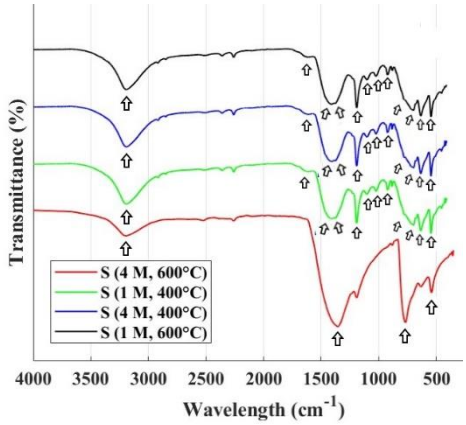

Fig.2 FTIR Spectra of S (1 M, 400°C), S (4 M, 400°C), S (1 M, 600°C), S (4 M, 600°C)

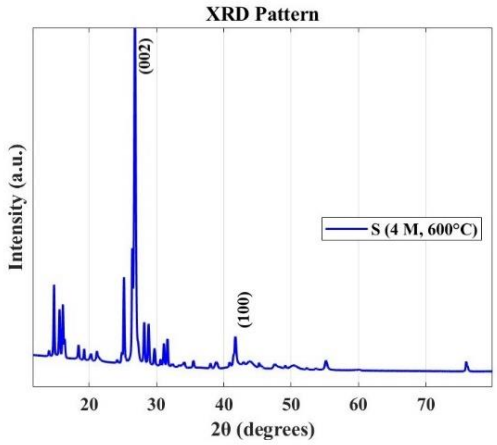

Fig.3 XRD pattern for S (4 M, 600°C)

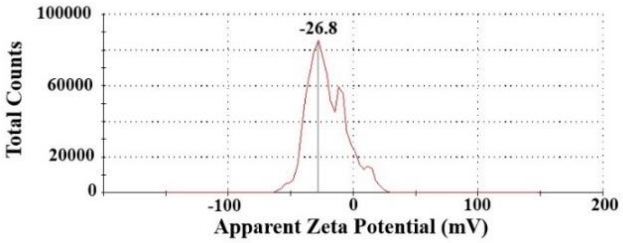

Fig.4 Zeta Potential curve for S (4 M, 600°C) at pH 7

3.2 Result

FTIR spectroscopy was executed with NICOLET iSS, ThermoScientific. In Fig. 2, the FTIR spectra are shown for sample S (1 M, 400°C), S (4 M, 400°C), S (1 M, 600°C), and S (4 M, 600°C). The FTIR spectra and the corresponding peaks of sample S (1 M, 400°C), S (4 M, 400°C), S (1 M, 600°C) suggest that ammonium pentaborate (APB) formation takes place here [11]. So, 400°C and 600°C (1 M) are not appropriate to synthesize hexagonal boron nitride. Table 1 and Table 2 show the comparison of FTIR peaks of all samples with the reference values.

Table 1 Vibrational band assignments of sample S (1 M, 400°C), S (4 M, 400°C), S (1 M, 600°C).

FTIR peaks (cm^{-1})	Ref. Values (APB) (cm^{-1}) [12]	Band assignments
3200	3326	(O-H) symmetric stretching
1651	1642	NH_4 asymmetric bending,
1425	1432	B-O terminal asymmetric stretching
1326	1354	B-O asymmetric stretching
1237	1244	CH_2 torsion
1091	1101	B-O terminal asymmetric stretching
1021	1024	B-O terminal symmetric stretching
912	924	B-O ring stretching
780	782	B-O ring stretching
689	695	O-B-Oring asymmetric bending
593	590	O-B-O terminal bending
546	504	O-B-O ring bending

In Fig. 2, the sample S (4 M, 600°C) exhibits two prominent peaks at 1358 and 767 cm^{-1}. The peaks at 3200 cm^{-1} in figure 2, which corresponds to the B-OH bond, was seen because of the moisture content in the bulk samples [13]. This FTIR spectrum confirms the synthesis of h-BN due the successful formation of B-N and B-N-B bonds which peaks match with the reference values [14, 15].

Table 2 Vibrational band assignments of sample S (4 M, 600°C).

FTIR peaks (cm^{-1})	Reference Values (BN) (cm^{-1}) [15]	Band assignments
3200	3200-3400	(O-H) stretching(oxidation)
1358	1378	B-N in-plane stretching
767	790	B-N-B out-of-plane bending

The h-BN sample further underwent two additional characterizations: XRD and Zeta Potential. The XRD belongs to Rigaku Smartlab with CuKα radiation at wavelength λ= 1.54 Å, scanning range 10°-80°, scanning speed 10°/min with 40 kV voltage and 40 mA applied current. In Fig. 3, XRD spectra confirm that all diffraction peaks correspond to standard BN (JCPDS Card No. 85-1068), exhibiting a layered hexagonal structure. The prominent peak at 2θ = 26.8° matches the h-BN (002) plane, which is the strongest peak of h-BN (JCPDS Card No. 85-1068). The lattice constants of sample S (4 M, 600°C) are in good agreement (Table 3) with the reported values of h-BN, namely a = 2.510 Å and c = 6.690 Å (JCPDS No. 85-1068) [16, 17]. From Fig. 3, maximum 2θ value is 26.80° for (002) crystal plane and full width at half maximum (FWHM) is 0.2944°. Size of the crystallite was determined using the Scherrer equation, which is given by [18]:

$$D = k\lambda/\beta\cos\theta \quad (1)$$

In this equation, D represents the crystallite size, k is a constant with a value of 0.94, β is the whole width at half maximum, θ is the Bragg angle of the (002) peak, and λ is the wavelength of CuKα.

The degree of crystallinity is determined by the formula [19],

$$X_c = 0.24/(\beta_{002})^2 \quad (2)$$

Dislocation density (δ) [20],

$$\delta = 1/D^2 \quad (3)$$

The lattice constants a, c, and the inter-planar spacing d_{hkl} are calculated using the following relations [21].

$$a = \frac{\lambda}{\sqrt{3}sin\theta} \quad (4)$$

$$c = \frac{\lambda}{sin\theta} \quad (5)$$

$$\frac{1}{d_{hkl}} = \left[\frac{4}{3a^2}(h^2 + k^2 + hk) + \frac{l^2}{c^2}\right]^{-\frac{1}{2}} \quad (6)$$

Dispersions with zeta potential values over ± 30 mV often demonstrate great physical stability [22]. In Fig. 4, the zeta potential of -26.8 mV (at pH 7) for h-BN suggests a significant level of electrostatic repulsion, which effectively prevents the particles from coming together and forming aggregates, thereby assuring good stability.

3.3 Discussion

The formation of ammonium pentaborate (APB) undergoes the reaction below:

$$5H_3BO_3 + NH_4OH \rightarrow NH_4[B_5O_8(OH)] + 3H_2O \quad (7)$$

The decomposition of APB starts at 600°C [23], and for 4 M based boric acid precursor solution, it undergoes the reaction below:

$$NH_4[B_5O_8(OH)] \xrightarrow{\Delta} BN + 5H_2O \quad (8)$$

So, the formation of h-BN takes place in two stages. Boric acid (H_3BO_3) reacts with ammonia solution (NH_4OH) to form ammonium pentaborate ($NH_4[B_5O_8(OH)]$). Upon heating at 600°C, APB decomposes to produce boron nitride (BN) and water (H_2O). Further heating of BN leads to the formation of hexagonal boron nitride (h-BN).

The calculated structural data (from XRD) such as crystal dimension, degree of crystallinity, strain, dislocation density, lattice constants a, c and interplanar spacing are presented in Table 3.

Table 3 Structural properties of sample S (4 M, 600°C).

Crystal dimensions, D (nm)	27.74
Degree of crystallinity,	2.18
Dislocation density, δ (nm^2) (10^{-4})	13
Lattice constant, a (Å)	2.50
Lattice constant, c (Å)	6.65
Interplanar spacing, d_{002} (Å)	0.30
Strain, ε (10^{-3})	1.25

The yield of h-BN may be enhanced by augmenting the concentration of reactants in accordance with Le Chatelier's principle. Nevertheless, increased concentrations of reactants often result in the formation of bigger crystals, hence requiring the need for optimization. Elevated temperatures and extended reaction durations provide increased yields by expediting reaction kinetics. Ammonium pentaborate undergoes decomposition at a temperature of 600°C [23], after that the conversion into h-BN starts . However, very high temperatures and extended reaction periods may have a negative impact on the size and shape of the crystals. Hence, it is crucial to create an ideal equilibrium between the concentration of reactants, temperature, and

time of the reaction to get the required yield and crystal properties of h-BN.

4. Conclusion

By adjusting two temperatures, this work sought to investigate a lab-scale, relatively inexpensive synthesis technique of h-BN. An easy sol-gel synthesis technique was employed to create h-BN. Zeta potential, FTIR, and XRD were used to characterize the synthesized h-BN. The production of BN at 600°C was verified by FTIR. According to XRD measurements, h-BN's crystal size was 27.74 nm. For h-BN, the observed zeta potential was -26.8 mV.

The zeta potential test demonstrated a negative value in h-BN. The h-BN negative zeta potential can physically disrupt the positively charged virus and bacteria, ultimately causing the death of bacterial cells [24]. It is a suitable candidate for antibiotic therapy. By introducing functional groups onto the surface of h-BN, the number of

reactive sites can be enhanced. In addition, h-BN is a great adsorbent for wastewater filtration [25]. So, this easy synthesis method can help the researchers experiment in a laboratory with h-BN and make great contribution to the field of drug-delivery, medicinal chemistry and environmental remediation.

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NOMENCLATURE

XRD : X-ray diffraction

FTIR : Fourier Transform Infrared Spectroscopy

h-BN: Hexagonal boron nitride