

T.R.
GEBZE TECHNICAL UNIVERSITY
INSTITUTE OF NANOTECHNOLOGY

**SYNTHESIS AND CHARACTERIZATION OF HEXAGONAL
BORON NITRIDE NANOPATES**

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NANOPLATES

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SUMMARY

Hexagonal boron nitride [h-BN] has attracted great interest as a two-dimensional material due to its unique combination of excellent thermal conductivity, electrical insulation, low dielectric constant, and chemical stability. Fabricating tiny, few-layer h-BN nanoplates (h-BNNs) is challenging because of the strong intramolecular and intermolecular interactions within the hBN structure. Common h-BNN fabrication techniques include chemical vapor deposition, solid phase exfoliation, and liquid phase exfoliation (LPE). Among such methods, LPE stands out among these techniques as the simplest and most extensively employed method for manufacturing these two-dimensional nanoplates.

This thesis aims to investigate in depth the LPE process conditions in an attempt to control the ultrasound exfoliation process in order to obtain h-BNNs with nanometer-thick walls. Our ultimate goal was to understand the viability of producing thin-layer h-BNNs via the probe ultrasound method, specifically for applications involving the fabrication of nanocomposites for energy storage. h-BNNs with ideal thickness at nanometer scale were synthesized using a variety of solvents and their concentrations using this approach. Shape, size, thickness, and chemical composition of as produced h-BNNs were examined using a variety of characterization techniques, namely, with Atomic Force Microscopy (AFM), Scanning Electron Microscopy (SEM), and Fourier Transform Infrared Spectroscopy (FTIR). The thickness of h-BNNs was found to increase with decreasing ultrasound duration.

Keywords: Hexagonal Boron Nitride, Liquid Phase Exfoliation, Nanoplates, Ultrasound-Assisted Exfoliation, Thin-Layer H-Bnns, Nanocomposites, Applications.

ÖZET

Altıgen bor nitrür [h-BN], öncelikle mükemmel termal iletkenlik, elektrik yalıtımı, düşük dielektrik sabiti ve kimyasal kararlılığın benzersiz kombinasyonu nedeniyle iki boyutlu bir malzeme olarak büyük ilgi görmüştür. İnce, az katmanlı h-BN nanoplakaların [h-BNN'ler] üretilmesi, hBN yapısı içindeki güçlü molekül içi ve moleküller arası etkileşimler nedeniyle zordur. Yaygın h-BNN üretimi teknikleri arasında kimyasal buhar biriktirme [CVD], katı faz eksfoliasyonu ve sıvı faz eksfoliasyonu [LPE] bulunmaktadır. Bu yöntemler arasında LPE, iki boyutlu nanoplakaları üretmek için en basit ve en yaygın kullanılan teknik olarak öne çıkmaktadır.

Bu tez çalışması, nanometre kalınlığında duvarlara sahip h-BNN'ler elde etmek için ultrasonik pul pul dökülme sürecini etkili bir şekilde kontrol etmek amacıyla LPE işleme koşullarını araştırmaya odaklanmaktadır. Nihai hedefimiz, enerji depolama için kompozitlerin kullanımını içeren uygulamalar için prop ultrason yöntemi ile ince h-BNN'ler üretmenin uygulanabilirliğini anlamaktır. Nanometre ölçeğinde ideal kalınlığa sahip h-BNN'ler, bu yaklaşım kullanılarak çeşitli çözücüler ve konsantrasyonları kullanılarak sentezlendi. Üretilen h-BNN'lerin şekli, boyutu, kalınlığı ve kimyasal bileşimi Atomik Kuvvet Mikroskobu (AFM), Taramalı Elektron Mikroskobu (SEM) ve Fourier Dönüştümlü Kızılötesi Spektroskopisi (FTIR) gibi çeşitli karakterizasyon teknikleri kullanılarak incelenmiştir. h-BNN'lerin kalınlığının azalan ultrason süresi ile arttığı bulunmuştur.

Anahtar kelimeler: Altıgen Bor Nitrür, Sıvı Faz Eksfoliyasyonu, Nanoplakalar, Ultrason Destekli Eksfoliyasyon, İnce Tabaka H-BNN'ler, Nanokompozitler, Enerji Depolama Uygulamaları.

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LIST OF ABBREVIATIONS AND ACRONYMS

<u>Abbreviations</u>	<u>Explanations</u>
<u>and Acronyms</u>	
AFM	: Atomic Force Microscopy
CHP	: 1-Cyclohexyl-2-Pyrrolidone
CVD	: Chemical Vapor Deposition
DMF	: Dimethylformamide
FTIR	: Fourier Transform Infrared Spectroscopy
hBN	: Hexagonal Boron Nitride
H BNNS	: Hexagonal Boron Nitride Nanoplates
H ₂ SO ₄	: Sulfuric Acid
KMnO ₄	: Potassium Permanganate
LPE	: Liquid Phase Exfoliation
NMP	: N-Methyl-2 Pyrrolidone
hBN	: Hexagonal Boron Nitride
nm	: Nanometer
PVD	: Physical Vapor Deposition
SEM	: Scanning Electron Microscopy
XRD	: X-Ray Diffraction Spectroscopy
GTÜ	Gebze Technical University

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1. INTRODUCTION

One of the most astonishing categories of materials that have emerged in recent years is that of the two dimensional (2D) nano structured materials. A great number of distinctive characteristics may be found within the structures such as graphene, molybdenum disulfide, boron nitride, tungsten disulfide, etc. Due to thickness and size of these 2D nanomaterials on both the macro and nanoscales, they are the thinnest of the 2D nanomaterials. These nanostructures are clustered with strong designed bonds that are sandwiched between layers and weak van der Waals forces [1]. In spite of the fact that a single layer is the ideal configuration for two-dimensional nanomaterials, these nanolayers usually consist of a number of layers [2],[3]. The number of layers affects numerous characteristics of such nanomaterials, including optical band gaps, electronic properties, mechanical strength and catalytic performance.. Because of this, a significant amount of research has been conducted on the differences in the numbers of these layers. The hexagonal crystal structure of hexagonal boron nitride nanoplates, which are a subset of two-dimensional nanomaterials, is made up of boron and nitrogen atoms organized on parallel planes. Important characteristics of h-BNNSs are their high dielectric constant, thermal conductivity, optical transmittance, and chemical resistance. Interest in possible applications for these characteristics has grown in a number of fields, including thermal management, optoelectronics, and electronics. The structure of hexagonal boron nitrite (hBN) is similar to that of graphite (Figure 1). Also known as white graphene, hBN has unique properties of superior electrical insulation, wide bandwidth, exceptional chemical and thermal stability, optical properties and excellent lubricance [3]. There are numerous methods for producing hexagon boron nitrite nanoplates such as chemical vapor deposition (CVD) and exfoliation. CVD is one of the bottom-up techniques involving vapor deposition of solid material, where chemical processes take place on the surface of the substrate, resulting in the growth of thin films and nanostructures. On the other hand, during mechanical exfoliation or otherwise known as ball mill procedure, the particles present in the mixture remain under the impact of high-energy balls. This process is used for the mechanical separation of solid materials. In the liquid phase exfoliation (LPE) technique, ultrasonic sound waves are used to dissolve adhesions between layers to

carry out the breakdown process. All of these techniques can be used to create hBN nanoplates (h-BNNS).

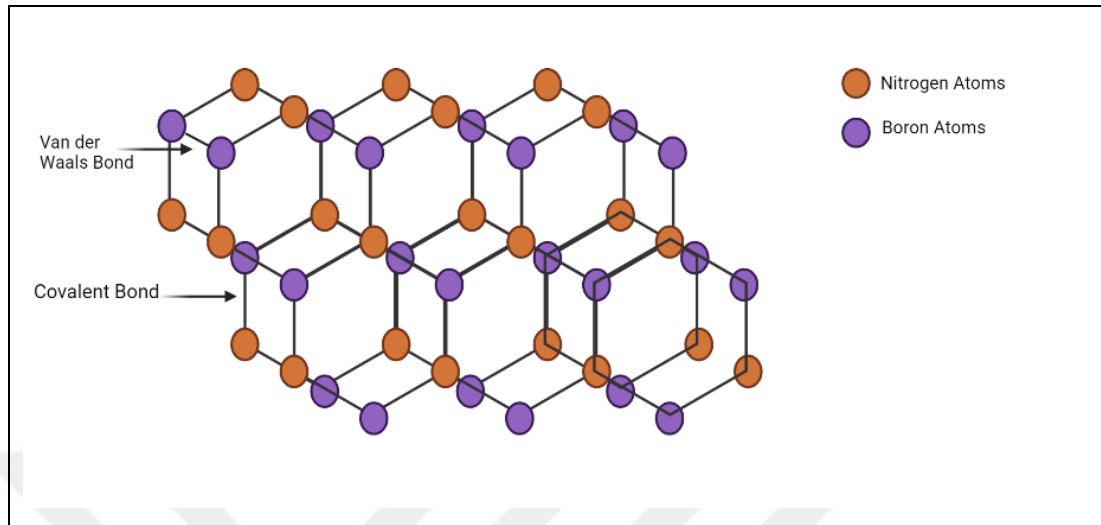


Figure 1.1: h-BNNs structure.

During the course of this thesis research, many variables, including processing time, concentration, and the polarity of solvents used, were altered in order to investigate the effect of the production process conditions on the 2D structure of hexagonal boron nitride nanoplates (h-BNNs). In our investigation, liquid phase exfoliation method utilizing ultrasonic sound waves were used as a cost-effective and facile approach [4]. We believe that this approach has some advantages in comparison to other production methods such as CVD, ballmilling and Hummers method since it shortens the amount of time required to manufacture numerous layers of material while simultaneously reducing the number of flaws and increasing the yield values [5]. Optimization of production method according to the application required (e.g. energy storage and biomedical applications) for 2D nanomaterials is vital for further studies.

2. 2D NANOMATERIAL

Nanomaterials are substances with at least one dimension between 1-100 nm and they have distinctive properties compared to their bulk state [6]. Typically, these materials are grouped according to their nanoscale dimensions. There are three different types of nanomaterials. Nanoparticles, which include compounds with all dimensions above the nanoscale, are the first group. For example, the nanoparticle fullerene can be mixed with crystalline solids to form nanocomposites with dimensions entirely on the nanometer scale. Carbon nanotubes are an example of this category; they are classified as nanotubes if they have two dimensions larger than the nanoscale. The third group consists of 2D components that are only a few atoms or molecules thick. These nanoparticles are substances that are only a few atoms thick and have widths and lengths on the nanometer scale. Some of the best known 2D nanomaterials are graphene and boron nitride. Boron nitride has a monolayer structure composed of boron and nitrogen atoms, while graphene is composed entirely of carbon.

Three-dimensional nanomaterials form the third group. These nanomaterials are usually in the form of cubes, cylinders or other complex geometric forms with at least one dimension at the nanoscale. Examples of 3D nanomaterials are metal nanoparticles or nanolamels.

These materials are of great interest in a number of different application areas. In the electronics sector, they have potential for nanoelectronic devices due to their high conductivity. They are also used in many fields such as energy storage (supercapacitors, battery technologies), materials science research, optoelectronic devices and biomedical applications. Examples include 2D materials such as graphene, boron nitride, molybdenum disulphide (MoS_2) and tungsten disulphide (WS_2).

2.1. Graphene

Graphene is one of the most promising 2D nanomaterials for the future due to its unique properties. In addition, graphene is the most important member of the family of multidimensional carbon materials, which also includes fullerene, a nanomaterial with zero dimensions, carbon nanotubes, a nanomaterial with one dimension, and

graphite, a nanomaterial with three dimensions [7]. Graphene is the narrowest material ever discovered, with a molecule-thick thickness. It is also known as one of the strongest materials; its tensile strength is 200 times that of steel [8]. Additionally, it has extremely high thermal and electrical conductivity. Graphene has begun to be used in numerous aspects of human life, the most essential of which are energy storage, catalysis while current study looks into its medicinal use potential.[9-11]. Since graphene is a translucent, flexible, and, most importantly, lightweight material, it can be utilized in the majority of electronic devices of daily use, including touch screens, batteries, and solar cells. Graphene is also known to be used in sensors as medical tests, food safety checks, and the identification of compounds and gases [12]. Therefore numerous graphene synthesis strategies have been investigated [12].

One of the common production method for graphene is the chemical vapor deposition, in which the surface of a thin layer of metal at high temperature interact with the carbon atoms in the gas (e.g. methane) given in the CVD chamber to form graphene on the metal surface [13]. The graphene can then be transferred to a different substrate and utilized for other purposes. Mechanical exfoliation is another method used alongside CVD for graphene production. Although this method is a straightforward one, it is a time-consuming process that entails removing small graphene particles from a graphite surface using tape or a similar substance. This process is highly limited as it is difficult to control the size and thickness of the graphene particles. Another technique used for graphene production is laser-induced graphene production. Laser-induced graphene production is another method that involves laser heating of a carbon-containing material, such as a polymer, to produce graphene. The laser heats the material to a high temperature, which arranges the carbon atoms into a graphene lattice. All these methods have advantages and disadvantages for mass production of graphene at low cost [14].

2.2. Molybdenum Disulfide

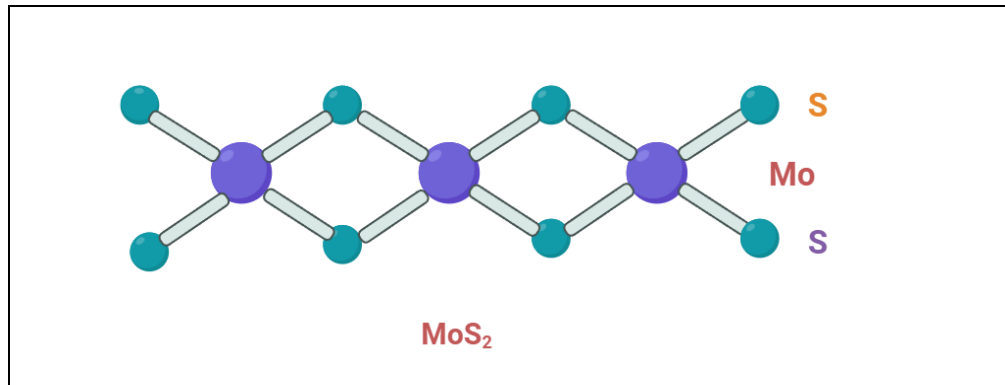


Figure 2.1: Molybdenum Disulfide structure.

Molybdenum disulfide (MoS_2) is a nanomaterial with a 2D structure that has recently garnered considerable interest. Molybdenum Disulfide, which is abundant in minerals and soil, has the same honeycomb hexagonal structure as graphene [15]. In between two layers of sulfur atoms is a layer of molybdenum atoms. It has many essential properties, the most significant of which is its high mechanical strength, which allows it to be used in nanoelectronic and nanomechanical devices. In addition, it is used as a semiconductor in electronic devices and as a coating to enhance the properties of a variety of surfaces [16]. Their optical properties, such as intense absorption and emission, make them stand out in the optoelectronic and photonic domains, where they are widely employed [17]. In addition, the minimal friction between its stratified sheets makes MoS_2 a useful lubricant [18]. The strong covalent bond within each sheet makes it an excellent conductor of heat and electricity. In the industrial sector, it is utilized as a solid lubricant in mechanical devices such as bearings and gearboxes.

MoS_2 is produced through a variety of processes, which are commonly CVD, hydrothermal technique, and solvothermal method [19-21]. Hydrothermal synthesis of MoS_2 nanosheets involves the reaction of molybdenum oxide and sulphur at high temperatures and pressures [24]. Molybdenum disulfide nanosheets of superior quality and high aspect ratio can be produced hydrothermally. The selected method is determined by the specific application and desired properties of the resulting material.

2.3. Boron Nitride

One of the most important nanomaterials, 2D hexagonal boron nitride, emerges as a new class of 2D nanomaterial with its resemblance to graphite. Equal amounts of N and B atoms make up boron nitride (BN) and are arranged in a hexagonal pattern, like carbon atoms in graphite [22],[23]. Figure 2.1 displays the structure of a h-BN nanosheet [23]. There are several different crystal forms of boron nitride, including hexagonal (hBN), cubic (c-BN), wurtzite (w-BN) and amorphous (a-BN) [25]. In hBN, boron and nitrogen atoms are covalently bonded together to form sheets, while van der Waals forces hold the sheets together. This is similar to the crystal structure of graphite, but the slight ionic bond that hBN has distinguishes hBN from graphite. While graphite is electrically a semimetal and has a high conductivity within layers, hBN has a wide bandgap and is an insulator both between layers and within layers. Hexagonal boron nitride does not occur in nature and must be synthesized.

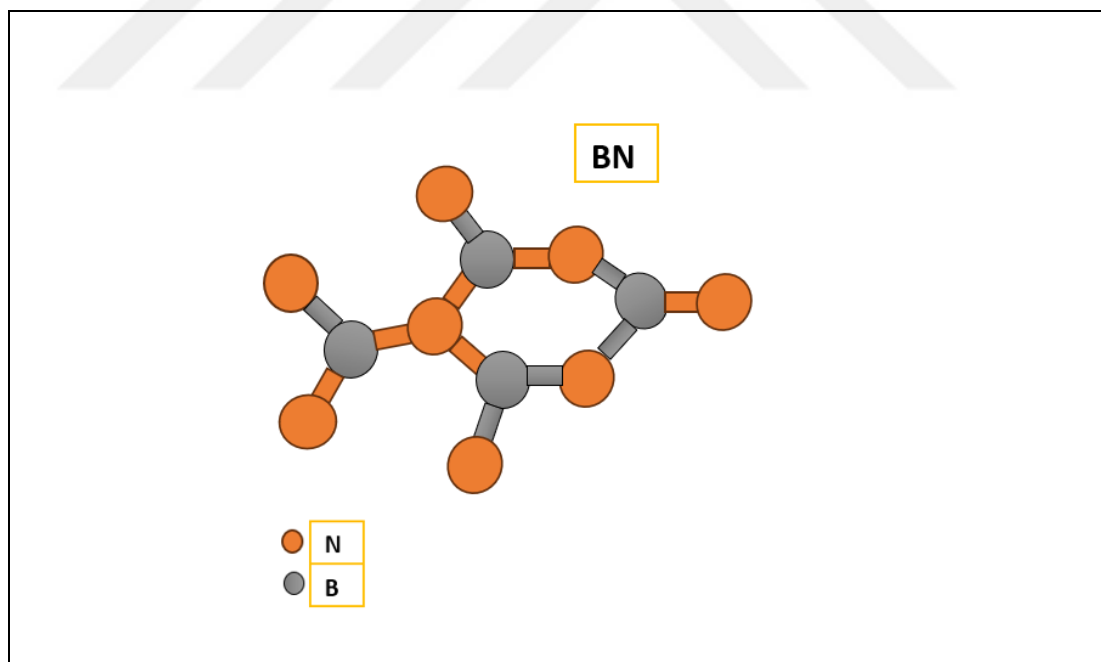


Figure 2.2: Structure of boron nitride (BN).

Hexagonal boron nitride does not occur in nature and therefore needs to be produced. The thermal conductivity of boron nitride can reach 600 W/mK, which is

higher than most metals such as copper and aluminum, which have thermal conductivities in the range of 200-400 W/mK [26]. Boron nitride is a superior electrical barrier due to its high dielectric strength of up to 1 MV/cm² [27]. hBN has a wide range of industrial applications in insulators, composites, lubricants, and surface coatings as a result of these characteristics and its unique qualities, such as high oxidation resistance, exceptional lubricity, chemical inertness, non-toxicity, and eco-friendliness [28]. Boron nitride also has a wide range of applications, particularly in the energy storage, aerospace, and biomedical industries [29],[30]. Boron nitride is frequently used in conjunction with composites in energy storage. It is preferable in tissue engineering and drug delivery systems [31] due to its biocompatibility, which is the most essential quality in the biomedical field. Due to the extraordinary properties of nanoscale materials and the development of their industrial applications, the discovery of new techniques for the synthesis of nanomaterials is an ongoing area of research.

"Bottom-up" vapor deposition, chemical exfoliation, and "top-down" ultrasound-assisted solvent exfoliation and mechanical exfoliation are the primary techniques used in boron nitride synthesis. In order to deposit boron and nitrogen precursor vapor onto a substrate such as silicon or sapphire, CVD necessitates extremely high temperatures [32]. This method has the capability to generate high-quality, low-defect, large-area boron nitride layers, but it is not preferred due to its high cost. On the other hand, chemical exfoliation using substances like sulfuric acid (H_2SO_4), potassium permanganate ($KMnO_4$), and hydrogen peroxide (H_2O_2), represents an environmentally friendly approach [32], albeit yielding minimal quantities. The most common method, ultrasound-assisted solvent exfoliation, is considered the simplest and most effective technique and can be used to form boron nitride with large surface area [34-35].

3. 2D NANOMATERIAL PRODUCTION METHODS

Due to their superior thermal and electrical conductivity, 2D materials offer a number of benefits over bulk materials [36]. These advantages make 2D materials more appropriate for use in scientific research. As a result of these considerations, the fast development of methodologies for synthesis of 2D materials is now taking place. How the nanomaterials are manufactured has a considerable impact on their surface characteristics, chemical structures, and morphologies.

In a broader sense, the manufacturing of such nanomaterials may be categorized into top-down and bottom-up processes. In the top-down synthesis approach, there is the exfoliation of bulk materials in fewer layers whereas at the bottom-up method, the production of 2D materials start from their precursor molecules [37]. When looking at the several ways that may be utilized to create BNNS from boron nitride, the synthesis process that is employed is the primary factor that dictates the quality of the 2D-hBN nanosheets. As a result, achieving a high level of quality in the 2D-hBN nanosheets that are created is essential for the majority of the applications that make use of it. The production of a 2D hBN nanosheet may be accomplished by either a bottom-up or a top-down strategy [38].

3.1. Bottom - Up Approach

The bottom-up synthesis method, sometimes referred to as chemical synthesis techniques, involves the careful stacking of atoms to form nanostructures. The bottom-up synthesis strategies used for 2D hBN nanosheets will be described later [39].

Chemical Vapor Deposition

Chemical vapor deposition (CVD) is a reliable chemical method that may be used to produce 2D nanomaterials and thin films on a variety of substrates. Filling the reaction chamber with the vapor of a gaseous or liquid reactant that contains the gases and film components necessary for the reaction is the fundamental concept that underpins this approach. To produce new solid materials that can be deposited on the surface, chemical processes may be generated on the substrate surface during the process of chemical vapor deposition by raising the temperature, generating a plasma effect, exposing the surface to laser radiation, or using some other kind of energy [40-42].

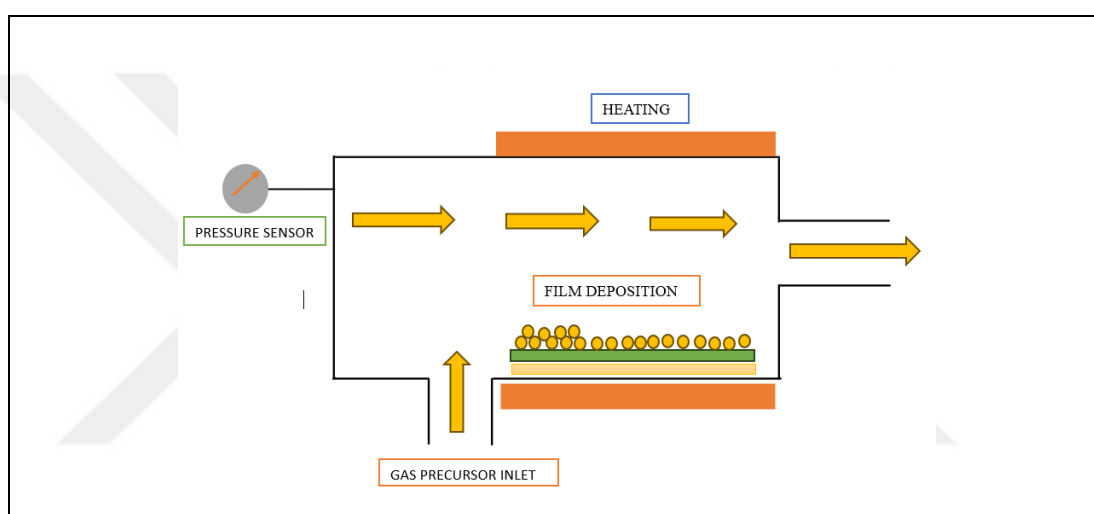


Figure 3.1: Schematic Representation of the Chemical Vapor Deposition Technique.

The CVD process is one of the most common technique for the production of h-BN nanosheets. The fundamental step in the process involves a gas-phase reaction that results in the deposition of boron nitride on a substrate. In this chemical process, a precursor gas that contains boron (eg. boron trichloride or boron tribromide) and a precursor gas that contains nitrogen (eg. ammonia or nitrogen gas) are often used [42]. CVD process may be carried out at a wide range of temperature and pressure in order to produce BNNS of the necessary size and shape. Higher temperatures and lower pressures, in general, result in the production of BNNS that are smaller and more uniform in size [43]. Depending on the parameters of the reaction, BNNSs may have a crystal structure that is either hexagonal or cubic. After the CVD process is finished, the BNNS may be scraped off from the substrate using a variety of methods, such as sonication or mechanical scraping, depending on the method chosen. In order to

characterize the BNNS produced, one may use X-ray diffraction spectroscopy (XRD), transmission electron microscopy (TEM), and scanning electron microscopy (SEM) are some of the examples of techniques that may be used in the process of analyzing the size, shape, and crystal structure of BNNS.

In general, the CVD process provides a versatile and scalable method for the production of BNNSs. This method can generate BNNSs with a broad variety of variations and characteristics, all of which may be tweaked to provide particular qualities and applications.

3.1.2. Physical Vapor Deposition

Physical vapor deposition (PVD) is an evaporation coating technology that involves the atomic-scale transfer of material in vacuum. The procedure is comparable to CVD in several ways but unlike CVD, which introduces precursors into the reaction chamber in gaseous form, PVD is in solid form with the precursors or the material to be deposited (Figure 3.2) [44].

PVD process consists of four steps:

- Atoms on the surface of the material to be deposited are vaporized by a high-energy source such as an electron beam or ions,
- The vapor is transported to the substrate to be coated,
- During the transport step the metal atoms react with the appropriate reactive gas (eg. oxygen, nitrogen or methane), and
- the coating is then applied to the substrate surface.

PVD has a number of benefits: [i] coatings created by PVD can have better properties than the substrate material; [ii] all inorganic and some organic materials can be used; and [iii] the process is more environmentally friendly than many other processes such as electroplating. However, PVD also has several disadvantages such

as difficulties in coating complex forms, high process costs and poor production, and process complexity [45-47].

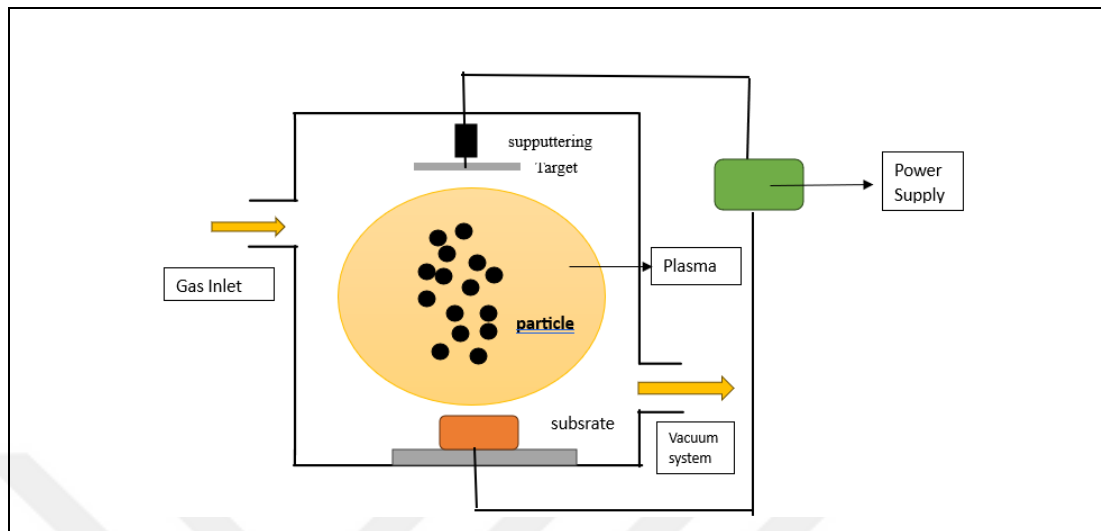


Figure 3.2: Schematic presentation of the physical vapor deposition technique.

In the PVD technique used to create h-BN, a boron nitride source material, such as boron nitride powder, is heated in a vacuum chamber. After that, the vaporized material condenses on a substrate to form a thin layer of h-BN. During deposition, the substrate can be heated to regulate the crystal structure and orientation of the h-BN film[48].

PVD is a widely used technology for producing h-BN thin films and coatings, as it provides exceptional control over film thickness, uniformity and purity. In addition, h-BN films can be deposited by PVD on various substrates such as silicon, glass and metals. However, the lack of high-quality h-BN source materials and the requirement for specialized vacuum equipment can put a limit to PVD.

3.1.3. Plasma-Assisted Synthesis

Materials may be synthesized utilizing plasma energy through a process called plasma-assisted synthesis. In a high-energy state of matter called plasma, some or all of the atoms in a gas get ionized and combine with other particles to produce an assortment of electrons, ions, and neutral particles [49]. Depending on the particular needs of the synthesis process, plasma can be produced using a variety of techniques,

including radio frequency (RF), direct current (DC), microwave (MW), or inductively coupled plasma (ICP) [50].

In plasma-assisted synthesis, chemical processes that result in the desired substance are facilitated by the plasma. By breaking chemical bonds, ionizing atoms and molecules, and exciting them to higher energy levels, plasma energy can trigger novel chemical processes that might not take place under typical circumstances [49]. A regulated environment for the synthesis process, such as low pressure or certain gas compositions, can also be provided by the plasma. Plasma-assisted synthesis of hexagonal boron nitride nanoplates requires boron and nitrogen precursors being introduced into a plasma reactor chamber, where they are ionized by the plasma energy. Following this, the ionized precursors combine to create h-BN nanoplates, which are subsequently placed on a substrate. The particular precursors and plasma conditions employed determine the exact reaction process.

Compared to conventional synthesis techniques, plasma-assisted synthesis has a number of benefits, including the capacity to synthesize materials at lower temperatures, quicker reaction rates, and improved control over the size and form of the final product. Additionally, a variety of materials, including metals, ceramics, and semiconductors, may be created via plasma-assisted synthesis. However, the availability of acceptable precursors, the requirement for specialized plasma equipment, and the possibility of unintended side effects or contamination can all put a cap on plasma-assisted synthesis [51].

Overall, plasma-assisted synthesis is a potent technique for creating materials with precise structural and physical characteristics, and it has applications in a wide range of industries, including electronics, energy storage, catalysis, and biomedical engineering.

3.1.5 Hydrothermal Synthesis

The process that takes place in a high-pressure and high-temperature water-based solution used for material synthesis is called hydrothermal synthesis and is another frequently used bottom-up method. In order to trigger the chemical processes that lead to the formation of the desired substance, this approach requires dissolving

precursor materials in water and heating the solution in a closed vessel (Figure 3.3 [52].

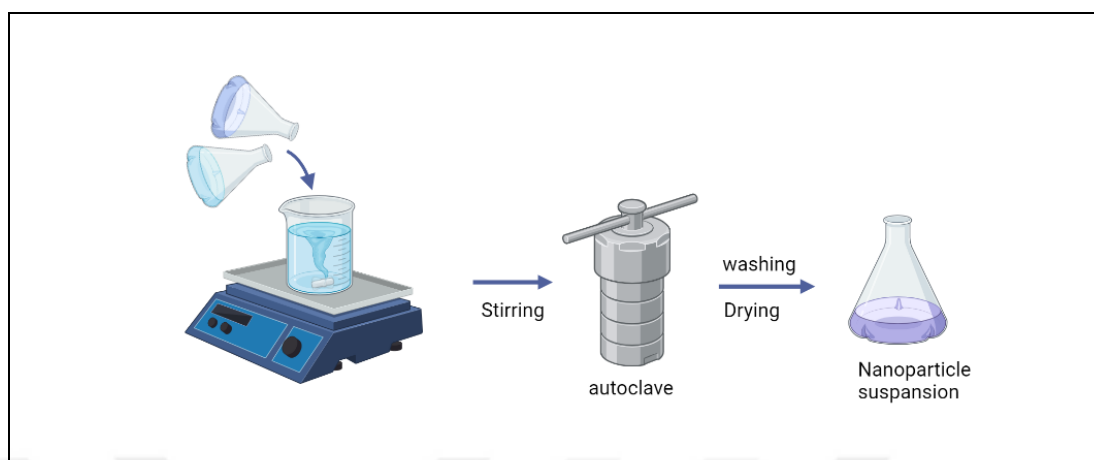


Figure 3.3: Schematic Representation of the Hydrothermal Synthesis Method.

Due to its capacity to produce high-quality and homogeneous materials with ordered morphology and crystal structure, the hydrothermal process is frequently used for the synthesis of a variety of materials, including metal oxides, metal sulfides and ceramics. A typical process for hydrothermal synthesis involves dissolving precursor components in water, usually with a small amount of acid or base for the stabilization of the pH and regulation of the reaction rate [53]

The precursor solution is later transported into a closed vessel, which is an autoclave made of a material (usually stainless steel) resistant to high pressure and temperature. The reaction vessel is heated to the required temperature and pressure, usually between 100 and 300°C and 1 and 10MPa, respectively [54]. Hydrothermal synthesis is a bottom-up method that can be used to create hexagonal boron nitride. This process involves dissolving boron and nitrogen precursors in a water-based solution and heating them at high pressures and temperatures in a tightly sealed reaction vessel. The reaction produces h-BN crystals of ordered size and shape. High purity and crystallinity h-BN has been produced through hydrothermal synthesis in various shapes and forms, including nanoplates, nanofibers and nanotubes. Adjusting the hydrothermal conditions such as temperature, pressure and reaction time, as well as the precursors used, can affect the shape and crystal structure of the h-BN produced [55]. The hydrothermal process can be difficult to use, requiring

specialized equipment, and the reaction time can be prolonged, which can limit the scaling capacity of the synthesis.

It is also possible to produce h-BN using other bottom-up techniques such as chemical vapor deposition and plasma-assisted synthesis, each with their own advantages and disadvantages.

3.2. Top - Down Approach

The production of nanostructured material from large bulk materials involves the employment of size reduction strategies, such as top-down or physical operations [56]. One advantage of the top-down technique is the capacity to synthesize enormous amounts of materials. However, this approach also makes it challenging to regulate form and size [57]. This method is often helpful in the production of nanostructured bulk materials rather than of nanoparticles.

3.2.1. Mechanical Exfoliation

For the top-down synthesis of two-dimensional materials such as hexagonal boron nitride, graphene, and transition metal dichalcogenides, mechanical exfoliation may be utilized as well. In this technique, adhesive tape or a similar technology is employed to physically separate atomically thin layers from the bulk crystal of the desired material [58]. An adhesive tape such as Scotch tape is cut in half with the adhesive side facing out. Application of the tape to the bulk crystal by pressing the tape's adhesive side securely against the bulk crystal's surface enables the tape to adhere to the material's surface and acquire a thin coating. This ensures the tape adheres to the material's surface and receives a thin coating. The tape is then rapidly stripped off, revealing a thin layer of material that has adhered to the tape. Place the tape containing the thin layer onto the substrate in order to transfer it to a spotless substrate, such as a silicon wafer or glass slide. To ensure appropriate contact between the layer and the substrate, this process is gently pressed downwards. Repeat steps 3 through 5 multiple times to create a denser layer. Multiple layers can be stacked on top of one another to produce a denser film. Finalize the procedure by annealing the sample by heating it to

a high temperature [typically 600 to 1000 °C] in nitrogen or argon. This procedure can enhance the quality of the film by removing any impurities or flaws[59].

Mechanical exfoliation is a quick and efficient technique for producing high-quality two-dimensional materials, such as hBN, with exceptional control over layer thickness[60]. This technique is especially effective for investigating the electrical and optical properties of atomic-scale materials. Thin coatings of hexagonal boron nitride [hBN] can be produced by means of top-down mechanical exfoliation. Using adhesive tape or a similar method, hBN layers are peeled off a bulk crystal in this procedure. By transferring the resulting layers onto a substrate, it is possible to generate a thin hBN film. The initial stage is to acquire a bulk hBN crystal, which can be manufactured commercially or synthetically using techniques such as chemical vapor deposition or hydrothermal synthesis. The sticky side should be facing out as you cut the adhesive tape strip in two. The tape immediately separates from the hBN crystal's surface, leaving a very thin film of hBN attached. The hBN layer on the substrate can be made thicker by repeatedly performing this procedure or by layering additional hBN layers. After the HBN layers have been applied to the substrate, the sample is annealed at a high temperature (usually between 600 °C and 1000 °C) under nitrogen or argon atmosphere. This procedure enhances the quality of the hBN film by removing any flaws or defects. The hBN thin films produced by mechanical exfoliation have exceptional optical and electrical properties, making them appropriate for a variety of applications in electronics, optics, and nanotechnology.

3.2.2. Ball Milling

Ball milling is a mechanical procedure in which balls are used as a grinding medium for the pulverization of the solid materials into finer particles in a ball mill. The ball mill machine comprises of a cylinder containing the grinding media (balls) that rotates on its own axis (Figure 3.4). The revolving spheres within a ball mill pulverize the material being processed through friction and impact, thereby reducing the particulate size [61].

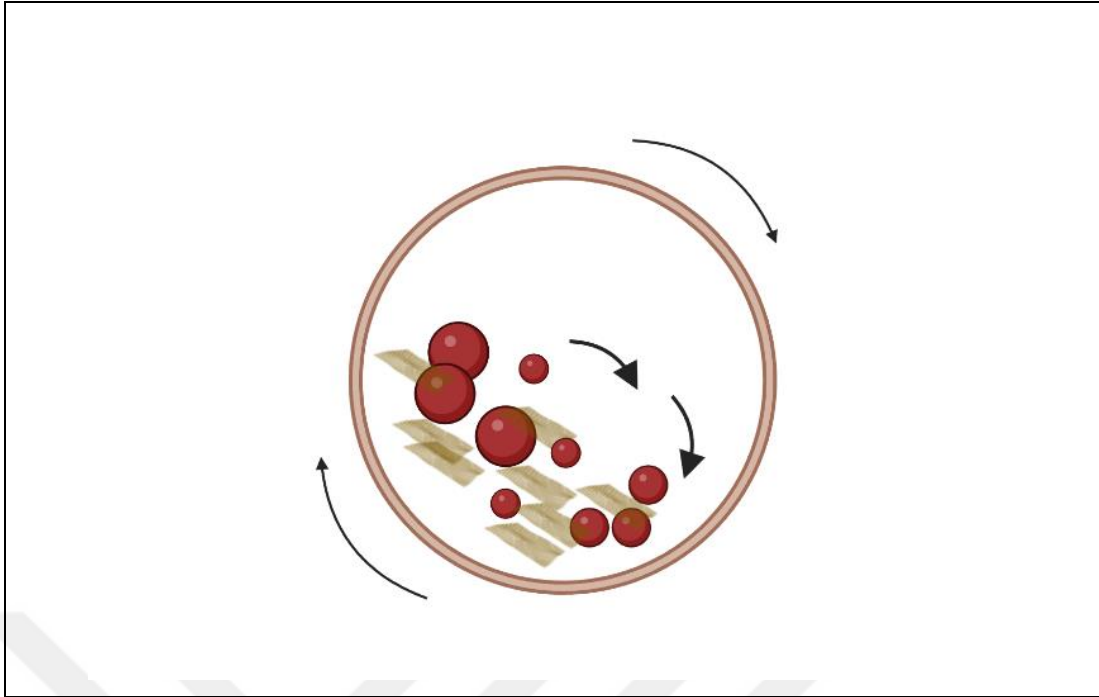


Figure 3.4: Demonstration of the Ball Milling Technique.

Metal alloys, ceramics, and composites are a few of the numerous materials with different properties that can be produced by the ball milling process [62]. The two most important phases of the procedure are the initial milling and ultimate consolidation steps. During the first milling process, the primary material and grinding medium are introduced into the ball mill equipment together. As a consequence of the grinding media's movement inside the rotating container of the ball mill, the material is pulverized and ground into smaller fragments. Variables of the ball milling process, such as milling duration, milling speed, and the size and composition of the grinding medium, can be altered to modify the particulate size produced during this phase. Typically, the powder resulting from the initial pulverizing stage is annealed or sintered to make the particulates more cohesive. During the final consolidation stage, the powder is heated to a high temperature to bond the particles together and produce a denser and stronger substance. The consolidation process can also be utilized to prepare composites by combining multiple materials during the milling phase and then consolidating them during the final stage. Milling with balls is a versatile and common technique for producing a variety of materials with varying attributes. It is also scalable and cost-effective, and can be used for both research and commercial purposes. The technique is an effective instrument for materials science and engineering because it

can be adapted to produce materials with specific properties, such as particle size, shape, and composition.

Ball milling is a top-down process in which boron nitride powder is mechanically ground with graphite spheres to produce hexagonal boron nitride, hBN. After milling, the hBN particles can be separated from the graphite spheres via centrifugation or sedimentation, and then refined via thermal annealing, chemical vapor deposition, acid treatment, or impurity removal. The ball milling method produces hBN particulates with a narrow size distribution at a low cost and on a large scale [63].

3.2.3. Ultrasonic Liquid Exfoliation

Graphene, boron nitride, and molybdenum disulfide are layered materials that may be converted into 2D nanosheets using the ultrasonic liquid exfoliation. In this technique as a the top-down technique. In this method, the bulk material is disseminated in a liquid medium and then ultrasonic energy is used to separate the layers and exfoliate the material into individual nanosheets [64].

Ultrasonic energy is transmitted by a submerged high-frequency ultrasonic transducer in a liquid medium. When the transducer is activated, high-frequency sound waves are produced, which cause cavitation bubbles to form in the liquid [65]. The rapid bursting of these bubbles generates microjets and high shear pressures capable of exfoliating the stratified material (Figure 3.5). The solvent employed during the exfoliation procedure has a substantial impact on the quality and the yield of the produced nanosheets. The solvent should be carefully chosen such that it must be effective at both stabilizing and dispersing the exfoliated nanosheets as well as dispersing the bulk material. Typical ultrasonic liquid exfoliation solvents include water, ethanol, isopropanol (IPA), and N-methyl-2 pyrrolidone (NMP) [66-68]. The produced nanosheets can be further purified utilizing techniques such as centrifugation and filtration. By altering the duration and intensity of ultrasonic energy as well as the concentration of the bulk material in the solvent, it is possible to manipulate the the thickness of the produced nanosheets and their lateral dimensions. Ultrasonic liquid exfoliation is a versatile and adaptable technique with applications in numerous industries, such as electronics, energy, catalysis, and biomedicine [69-70]. Nanosheets produced with this technique are intriguing for a variety of applications, including

electrical devices, composites, coatings, sensors, and drug delivery systems, due to their unique physical, chemical, and mechanical properties.

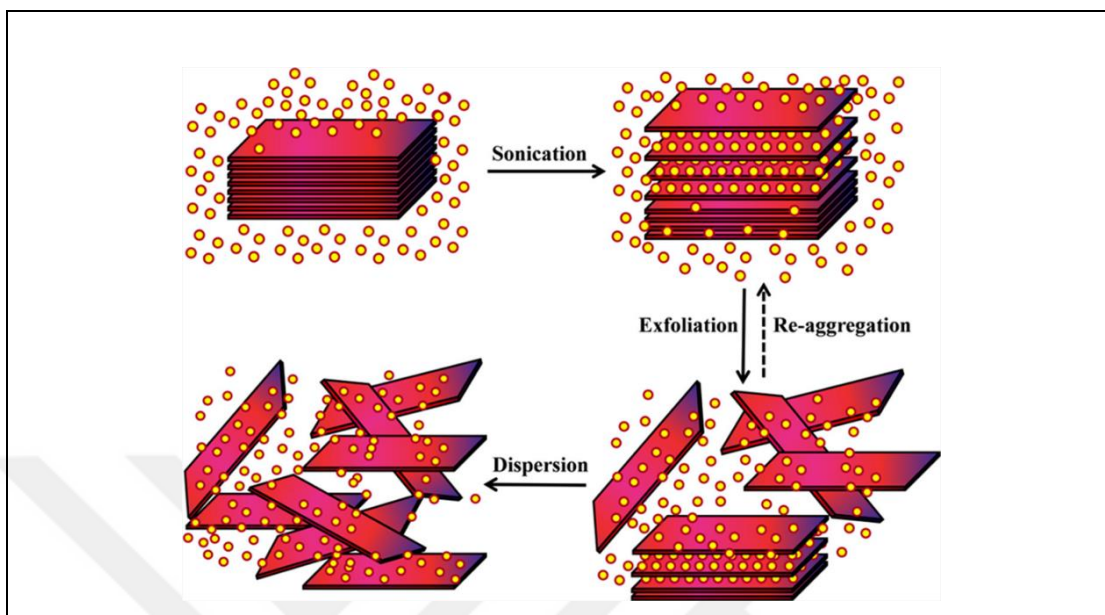


Figure 3.5: Schematic Representation of the Ultrasonic Liquid Exfoliation Adapted with permission from reference [71]. Copyright (2020) American Chemical Society.

The first stage in the ultrasonic liquid exfoliation method of hBN synthesis is obtaining bulk hBN crystals. After obtaining hBN crystals in bulk, the next step is to disperse them in a solvent [72]. N-methyl-2-pyrrolidone, NMP, is a common solvent for disseminating hBN crystals, but other solvents such as dimethylformamide (DMF) can also be used [73]. The aggregate hBN crystals are combined with the solvent and sonicated for a number of hours to evenly distribute the crystals throughout the solvent. Using sonication, large hBN crystals are broken down into smaller pieces. Once the hBN crystals have been uniformly dispersed in the initial solvent, the mixture is sonicated again, this time in a different solvent, such as water or ethanol. hBN crystals are exfoliated into individual hBN nanosheets using ultrasonic energy. This phase is necessary for the production of high-quality hBN nanosheets, and it requires careful management of the sonication duration and intensity to prevent nanosheet damage. Upon completion of exfoliation, a mixture of hBN nanosheets and other particles will be present. To purify hBN nanosheets, centrifugation or filtration techniques can be used to separate them from other particles. Using techniques such as AFM or TEM, the size and morphology of unadulterated hBN nanosheets can then be confirmed.

Using ultrasonic liquid exfoliation, the production of high-quality hBN nanosheets with restricted size distribution is scalable and cost-effective. This method can produce hBN nanosheets with diverse morphologies and properties for a variety of applications, including electronics, optics, and catalysis. By meticulously modulating the sonication duration and intensity, the characteristics of the generated hBN nanosheets can be precisely tailored to the requirements of each application [74]. Overall, ultrasonic liquid exfoliation is an efficient method for producing high-quality hBN nanosheets that can be utilized in a variety of disciplines [75].



4. SYNTHESIS and METHODS

4.1. Materials

Boron nitride (h-BN, 98.5%, 65-75nm particle size) was purchased from Nanography Ltd. Isopropyl alcohol (IPA, 99.5%), dimethylformamide (DMF, 99%), 1-Methyl-2-pyrrolidone (NMP, 99%) were obtained from Tekkim Ltd. and 1-Cyclohexyl-2-pyrrolidone (CHP, 99%) was obtained from Sigma Aldrich. These chemicals were used directly without further purification. Distilled water was purified using Sartorius Arium 611UV (Millipore 18.2 MΩ/cm) and was used in all experiments

4.2. Instrumentations for Characterization

In this thesis study, Morphology of the hBN nanoplates were examined with scanning electron microscopy (SEM) using Philips XL 30 SFEG scanning electron microscope device. SEM-EDS analyses were done using the same instrument.

Atomic force microscopy (AFM) analyses about the surface morphology and thickness measurement of the nanoplates were investigated by AFM Bruker Corporation, (UK) controlled with the Nanoscope IV software V8.

FTIR analyses were carried out to determine the chemical bonds in the structure of the nanoplates obtained as a result of synthesis by using Perkin Elmer Spectrum 100 FTIR Spectrometer.

IKA magnetic stirrer is used in order to disperse powder materials. MMM VacuCell Vacuum Etuve is utilized for drying of the produced powders. Nanografi Ultrasonic Homogenizer ultrasonic device is used for sample preparation before microstructure characterizations (ultrasound power: 360 Watt, frequency: 20 kHz) (Figure 4.1).



Figure 4.1: Nanao Grafi Ultrasonic Homogenizer [NG-900N] model ultrasonic device used for LPE.

4.3. Experimental Procedure

Experiments were carried out by preparing different types of solvents. In the thesis study, h-BNNS were synthesized using the liquid phase exfoliation method using an ultrasonic probe at 20 KHz frequency and 30 W power (Figure 4.2). A comparison was made using 4 different solvents, namely, CHP with other solvents, NMP, IPA, DMF and their aqueous solutions with different dH₂O ratios.

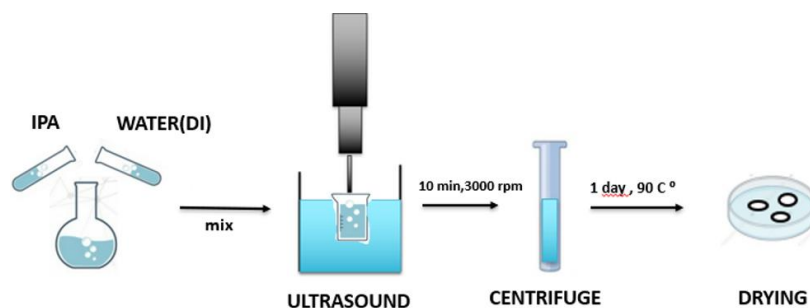


Figure 4.2 : Scheme of the synthesis method for the preparation of h-BNNs.

4.3.1 Synthesis of h-BNNS with isopropylalcohol Experimental Procedure

0.125 grams of boron nitride (BN) was dissolved in 50 mL of a mixture of isopropyl alcohol (IPA) and dH_2O with a 3:7 volumetric ratio of IPA: H_2O . The prepared solution was sonicated for 2 hours at a maximum of 30°C using a 30 W ultrasonic probe. At the end of the exfoliation period, the resulting mixture was centrifuged at 3000 rpm for 10 minutes. The collected precipitate was discarded and the supernatant was collected and dried oven for 24 hours. The product is named as hBNNS(IPA 3:7).

For the preparation of hBNNS(IPA 1:1), the same synthesis procedure was followed except that the solution was prepared with IPA: H_2O of 1:1 volumetric ratio.

Experiments were carried out using different solvents to obtain boron nitride nanoplates. Firstly, hBN synthesis was carried out using isopropyl alcohol due to its high solubility, low toxicity, volatility and low viscosity. Experimental procedure was carried out in a sequence as shown in the (Figure 4.2).

4.3.2. Synthesis of h-BNNS with N-Methyl-2-pyrrolidone

A similar experimental procedure was followed as for hBNNS(IPA 3:7), except the change of the solvent to N-methyl-2-pyrrolidone. In this synthesis, 50 mL solution with 3:7 volumetric ratio of NMP and dH_2O was used. After the exfoliation period of 2 h, the resulting mixture was centrifuged at 3000 rpm for 10 minutes. The collected precipitate was discarded and the supernatant was collected and dried oven for 24 hours. This product was named as hBNNS(NMP 3:7).

For hBNNS(NMP 1:1), same synthesis procedure was repeated except that the solution was prepared with a 1:1 volumetric ratio for NMP: dH_2O .

4.3.3. Synthesis of h-BNNS with Dimethylformamide

0.125 grams of boron nitride (BN) was dissolved in 50 mL dimethyl formamide (DMF) and dH₂O in a 3:7 volumetric ratio of DMF:H₂O. The prepared solution was sonicated for 2 hours at maximum 30°C using a 30 W ultrasonic probe. At the end of the exfoliation time, the resulting mixture was centrifuged at 3000 rpm for 10 min. The collected precipitate was discarded and the supernatant was collected and dried in an oven for 24 hours. The product was determined as hBNNS(DMF 3:7). For hBNNS(DMF 1:1), the same synthesis procedure was repeated except that the solution was prepared in DMF:dH₂O 1:1 volume ratio.

4.3.4. Synthesis of h-BNNS with 1-Cyclohexyl-2-pyrrolidone

For the preparation of hBNNS (CHP 1:20), 0.125 grams of boron nitride was dissolved in 50 mL of cyclohexylpyrrolidone (CHP) and dH₂O in a 1:20 volumetric ratio of CHP:H₂O. The prepared solution was sonicated for 2 hours at maximum 30° using a 30 W ultrasonic probe. At the end of the exfoliation time, the resulting mixture was centrifuged at 3000 rpm for 10 min. The collected precipitate was discarded and the supernatant was collected and dried in an oven for 24 h.

The process was repeated for comparison with hBNNS (CHP 1:20) for 10 h.

5. RESULTS AND DISCUSSION

It is possible to produce hBN nanoplates by chemical vapor deposition (CVD) and solid phase exfoliation methods, but due to the disadvantages such as high cost and long processing time, liquid phase exfoliation method which is a more convenient and cost effective technique is usually preferred. Presence of partial ionic bonds as well as van der Waals interactions between the nanoplates make lamellae more difficult to dissociate than graphene. Therefore, the production method and its steps are vital for the yield and the properties of the produced hBNNS [42].

Commercially available boron nitride (BN) powder particles were mixed with 0.1 M aqueous cyclohexylpyrrolidone solution, CHP:H₂O v/v 1:20, and a probe type ultrasound device (ultrasound power: 360 Watt, frequency: 20 kHz) was used for a 30 minute exfoliation period. During this period, the solution temperature was kept constant at 30°C. The solution obtained after sonication was filtered and the large particles remaining in the solution were eliminated. The filtered solution was then centrifuged at 3000 rpm [54]. The product obtained after centrifugation was dried oven overnight.

Based on literature, it is known that an increase in exfoliation efficiency is observed when the solvent is used with H₂O instead of using it in pure form [42]. Liquid phase exfoliation method was optimized according to the desired properties of hBNNS to be used in energy storage applications and the morphological properties of the hBNNS obtained by this method in various solvents (CHP, DMF; NMP, IPA) were investigated using advanced characterization tools. DMF, one of the solvents utilized, offers qualities such as high solubility, strong thermal stability, and good reaction medium [82]. NMP offers the benefits of high solubility, strong thermal stability, and high purity [81]. IPA has a high solubility, low toxicity, volatility, and viscosity. Finally, the CHP used has qualities such as high solubility, strong thermal stability, and a favorable reaction environment [82]. Table 5.1 displays the ultrasonic exfoliation process conditons for h-BNNS used in this thesis.

Table 5.1: Ultrasonic Liquid phase exfoliation process conditions for the preparation of hBNNS in general.

Process performed	Duration	Process Parameters
Mixing the solution in an ultrasonic mixer	24 Hours	Ultrasonic power: 30 Watts Rxn temperature: 30 °C
centrifuge	10 min	3000 rpm

Looking at the SEM images (Figure 5.1) and XRD analysis results (Figure 5.2), it is clearly observed that the commercially purchased BN powder is in an irregular bulk. The XRD results confirm that this BN sample shows a characteristic peak of 26.7 degrees [76]. This peak is a typical feature indicating the presence of BN.

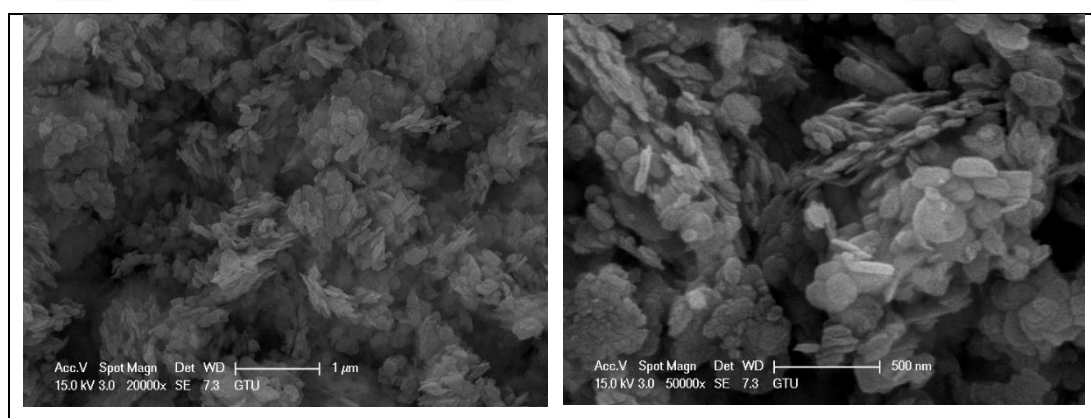


Figure 5.1: SEM Images of bulk h-BN as the starting material

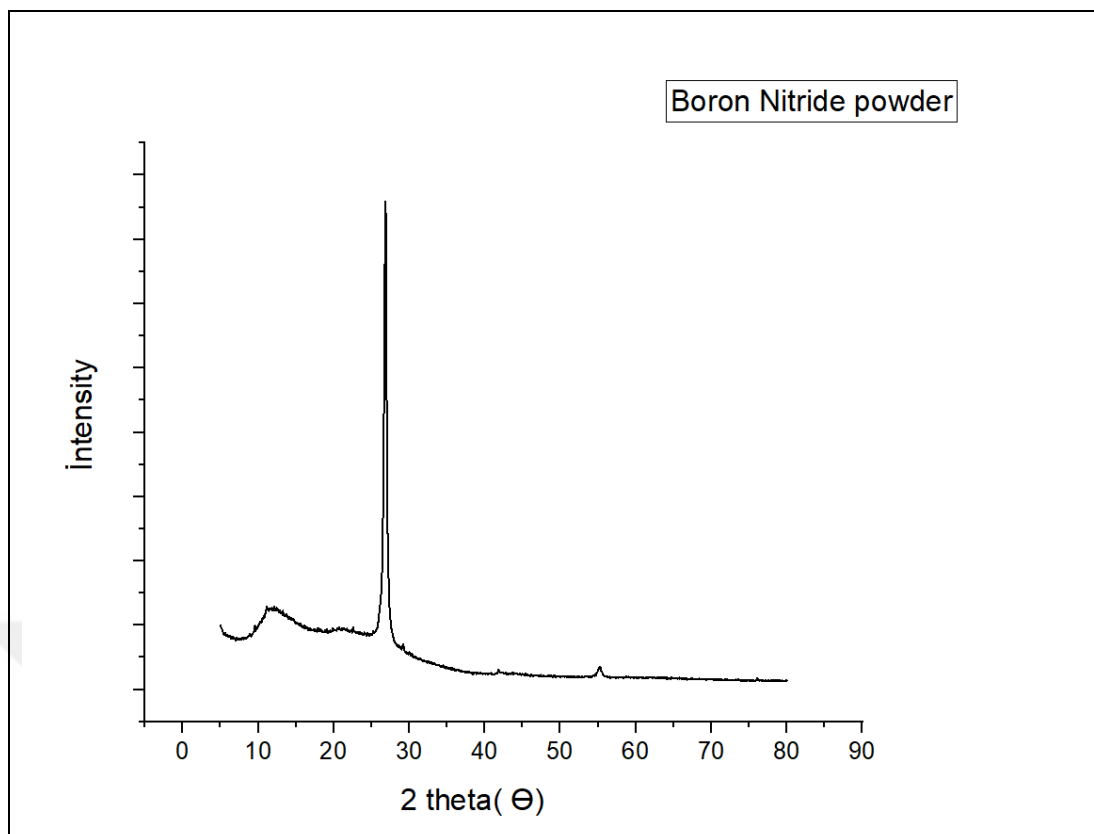


Figure 5.2: XRD image of bulk h-BN as the starting material.

Looking at the AFM images of the hBN nanoplate produced using DMF, nanoplate formation was low (Figure 5.3(a) and Figure 5.3(b)). The resulting nanoplates were likely to be layered again, depending on the waiting time between sonification and centrifugation. Although the particle distribution was not homogeneous, it predominantly had a thickness of 10 nm and above (Figures 5.3(c) and Figure 5.3(d)). In order to have a thickness of <10 layers, considering that the distance between the two layers is 0.34 nm, the nanoplate thicknesses obtained should not exceed 3 nm [79]. As seen in Figure-5.3(b), the nanoplate thicknesses are mostly above this value.

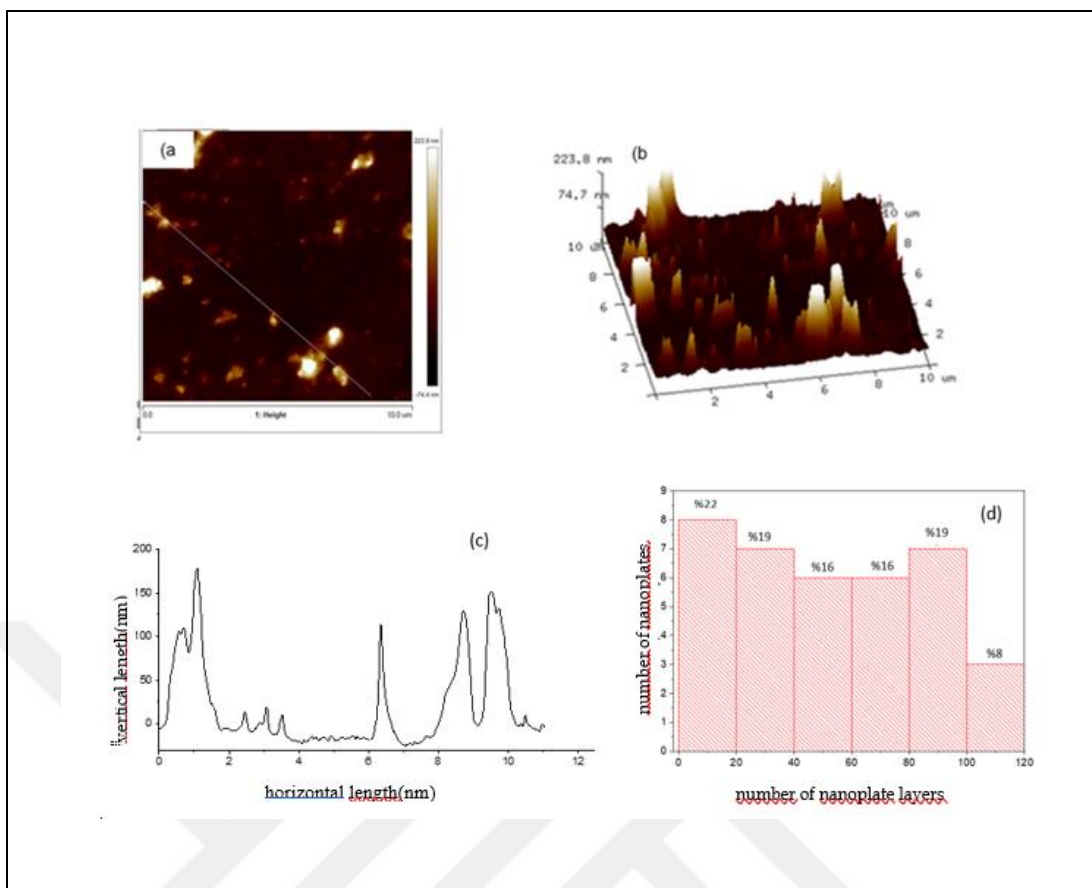


Figure 5.3: (a) a 2D AFM picture of hBNNS(DMF (1:1)) by scanning in a 10 micron region using contact mode. (b) A 3D quantitative AFM height analysis of hBNNS(DMF (1:1)). (c) A linear height profile analysis corresponding to the AFM picture shown in (a) as measured from the AFM image. (d) The equivalent percent distribution of the algorithm that was derived based on the AFM picture in (b).

SEM images of hBNNS(DMF 1:1) are presented in Figure 5.4.

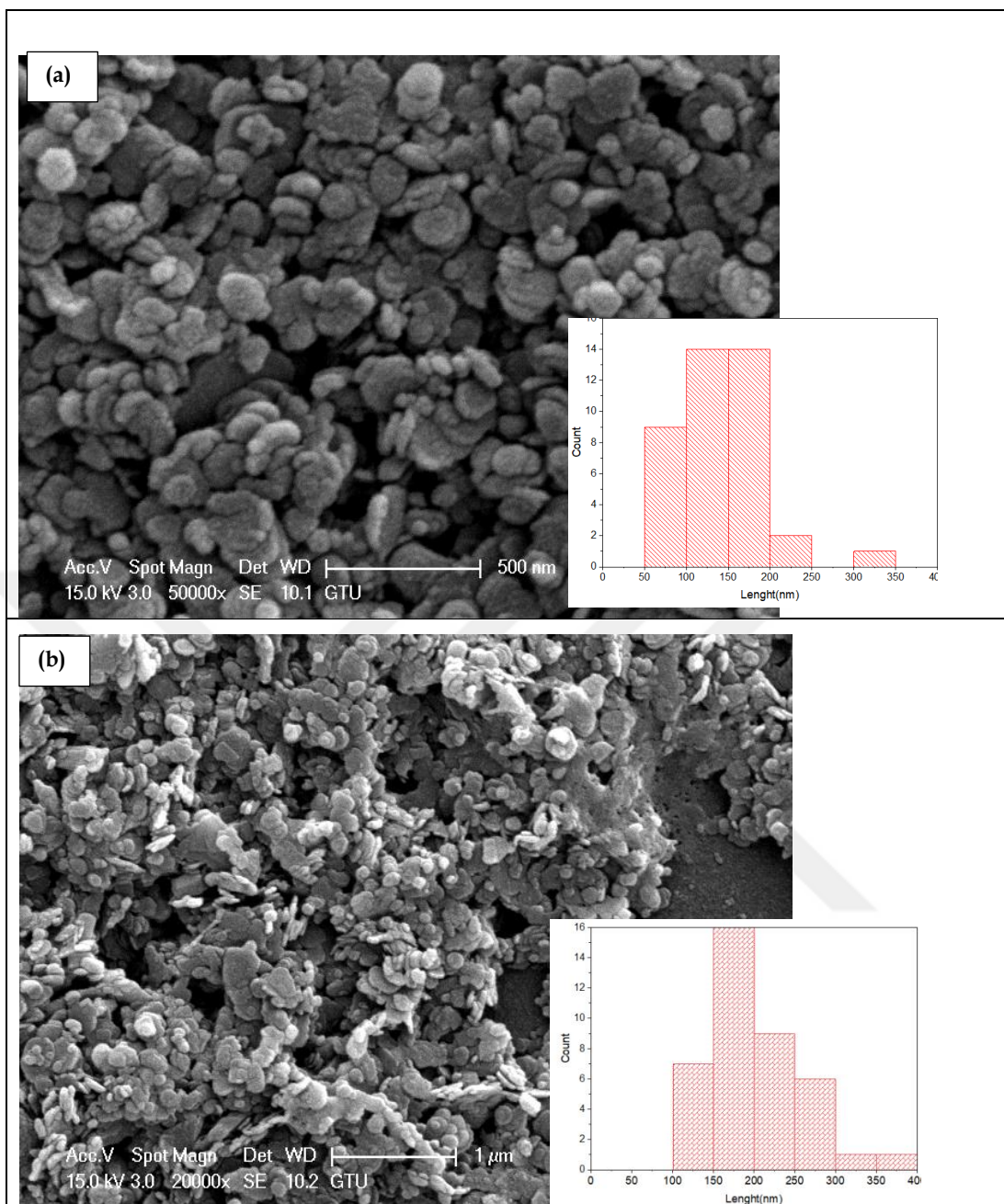


Figure 5.4: SEM images of hBNNS(DMF 1:1) at **(a)** 50000X and **(b)** at 20000X magnifications.

When AFM and SEM images are examined, it is seen that the thickness ratio of the nanoplates synthesized with DMF solution is 100 nm and above according to the AFM image. SEM image is in accordance with the morphology in the literature. According to the SEM image in Figure 5.4 (a) and Figure 5.4(b), it is seen that the nanoplates consist of nanoplates with a size of 100-200 nm. SEM images are consistent with the morphology in the literature.

FTIR analysis of hBNNS(DMF 1:1) is given in Figure 5.5 below. The FTIR results showed that the OH and C=O vibrations were at 3326.2 cm^{-1} and 1647.9 cm^{-1} , respectively. The B-N (in-plane) and B-N-B (out-of-plane) vibrations were at 1391 cm^{-1} and 661.5 cm^{-1} , respectively, in parallel with the literature results [77].

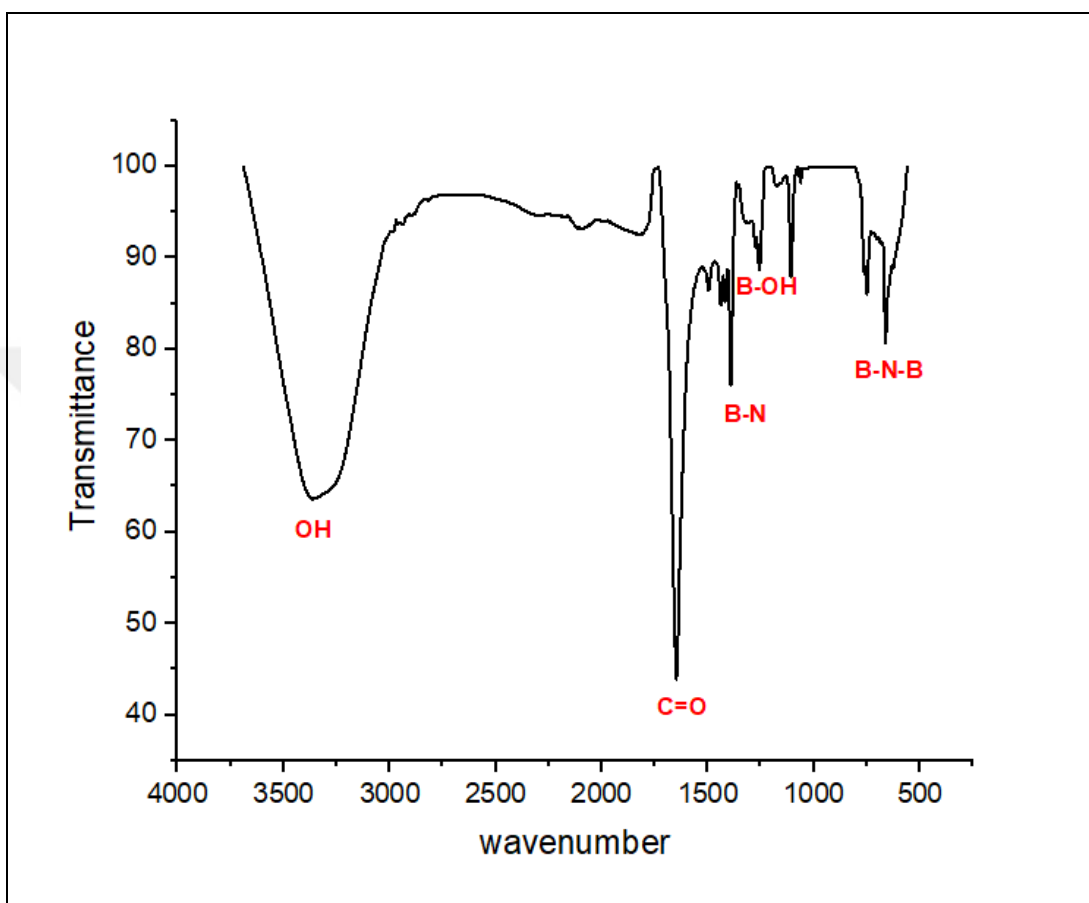


Figure 5.5: FTIR spectrum of hBNNS(DMF 1:1).

The peak seen at $\sim 1380\text{ cm}^{-1}$ is the characteristic hBN peak for B-N [77]. When all FTIR peak positions were examined, no interaction was found that caused structural deformation of the hBN nanoplates at the atomic scale. In the literature, hBN nanoplates obtained with similar solutions give results consistent with characteristic peaks [77].

Looking at the AFM images of hBNNS(DMF 3:7) are presented in Figure 5.4, nanoplate formation was low (Figure 5.6(a) and Figure 5.6(b)).

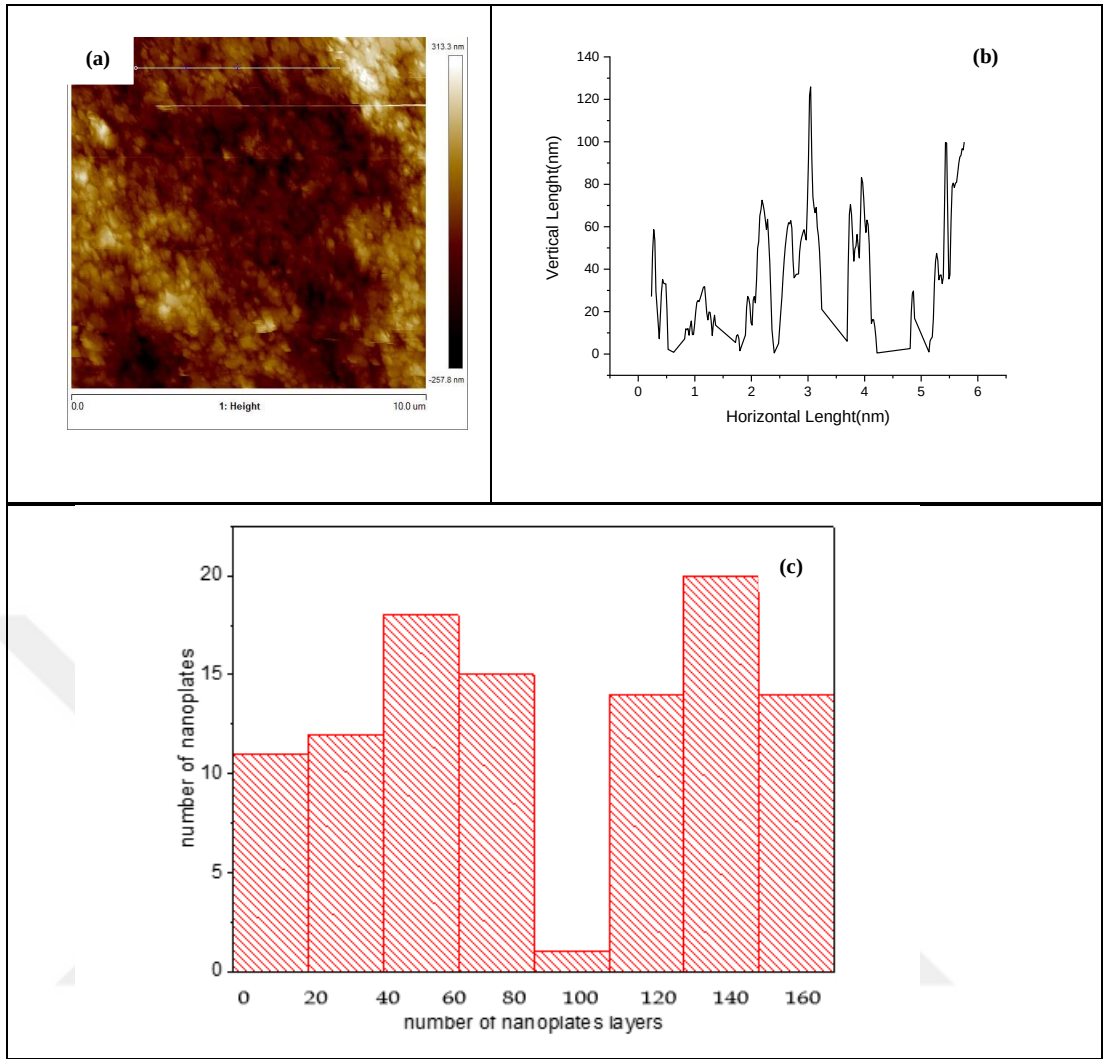


Figure 5.6: (a) a 2D AFM picture of hBNNS(DMF (3:7) by scanning in a 10 micron region using contact mode. (b) A linear height profile analysis corresponding to the AFM picture shown in (a) as measured from the AFM image. (c) The equivalent percent distribution of the algorithm that was derived based on the AFM picture in (a).

SEM image of hBNNS(DMF 3:7) are presented in Figure 5.7.

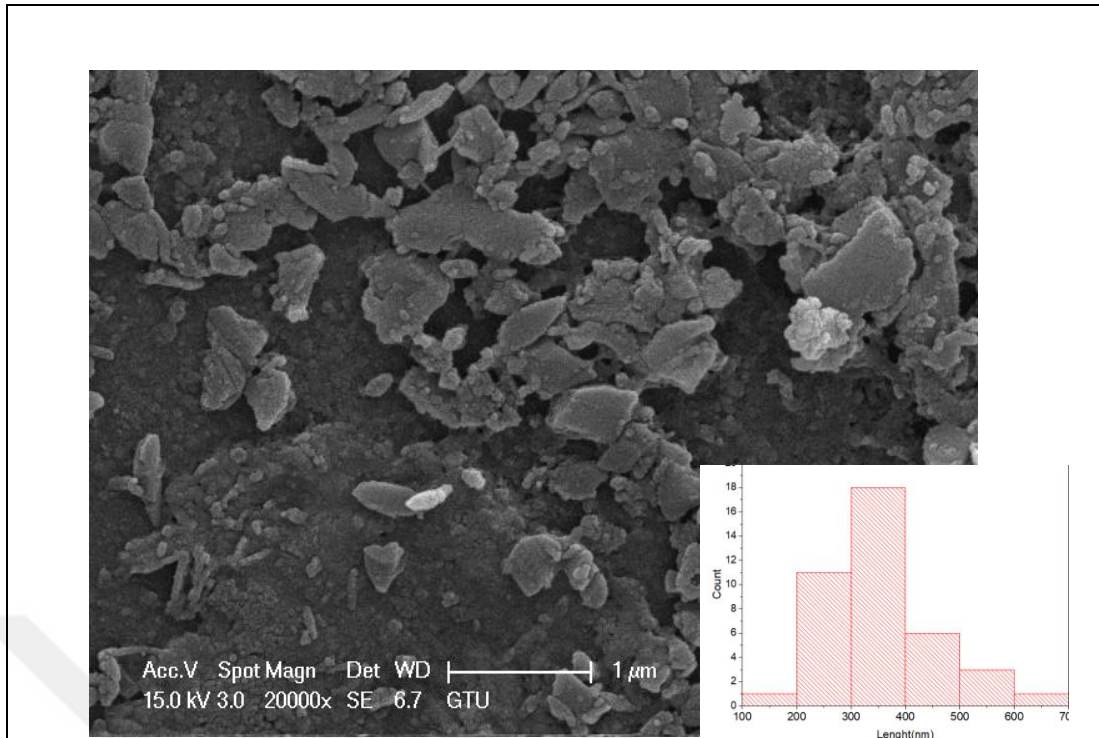


Figure 5.7: SEM images of hBNNS(DMF 3:7) at 20000X magnifications.

The SEM image obtained in our experiment is shown in Figure 5.7 and has a similar morphology and nanostructure compared to the SEM image in the literature, and the lateral dimension of 500 nm in the literature confirms that h-BNNs layers were successfully formed in our experiment[78].

When AFM images of hBNNS(DMF 1:1) and hBNNS(DMF 3:7) are compared, it is seen that the highest percentage of hBNNS(DMF 1:1) is in the 0-20 nm range according to figure 5.3(d), while the highest percentage of hBNNS(DMF 3:7) is in the 120-140 nm range according to figure 5.6(c). When the SEM images of hBNNS(DMF 1:1) and hBNNS(DMF 3:7) and SEM images in Figure 5.4 and Figure 5.7 are compared, it is seen that the thickness and surface width of the nanoplates increase in hBNNS(DMF 3:7) in accordance with the AFM results.

Two different hBNNS were prepared using IPA as the solvent; hBNNS(IPA 3:7) and hBNNS(IPA 1:1). AFM images of hBNNS(IPA 3:7) are shown in Figure 5.8.

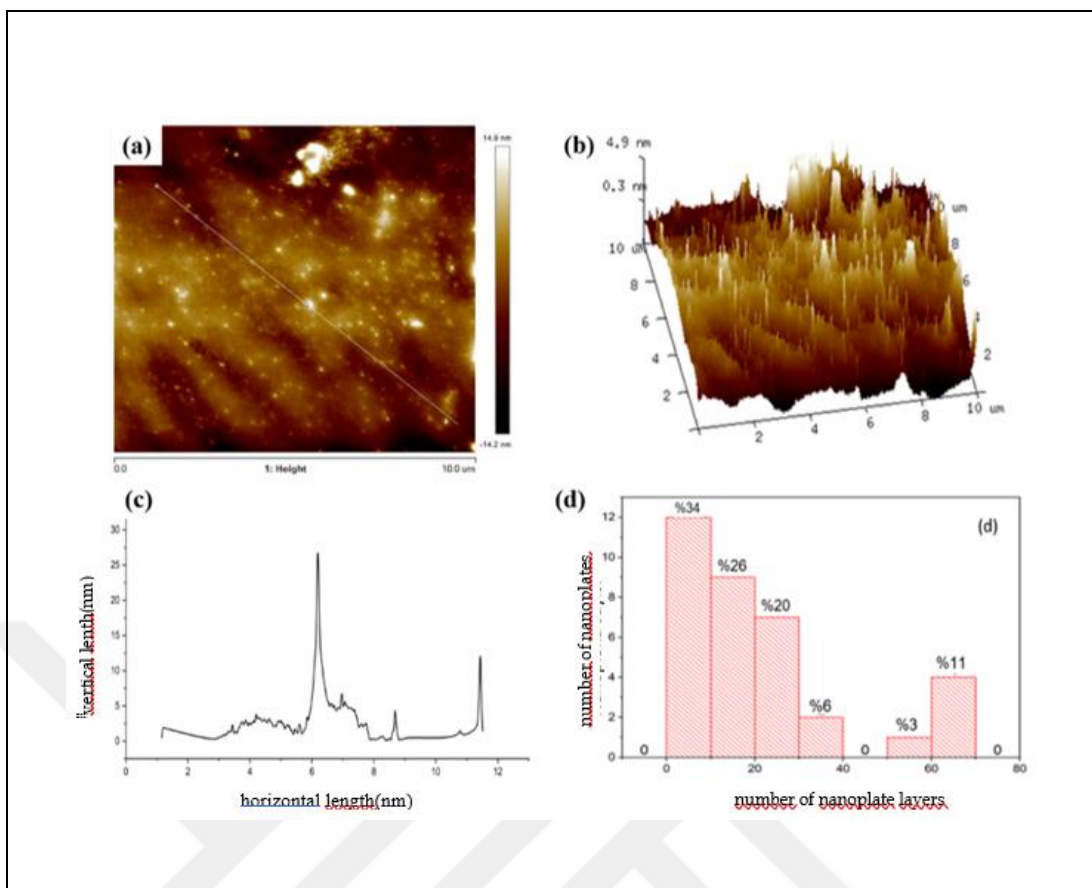


Figure 5.8: (a) 2D AFM image of hBNNS(IPA 3:7) by scanning in 10 micron area with contact mode, (b) 3D quantitative AFM height analysis, and (c) Corresponding linear height profile analysis of the AFM image in (a), (d) Percent distribution of the produced hBNNS layers derived from (b).

A significant thinning of the layers was observed in the obtained hBNNS relative to ones produced in DMF. Particle distribution was found to be quite homogeneous and the density was below 10 layers (Figure 5.8). For a better dispersion, it is possible to increase the centrifuge speed and reach the targeted thickness value with additional filter steps.

SEM results of hBNNS(IPA 3:7) are given in Figure 5.9. According to the SEM analysis, nanoplate width was found to be in the range of 50-200 nm. The fact that the nanostructures have a more or less round morphology shows that they are not fragmented nor damaged during the ultrasonic exfoliation process.

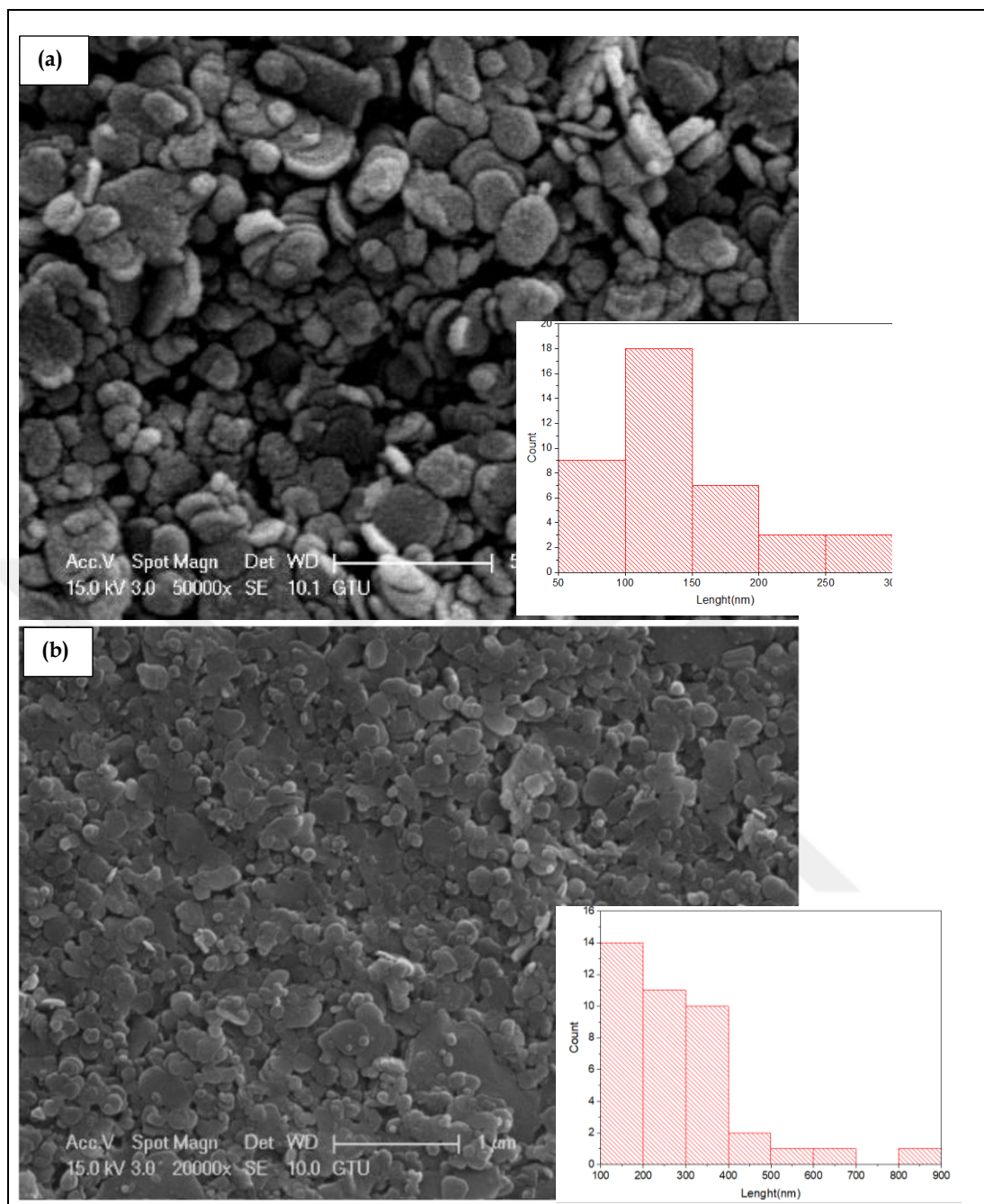


Figure 5.9: SEM images of hBNNS(IPA 3:7) at **(a)** 50000x and **(b)** 20000x magnifications.

Figure 5.10 displays the SEM-EDS analysis of hBNNS(IPA 3:7).

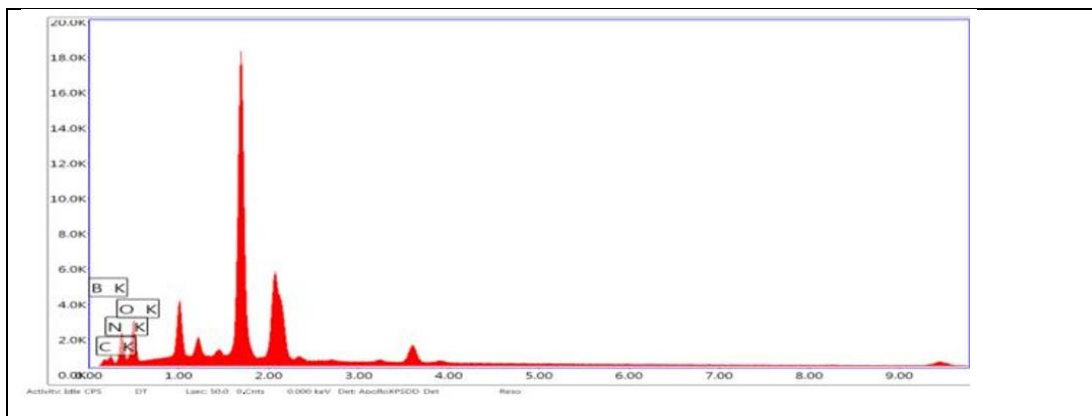


Figure 5.10: SEM-EDS analysis of hBNNS(IPA 3:7)

Figure 5.10 shows the SEM-EDS analysis of hBNNS(IPA 3:7) nanoplates. According to Table 5.2, the high carbon and oxygen element ratios confirm that there is a significant amount of IPA molecule on the hBN surface. Although the boiling point of the IPA solvent was low, it was understood that it could not be completely removed even after drying the sample overnight.

Table 5.2: Weight and atomic percentages corresponding to element peaks of hBNNS(IPA 3:7) calculated from the corresponding EDS analysis.

Element	Weight %	Atomic %	Net Int.	Net Int. Error
B K	28.31	34.43	53.17	0.03
C K	10.74	11.76	54.47	0.04
N K	31.68	29.75	199.25	0.02
O K	29.27	24.06	316.52	0.01

When the FTIR analysis of hBNNS(IPA 3:7) was examined, it was determined that the element boron (B) tended to bond with the OH⁻ anion (Figure 5.11). This has the effect of increasing the reaggregation rate of the nanoplates after exfoliation. Looking at the FTIR spectrum, the peak seen at $\sim 1385.9 \text{ cm}^{-1}$ is the characteristic hBN peak for B-N [77]. In addition, OH and C=O vibrations were found at $\sim 3310 \text{ cm}^{-1}$ and $\sim 1643.7 \text{ cm}^{-1}$, respectively. B-N (in-plane) and B-N-B (out-of-plane) stresses were observed at 1385 cm^{-1} and 659 cm^{-1} , respectively. When all FTIR peak positions were

examined, no interaction was found that caused structural deformation of the hBN nanoplates at the atomic scale. In the literature, hBN nanoplates obtained with similar solutions give results consistent with these characteristic peaks [77].

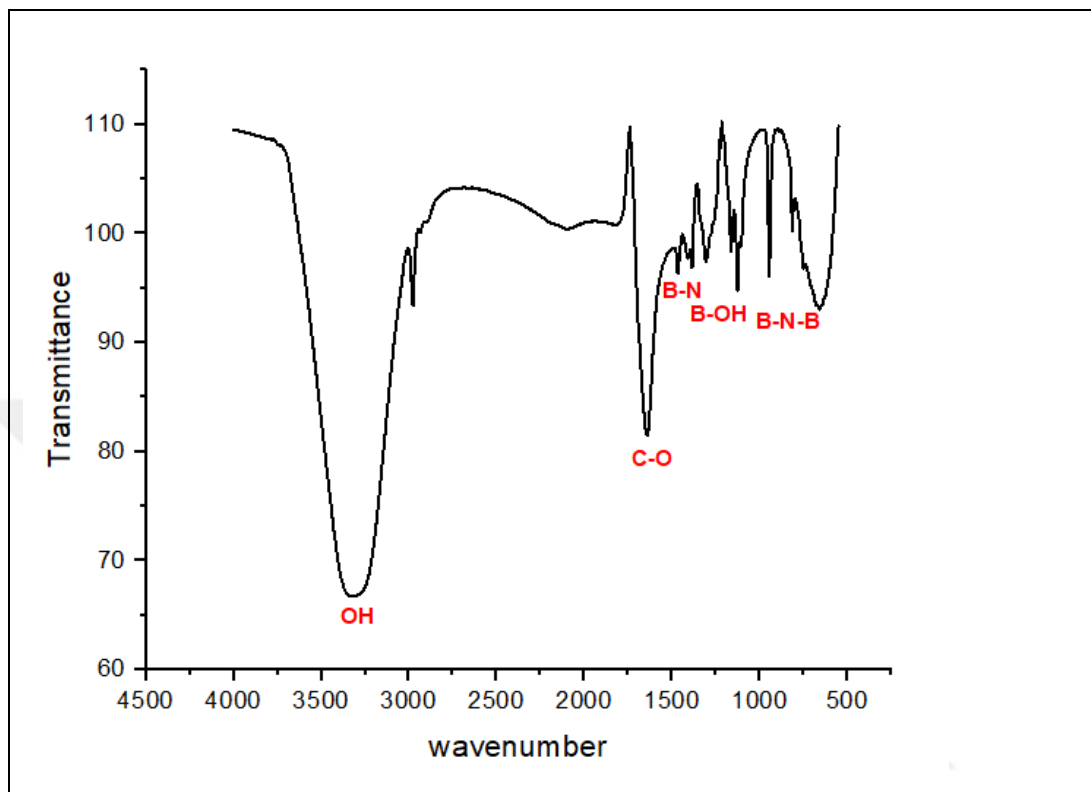


Figure 5.11: FTIR spectrum of hBNNS(IPA 3:7).

In a similar approach, hBNNS(IPA 1:1) was prepared using the 1:1 volumetric ratio of IPA:H₂O. A significant increase was observed in particle size and thickness. However, the AFM results showed a relatively homogeneous distribution overall (Figure 5.12).

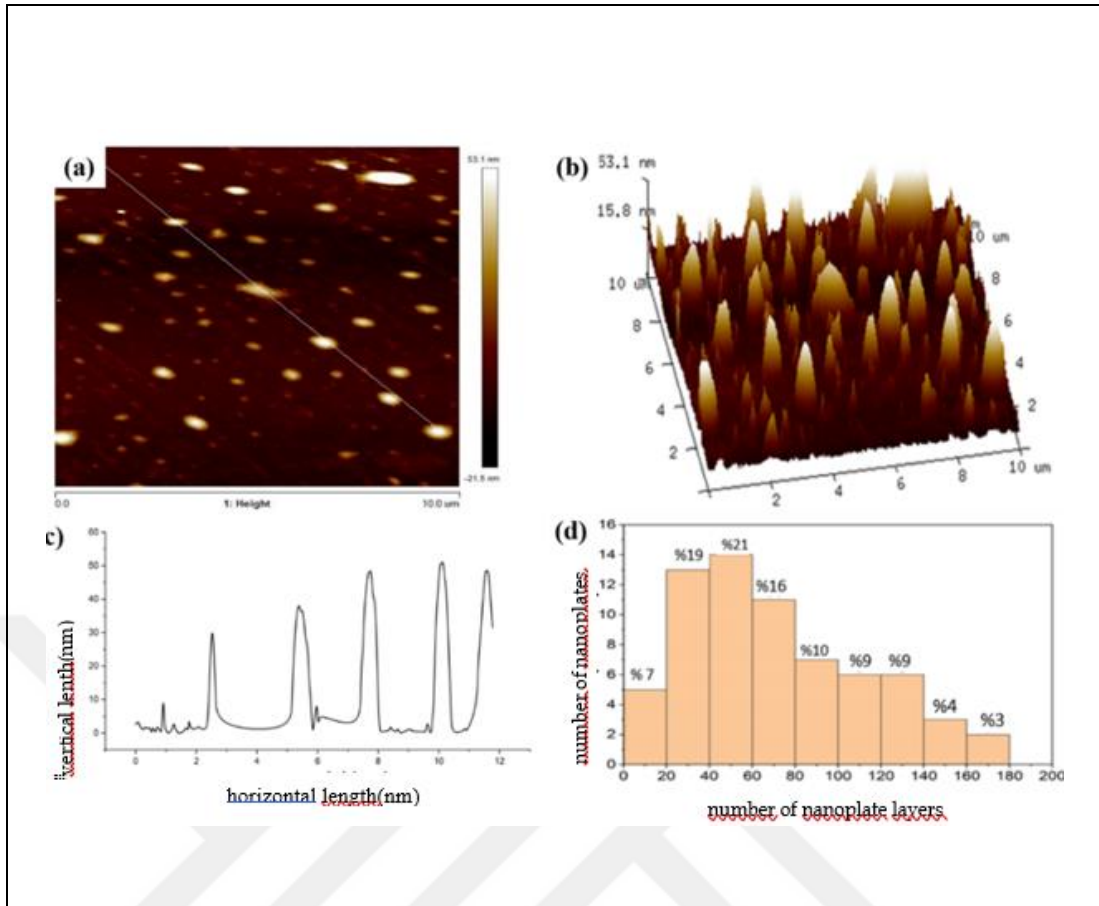


Figure 5.12: (a) 2D AFM image of hBNNS(IPA 1:1) by scanning in 10 micron area with contact mode, (b) 3D AFM image of of hBNNS(IPA 1:1), (c) Analysis of the corresponding linear height profile measured from the AFM image in (a). (d) The corresponding percent distribution of hBNNS(IPA 1:1) nanoplate layers estimated from the AFM image in (b).

SEM results of hBNNS(IPA 1:1) are given in Figure 5.13. According to SEM analysis, the nanoplate width was found to be in the range of 50-300 nm.

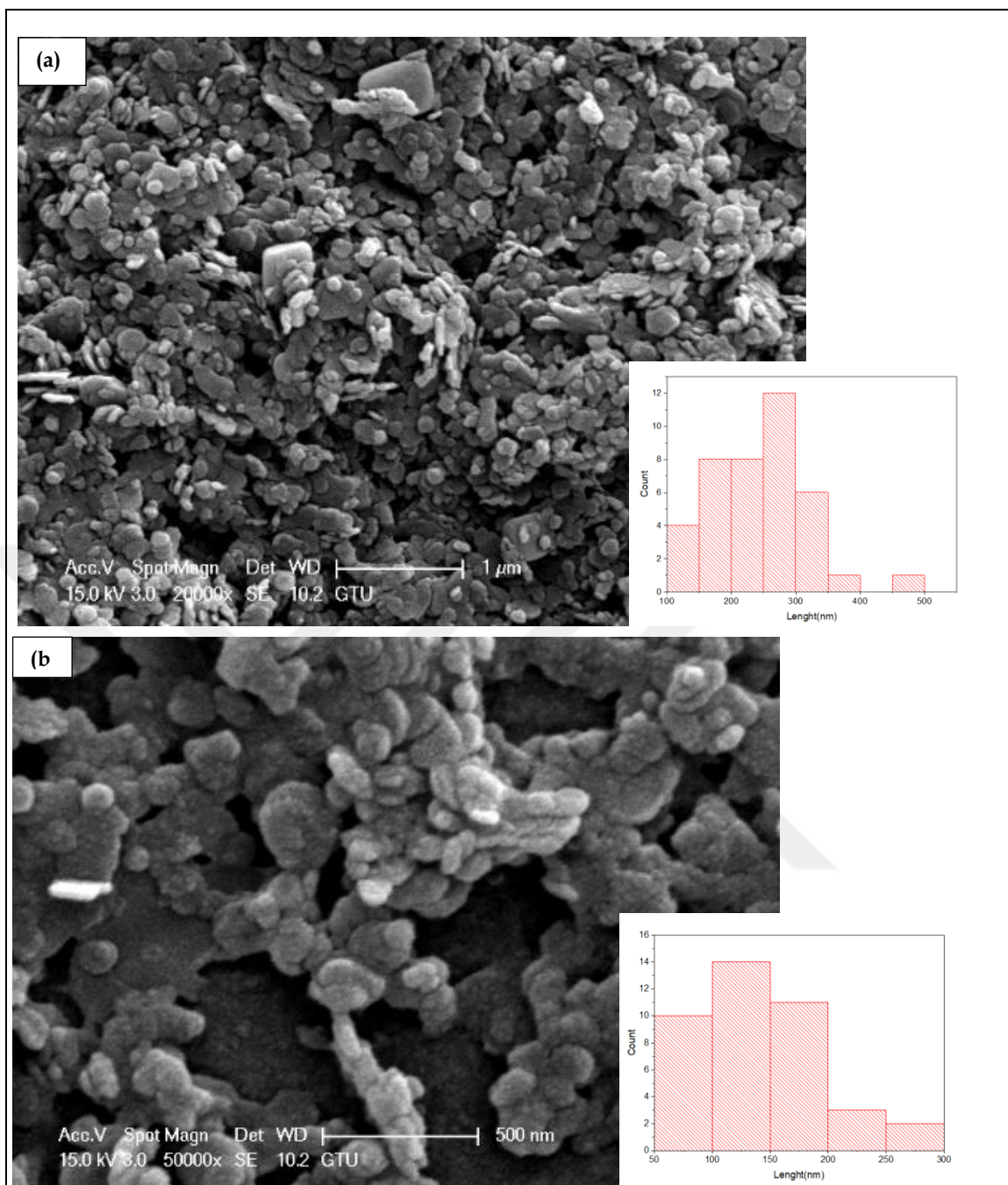


Figure 5.13: SEM images of hBNNS(IPA 1:1) at **(a)** 20000x and **(b)** 50000x magnifications.

When AFM and SEM images of hBNNS(IPA 3:7) and hBNNS(IPA 1:1) are examined, it is seen that the thickness ratio of the nanoplates synthesized with hBNNS(IPA 3:7) solution is 10 nm and below according to the AFM image. It was observed that as the IPA ratio increased, the thickness of the nanoplates increased.

When SEM images are compared, it is seen that the nanoplates obtained from two different solutions prepared with IPA are between 50-100 nm in size.

FTIR images of hBNNS(IPA 1:1) are shown in Figure 5.14. OH and C=O vibrations were detected at 3309.5 cm^{-1} and 1632.9 cm^{-1} , respectively, while B-N (in-plane) and B-N-B (out-of-plane) stresses were detected at 1380 cm^{-1} and 635.5 cm^{-1} , respectively [77].

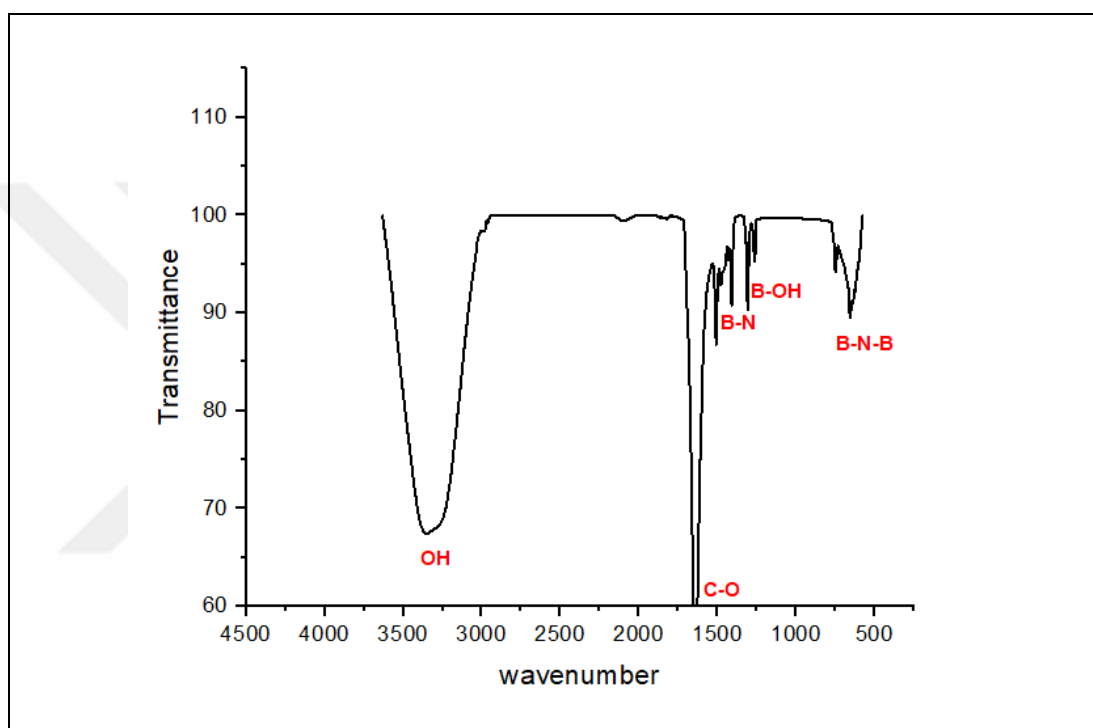


Figure 5.14: FTIR spectrum of hBNNS(IPA 1:1).

As a result of these analyses, it was observed that as the amount of water in the solution increases, nanoplate thickness decreases, in general.

When the SEM images of the nanoplates prepared with IPA solution and the SEM EDS images shown in Figure 5.10 are examined, it is seen that there are still residues at the end of the reaction. To solve this problem and to remove solvent residues, further filtration and washing were performed after the centrifugation step. The nanoplates remaining on the filter surface after filtration through a cellulose-based filter were washed 4 times with diluted HCl followed by distilled H_2O . According to the SEM images taken for the hBNNS(IPA 3:7) samples that gave good results after this process, it was observed that washing the sample with 20% HCl removed organic

residues to a greater extent compared to 10% HCl (Figure 5.15).

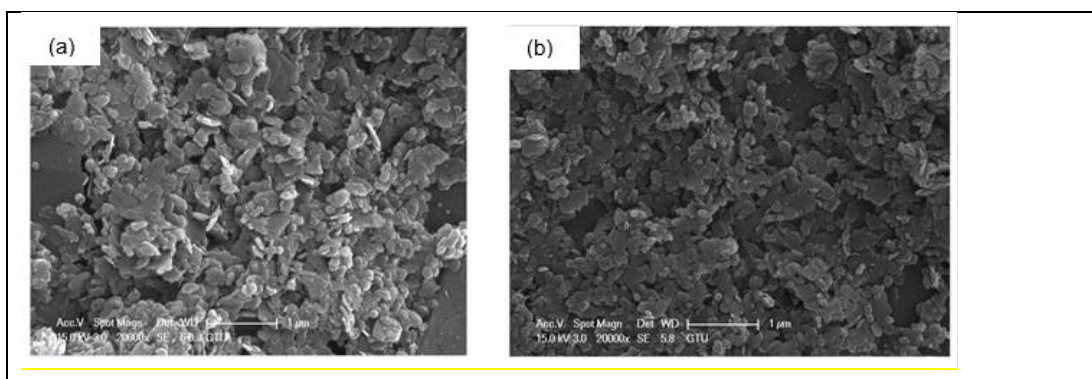


Figure 5.15: SEM images of hBNNS(IPA 3:7) washed with **(a)** 10% HCl and **(b)** 20% HCl (20000x).

AFM images of hBN nanoplates prepared by experimenting with two different ratios of N-Methyl-2-Pyrrolidone (NMP) solvent, namely, hBNNS(NMP 3:7) and hBNNS(NMP 1:1), are given in Figure 5.16 and Figure 5.19.

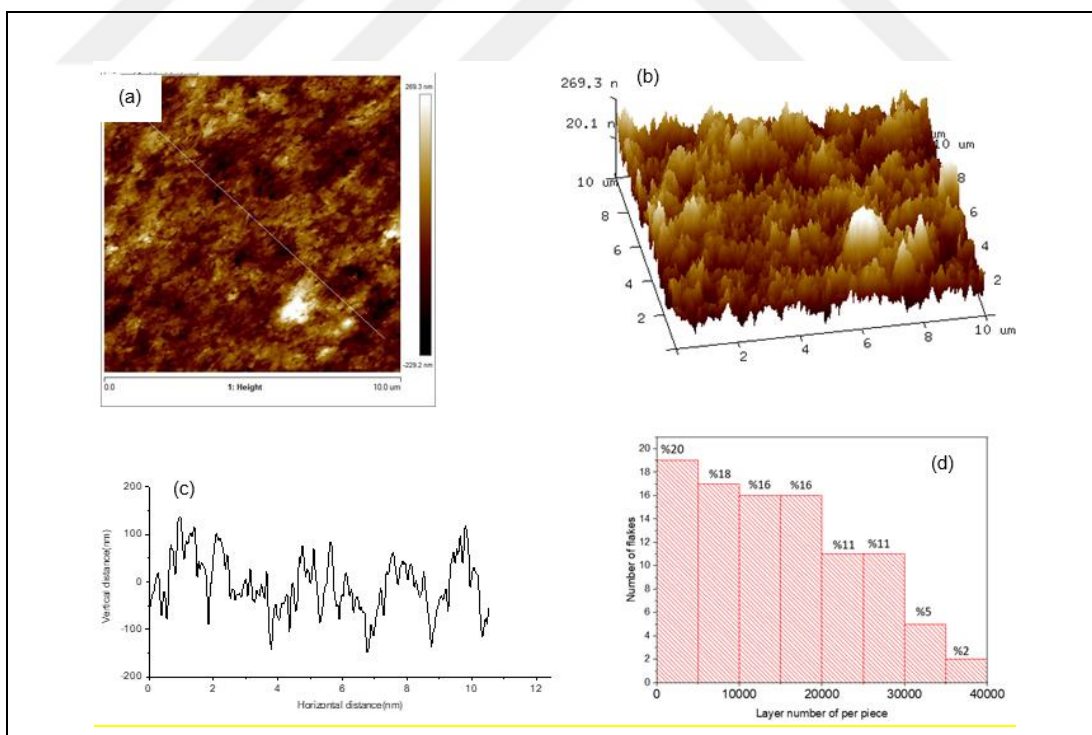


Figure 5.16: **(a)** 2D AFM image of hBNNS(NMP 3:7) by scanning in 10 micron area with contact mode, **(b)** 3D AFM image of hBNNS(NMP 3:7), **(c)** Analysis of the corresponding linear height profile measured from the AFM image in (a). **(d)** The

corresponding percent distribution of hBNNS(NMP 3:7) nanoplate layers estimated from the AFM image in (b).

SEM image of hBNNS(NMP 3:7) are presented in Figure 5.17

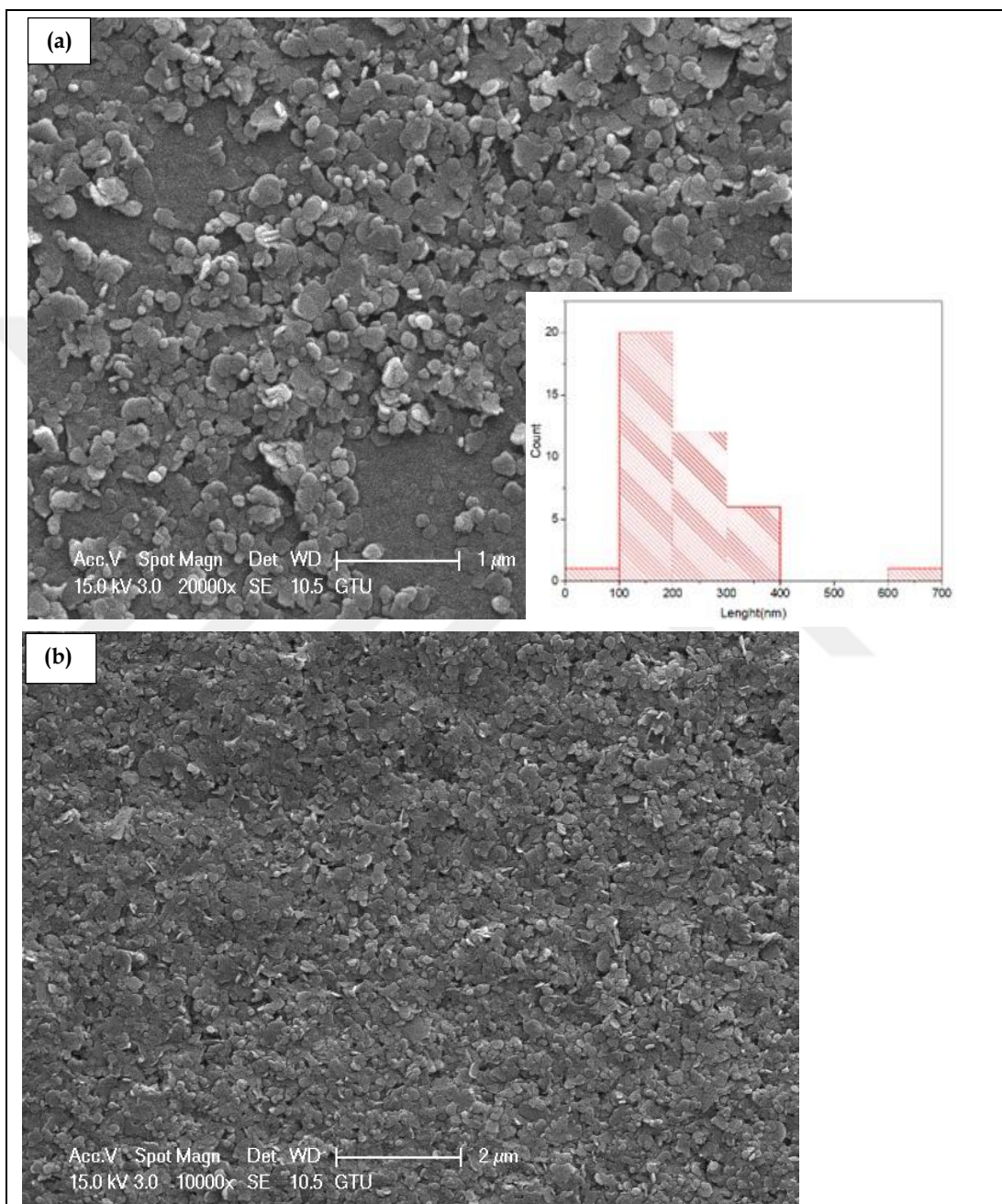


Figure 5.17: SEM images of hBNNS(NMP 3:7) at (a) 20000X and (b) 10000X magnifications.

FTIR analysis of hBNNS(NMP 3:7) is given in Figure 5.18. The FTIR study concluded that the vibrational peaks of the OH and C=O groups were at 3319.9 cm^{-1} and 1640.2 cm^{-1} , respectively, similar to the results obtained in other polar solvents. Additionally, the B-N bond was shown to extend in-plane at 1410 cm^{-1} and out-of-plane at 654.2 cm^{-1} . These results demonstrate that the hBN nanoplates used in the investigation do not experience atomic-scale structural deformation [79].

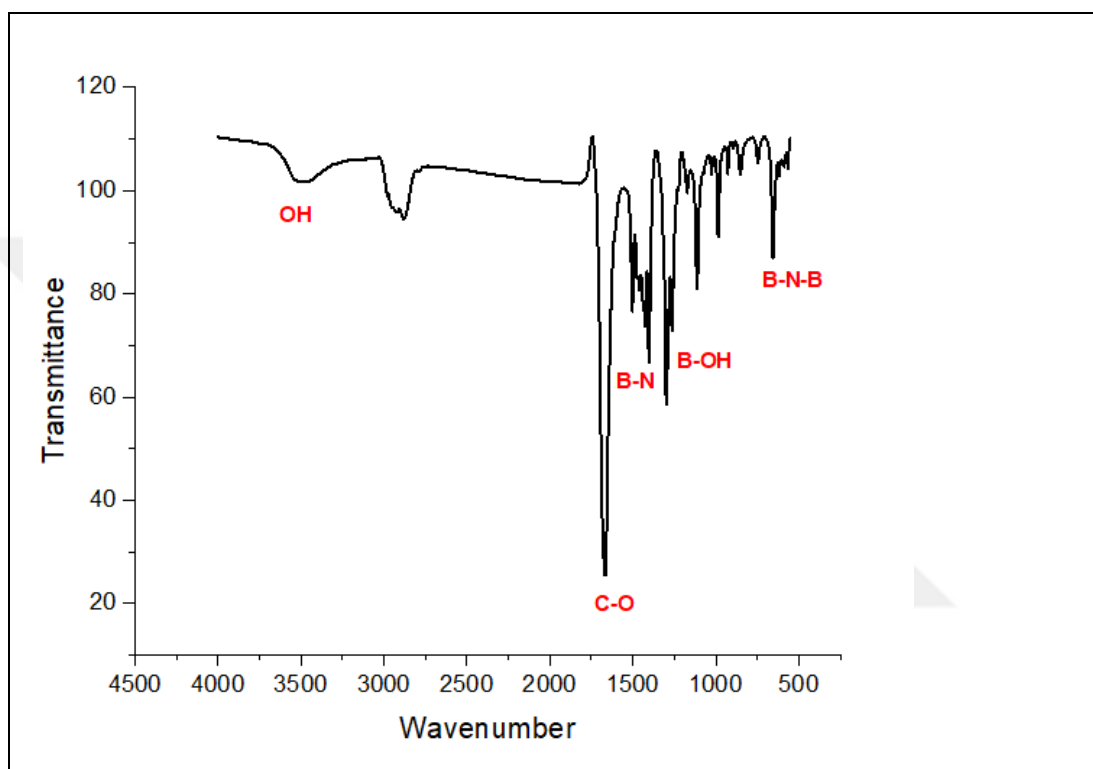


Figure 5.18: FTIR spectrum of hBNNS(NMP 3:7).

AFM image of hBNNS(NMP 3:7) are presented in Figure 5.19.

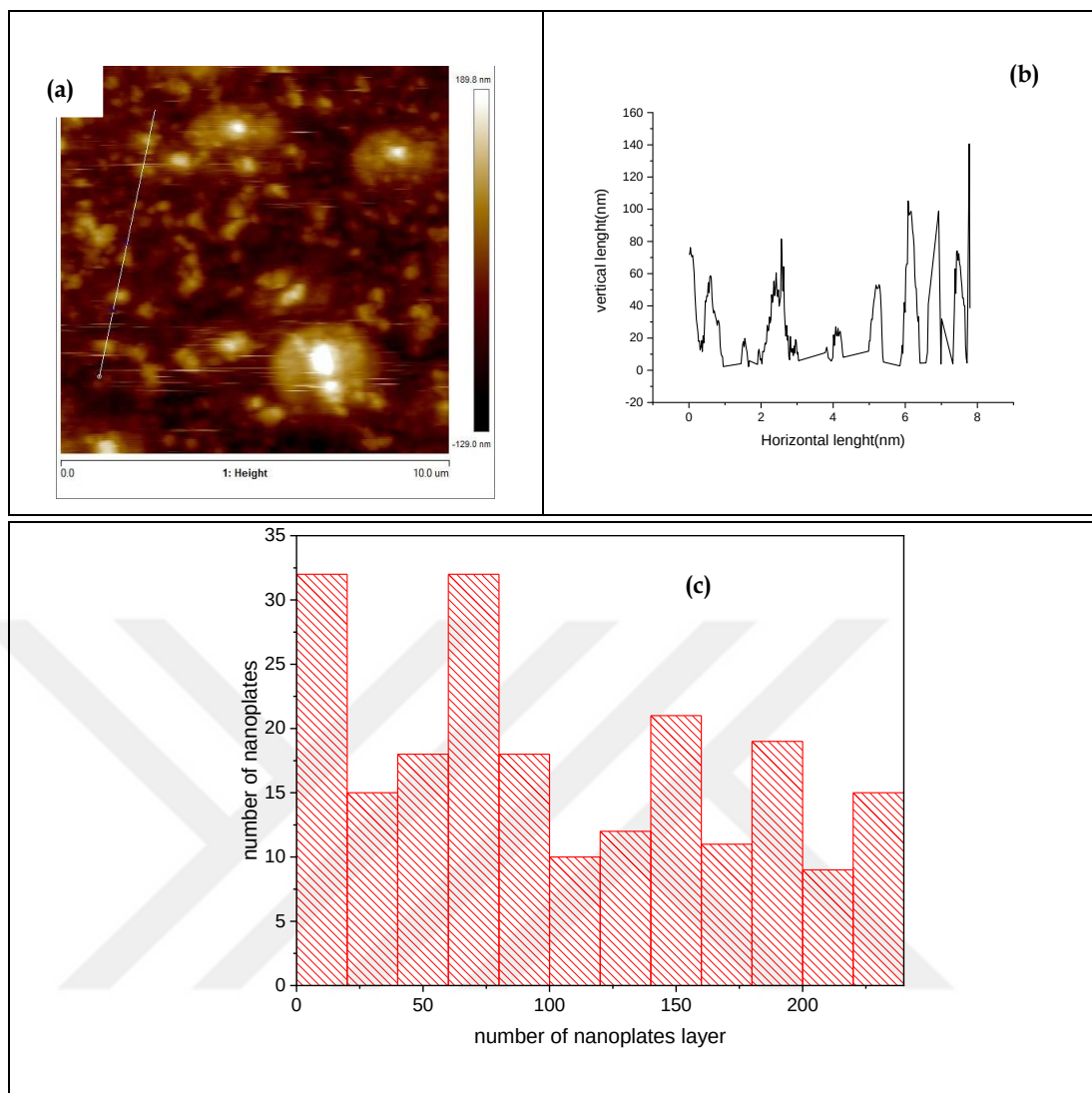


Figure 5.19: (a) a 2D AFM picture of hBN nanoplates generated with NMP/Water (1:1) solution by scanning in a 10 micron region using contact mode, and **(b)** A linear height profile analysis corresponding to the AFM picture shown in([a) as measured from the AFM image. **(c).**The corresponding percent distribution of hBNNS(NMP 1:1) nanoplate layers estimated from the AFM image in (a).

AFM images of hBN nanoplates prepared with N-Methyl-2-Pyrrolidone (NMP) solvent (hBNNS(NMP 3:7) and (hBNNS(NMP 1:1)) are given in Figure 5.16 and Figure 5.19. According to the results obtained, a homogeneous distribution of hBNNS was not observed (Figure 5.16(a) and Figure 5.19(a)). Also, thicker layers were obtained compared to DMF solvent (Figure 5.16(d)). During the treatment with NMP as solvent, it was also observed that the samples did not dry homogeneously on the glass substrate and agglomeration was observed.

SEM image of hBNNS(NMP 1:1) are presented in Figure 5.20.

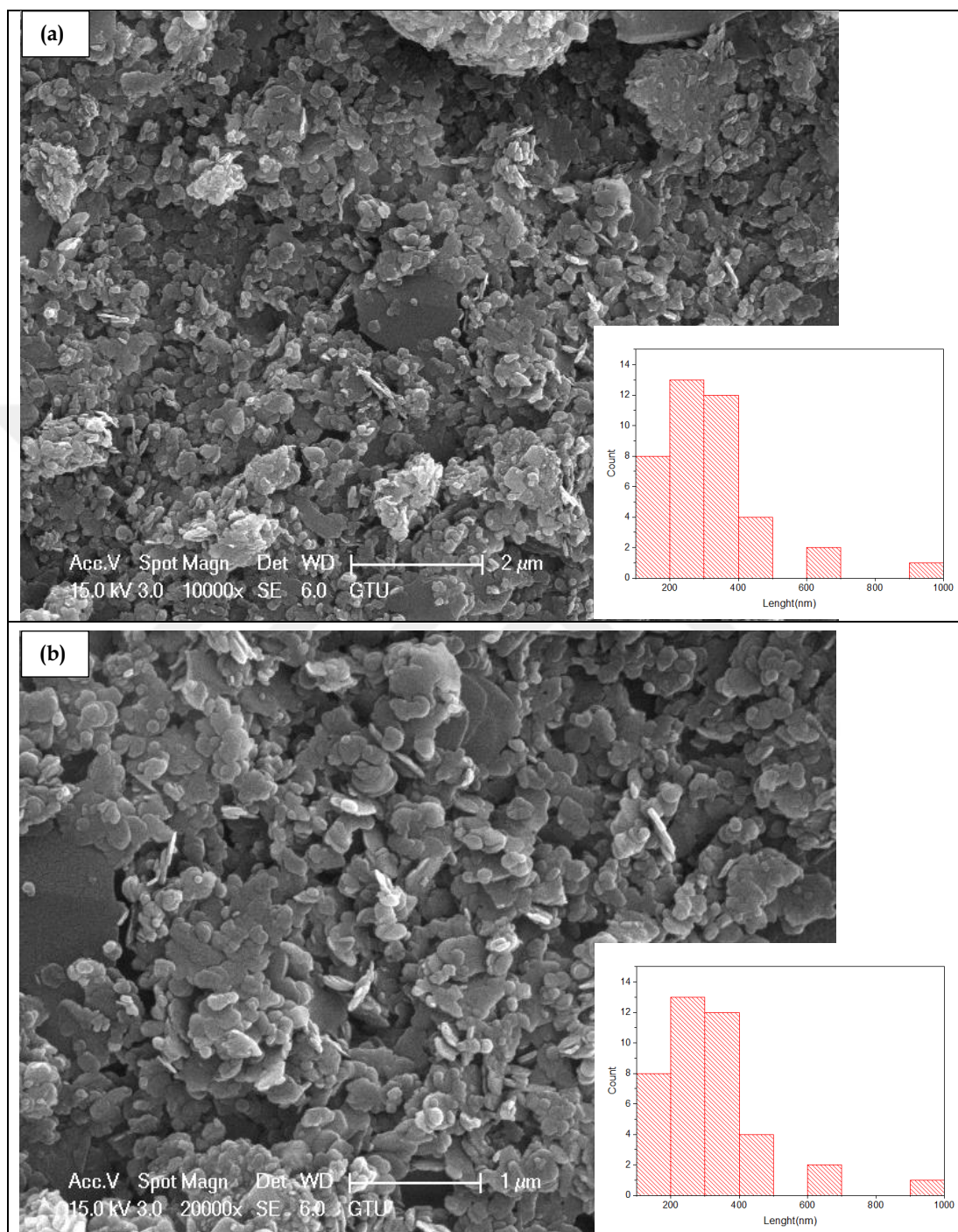


Figure 5.20: SEM images of hBNNS(NMP 1:1) at **(a)** 10000X and **(b)** 20000X magnifications.

According to SEM and AFM images, NMP gave hBN nanoplates with a thickness of 50-100 nm (Figure 5.17 and Figure 5.20).

Finally, AFM results of hBN nanoplates obtained using CHP solvent are given in Figures 5.21 and 5.25. According to the experiments performed at different times (2 h and 10 h), AFM studies show that the particle morphology is distinct and homogeneous (Figure 5.21(a)) and (Figure 5.25(a)).

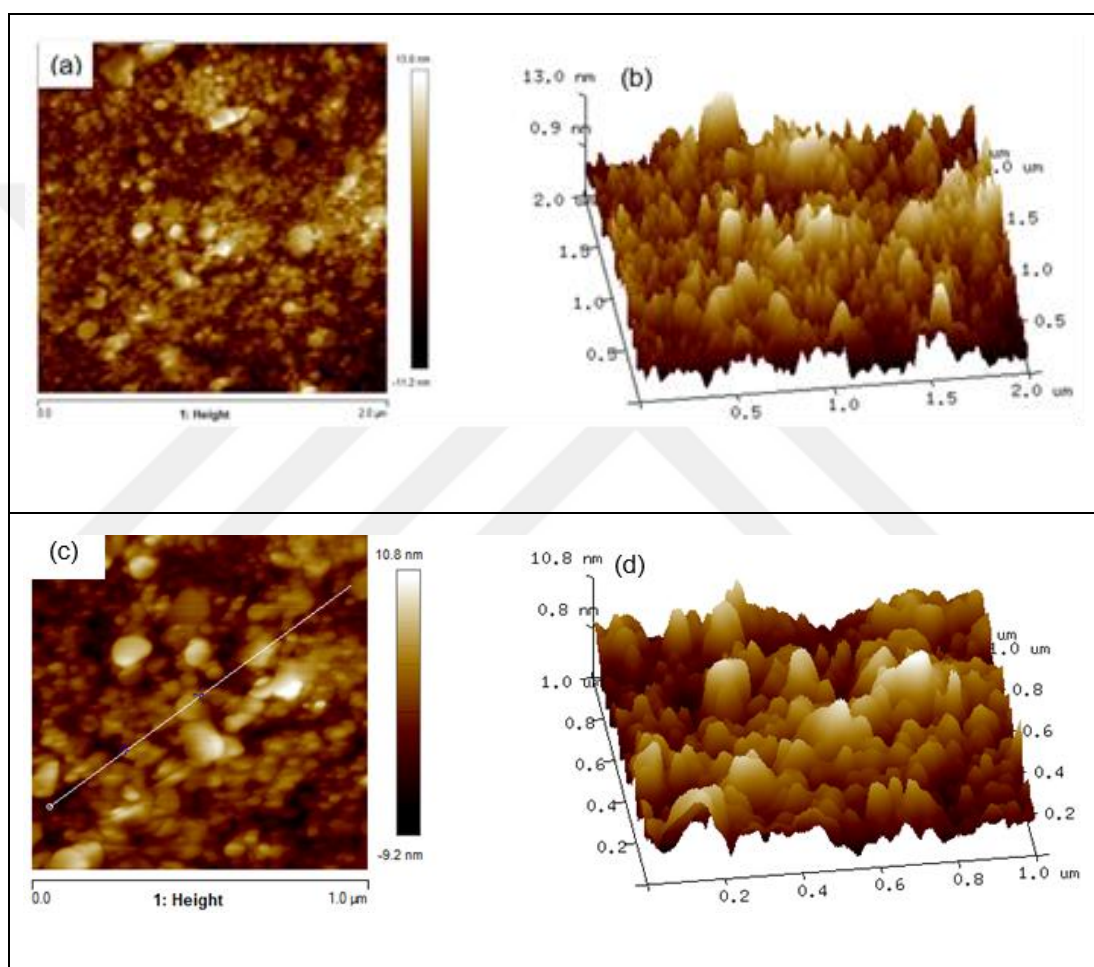


Figure 5.21: (a) 2D AFM image of hBNNS((CHP 1:20) for 2 h) by scanning with the contact mode in a 2-micron area. (b) 3D AFM image of of hBNNS(CHP 1:20), (c) 2D AFM image of hBNNS(CHP 1:20) obtained by scanning with contact mode in a 1 micron area. (d) 3D quantitative AFM height analysis of the corresponding sample.

In the linear height profile analysis of 1 μm length performed AFM image, it was observed that the nanoplate thickness is ~ 7 nm at most (Figure 5.22(a)). Again, on the same AFM image, in the height distribution graph made by Gaussian filtering method, it was determined that the nanoplate thicknesses were mostly below 5 nm (< 5 nm) (Figure 5.22(b)).

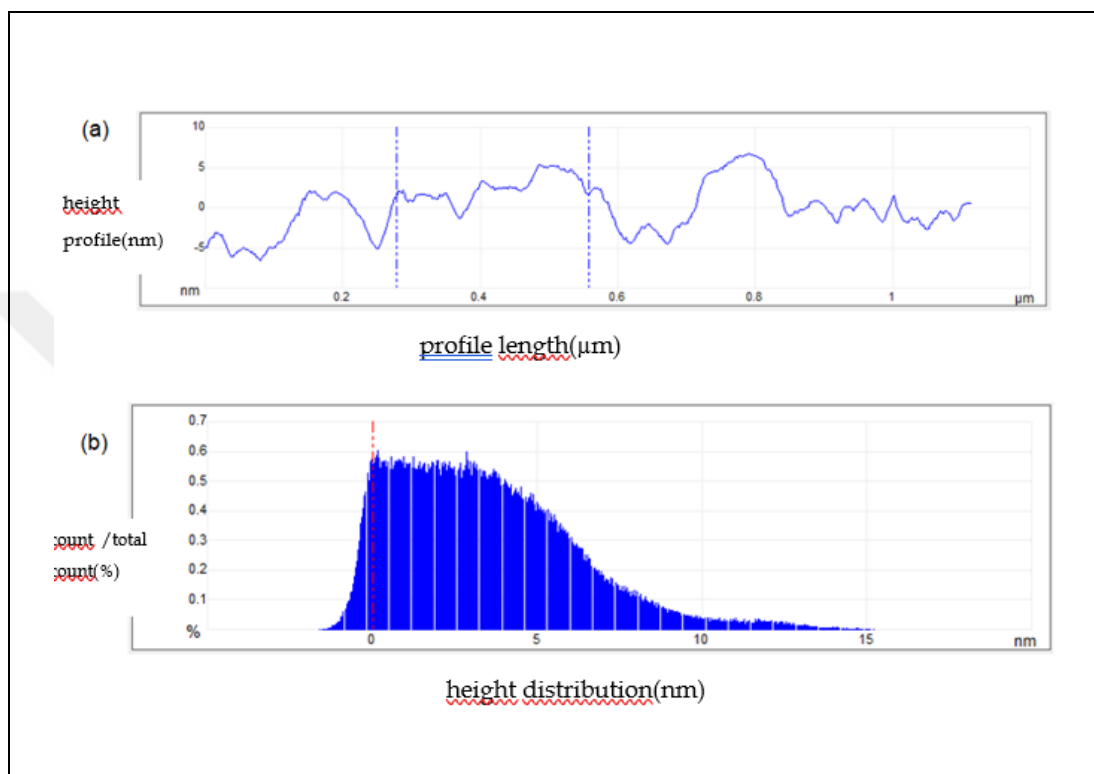


Figure 5.22: (a) An examination of the linear elevation profile using the AFM picture shown in Figure 5.21(c). **(b)** The percentage distribution of two-dimensional nanoplates by scanning at contact mode in a 1 μm region, according to their thickness.

AFM results of hBN nanoplates obtained using CHP solvent are given in Figure 5.21. AFM studies show that the particle morphology is distinct and homogeneous (Figure 5.21(a)). However, since the samples taken in the first place were not dilute, it is thought that the nanoplates overlapped. But even in this case, the height from the substrate surface is found to be ~ 5 nm (Figure 5.21(d)). Considering that the distance between the two layers is 0.34 nm, the nanoplates obtained are calculated to be ~ 16 layers [80].

SEM analysis of hBNNS((CHP 1:20) for 2 h) is shown in Figure 5.23. SEM analysis of hBNNS[(CHP 1:20) for 10 h) obtained for 10 hours is shown in Figure 5.26. In Figure 5.23, the nanoplate widths are in the range of 50-200 nm.

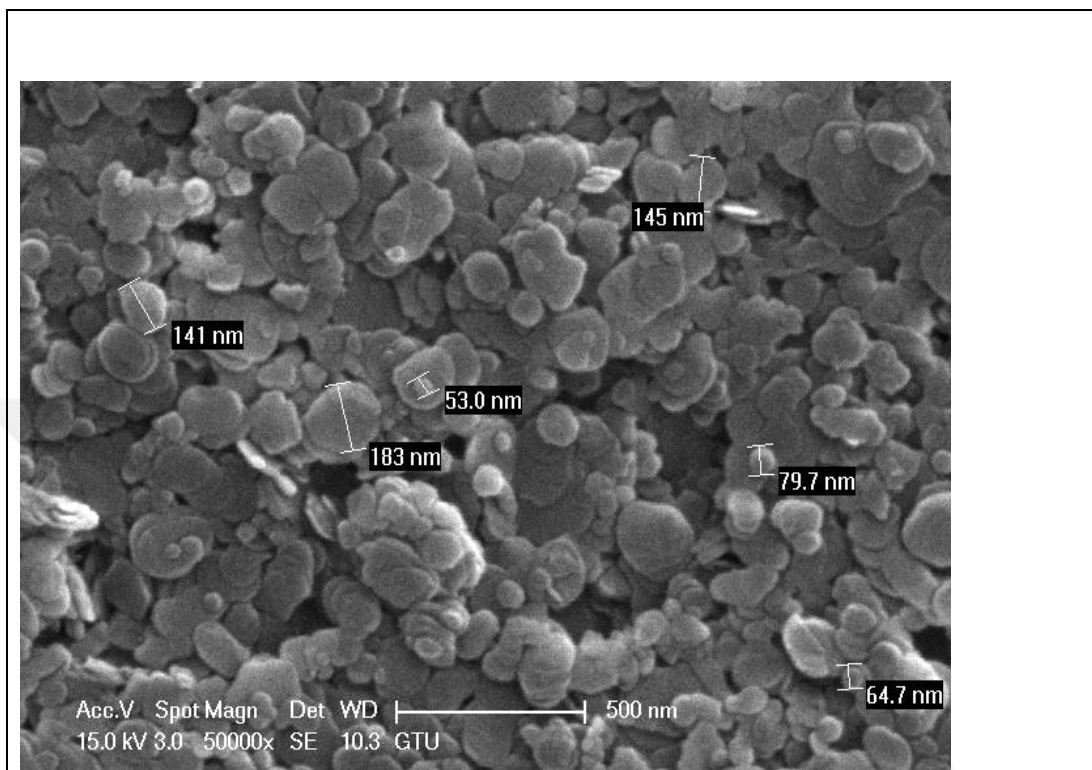


Figure 5.23: SEM image of hBNNS((CHP 1:20) for 2 h) at 50000x magnification.

FTIR image of the sample hBNNS((CHP 1:20) for 2 h) is shown below in Figure 5.24. According to the FTIR data, similar to the results obtained with other solvents, B-N (in-plane) and B-N-B (out-of-plane) strains were detected at 1380 and 635.5 cm^{-1} , respectively. Again, OH and C=O vibrations were detected at 3309.5 and 1632.9 cm^{-1} [79]. The 1380 cm^{-1} peak is the characteristic hBN peak for B-N.

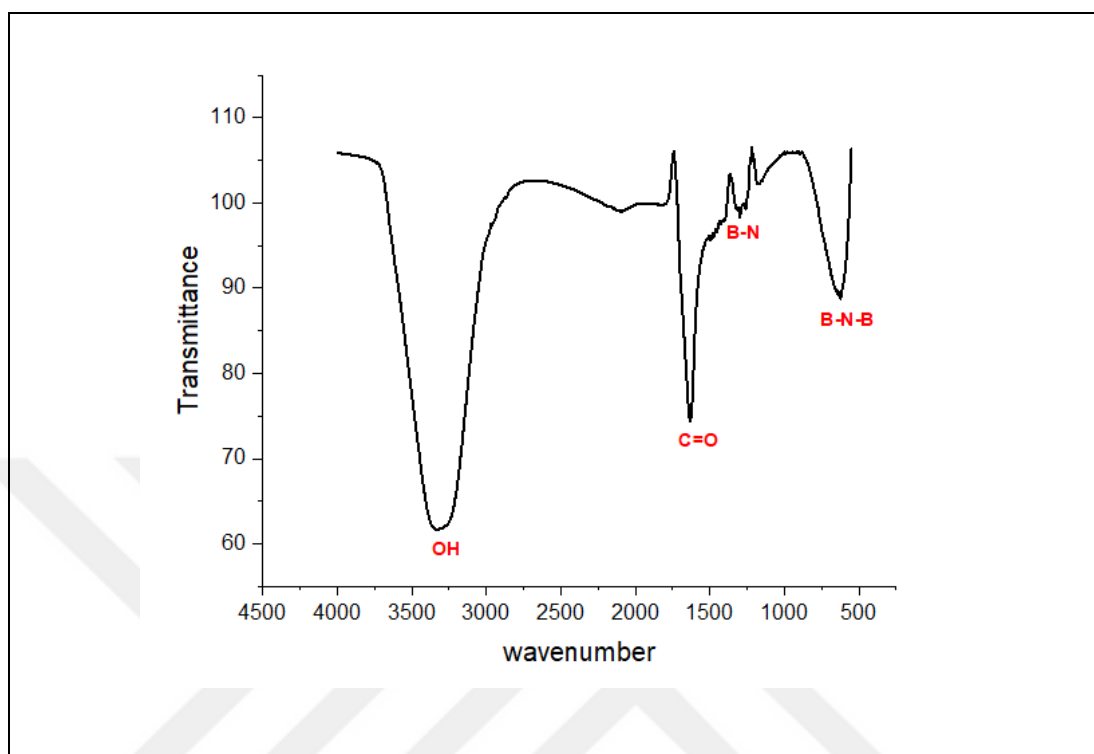


Figure 5.24: FTIR analysis of hBNNS((CHP 1:20) for 2 h).

The AFM image of hBNNS((CHP 1:20) for 10 h) is presented in Figure 5.25.

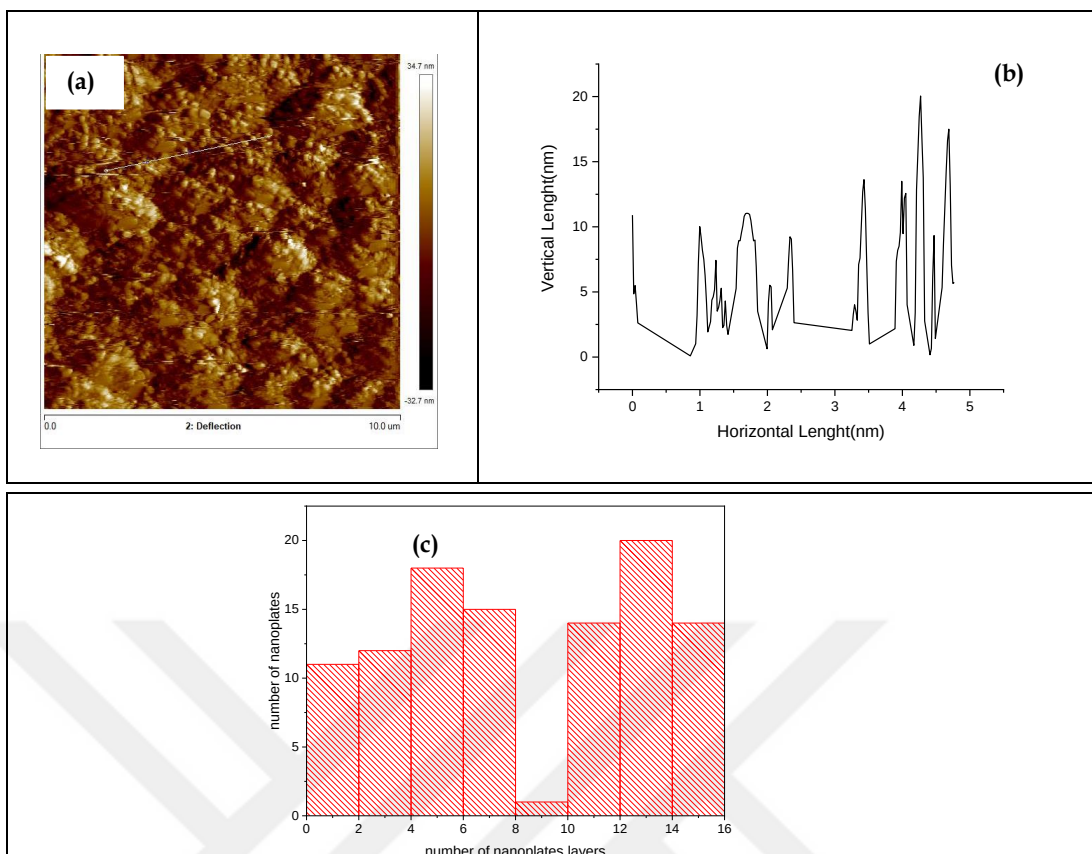


Figure 5.25: (a) 2D AFM image of hBNNS((CHP 1:20) for 10 h) by scanning with the contact mode in a 2-micron area **(b)** AFM height analysis. **(c)** The corresponding percent distribution of hBNNS((CHP 1:20) for 10 h) nanoplate layers estimated from the AFM image in (a).

AFM results of hBN nanoplates obtained using the same ratio of CHP solvent with 10 h exfoliation time are given in Figure 5.25. AFM studies show that the particle morphology is distinct and homogeneous (Figure 5.25(a)). The overall average thickness varies in the range of 0-10 nm as seen in (Figure 5.25(b)).

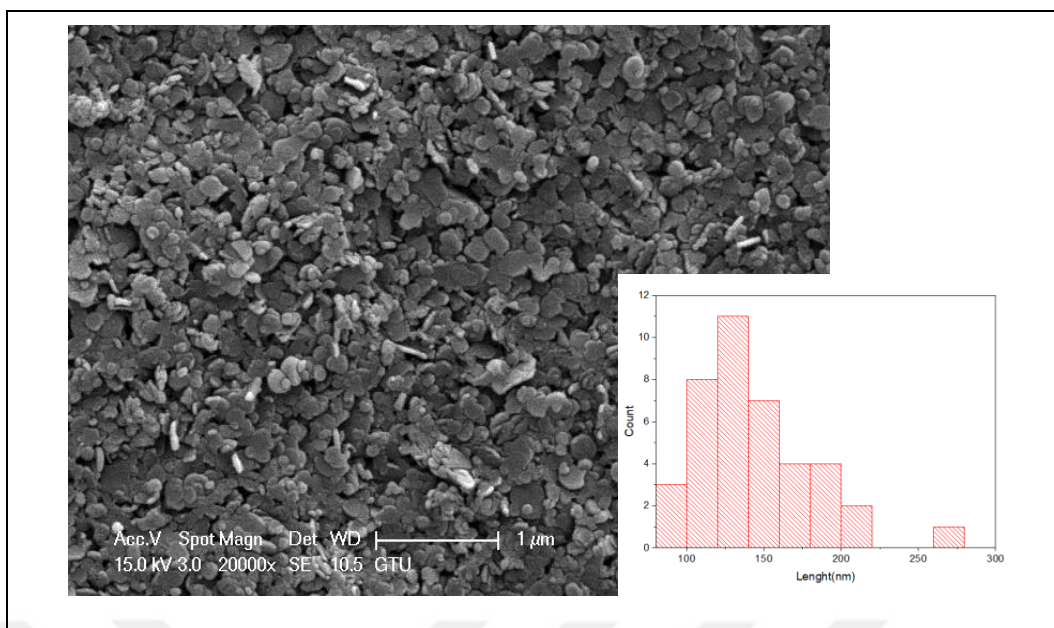


Figure 5.26: SEM image of hBNNS((CHP 1:20) (10 h) at 20000x magnification.

SEM analysis of hBNNS(CHP 1:20) is shown in Figure 5.23. Figure 5.26 shows the SEM analysis of hBNNS(CHP 1:20) obtained for 10 hours. In Figure 5.23, the nanoplate widths are in the range of 50-200 nm. In addition, when the SEM image in Figure 5.26 is examined, it is also seen that it has the same similar lateral dimensions. The fact that the nanostructures woven in Figure 5.23 and Figure 5.26 have a morphology close to round shows that they do not disintegrate and are not damaged during the ultrasound process. However, when figure 5.26 is examined, it is seen that contamination occurs with the prolongation of time and the nanoplates cannot be separated from each other

6. CONCLUSION

In this dissertation, a comparison was made between the properties of nanoplates produced with different solvents using the liquid phase exfoliation method. This technique is known to be economically viable and effective method in the production of 2D nanomaterials. The impact of varying the solvent (aqueous solutions of CHP, DMF, NMP, IPA) reagent content on exfoliation performance was investigated using ultrasonication at room temperature. After 2 hours of sonication at 30 W at 30 °C, the exfoliated and dispersed hBN particles in the investigated solution were further purified by various steps such as centrifugation, filtration and washing. The produced samples were characterized by AFM, SEM and FTIR techniques.

These investigations confirmed that the amount of H₂O in the reaction mixture using IPA decreased the layering. The energy barrier for lateral slippage between molecular layers has been reduced, hence facilitating the exfoliation of h-BN [80],[81].

SEM and AFM analyses were used to determine the size, shape, and thickness of the produced exfoliated h-BN nanosheets. The finest results were obtained from the solvent mixtures of CHP:H₂O (1:20) and IPA:H₂O (3:7).

When the FTIR analyses of IPA, DMF and NMP samples were examined, it was determined that boron element tended to bond with the OH⁻ anion. This increases the reaggregation rate of the nanoplates after exfoliation. This situation was visually confirmed in the samples that were kept for 2 hours or more without separating from the solution. In the CHP sample, on the other hand, the B-OH bond ratio is lower and the shelf life is therefore longer. According to the FTIR results, when CHP:H₂O, v/v 1:20 is used, -OH and C=O vibrations were found at 3309.5 cm⁻¹ and 1632.9 cm⁻¹, respectively. In addition, B-N (in-plane) and B-N-B (out-of-plane) stresses were observed at around 1380 cm⁻¹ and 635.5 cm⁻¹, respectively. The OH and C=O vibrations for IPA:H₂O (3:7) came at 3310 cm⁻¹ and 1643 cm⁻¹, respectively while B-N (in-plane) and B-N-B (out-of-plane) stresses were observed at 1385 cm⁻¹ and 659 cm⁻¹, respectively. The peak observed around 1380 cm⁻¹ for all the samples is the characteristic hBN peak for B-N [80].

The lateral dimensions of the nanosheets were on the order of tens of nanometers. Although there are very few publications using CHP solvent, to the best of our knowledge, we obtained the good results in terms of optimization of the process

conditions and the least nanoplate thickness using this solvent. The satisfactory results attained with IPA:H₂O (3:7) were in parallel with the literature [82],[83].

It is worth to mention that one of the difficulties encountered during the sonication process was the overheating of the solution, making it difficult to maintain a constant temperature for the reaction. The centrifugation phase was also essential for the production of nanosheets. Another challenge was the careful preparation of the AFM and SEM samples to get the precise results for the produced nanosheets.

Finally, during our studies, we obtained promising results from hBN nanoplates produced with CHP:H₂O v/v 1:20 and IPA:H₂O v/v 3:7 solutions. The hBN nanoplates obtained by using IPA:H₂O v/v 3:7 was found to be similar to the properties of the nanoplate produced in CHP aqueous solution. On the other hand, it is well known that IPA is less expensive than CHP, which is an advantage. We believe that such hBNNS may be further utilized in biomedical, energy, catalysis, and other applications. Our future efforts will be towards their investigation in energy storage applications.

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