



Effect of Laser Energies on the Performance of Exfoliation and Fragmentation for Hexagonal Boron Nitride by Laser

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ABSTRACT

A technique for exfoliating Boron nitride (BN) nanosheets was devised, which was then followed by a laser ablation-fragmentation process to produce lamellar hexagonal Boron nitride nanostructures (h-BNNs). The physicochemical properties of the nanoparticles were analysed to investigate the effect of laser energy and wavelength in the two-step pre-treatment procedure during BN synthesis. The X-ray diffraction (XRD) patterns showed no impurity phase structures, and only primary h-BN reflections were visible. It was discovered that the crystallite h-BNNs size ranged from 11 to 18 nm, and nanosecond laser energy was sufficient to transform BN into h-BNNs and a few nanotubes. Combining laser intensity and wavelength transformed the BN nanoparticle shape from haphazardly arranged platelets to melting-like formations. Fourier Transform infrared (FTIR) spectroscopy confirmed distinct observed changes in the size and melting behaviour in the h-BNNs and the sharp absorption peaks, which could indicate changes in their optical properties. Morphological characteristics and formation of the hexagonal phase of BN caused variations in optical properties and high-resolution transmission electron microscopy (HRTEM) results. Photoluminescence of h-BNNs was observed in the 250–600 nm range with peak emission at 485 nm. Due to its significant structural disorder, the h-BNNs exhibited a wide emission with a strong luminescence that remained largely continuous after 48 hours, resulting in a distinctive blue hue (470 and 485nm).

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1. Introduction

Quantum dots, also called (QD), containing the compound graphene quantum dots (GQD) and carbon nanodots, have distinctive chemical and physical characteristics. That makes them ideal for various apps like photocatalysis, sensor technology, bioimaging, bio-labelling, conversion of energy, and delivery of drugs. As the demand for these QD continues to grow, researchers are exploring Black phosphorus quantum dots (BPQD) and boron nitride quantum dots (BNQD) are two new forms of quantum dots, which offer exceptional features resulting from their

size, shape, edge, and layer [1]. A significant increase in interest has been seen in BNQD, particularly because of their distinct structure and intriguing physical and chemical characteristics. Created BNQD self-assembled from boron nitride (BN) nanosheets that had undergone exfoliation by high-intensity ultra-sonic [1]. Nanostructures made of hexagonal boron nitride (h-BN) have a specific crystal structure that has piqued the interest of scientists, as it closely resembles that of graphite/graphene (sp^2) h-BN, often known as "white graphene," is isoelectronic with graphene and comprises an equal amount of atoms of nitrogen (N) and boron (B), which form strong sp^2 covalent bonds within each layer. The forces generated by Van der Waals between the layers are weak. Due to its wide band gap range from 4-6 eV, hexagonal Boron nitride nanostructures (h-BNNs) are insulating materials, with electrical insulation demonstrated between the lowest unoccupied molecular orbit (LUMO) in a hexagonal arrangement and the highest occupied molecular orbit (HOMO). Neighbouring h-BN layers may also connect via lip-lip ionic bonding interactions [2, 3]. The characteristics of h-BN can be enhanced when the dimension is reduced to the nanoscale, much like graphene nanosheets. Exfoliating BNNs from bulk BN is far more difficult than doing the same for graphene from bulk graphite. BN has been considered the perfect material for creating and manufacturing various nanodevices for decades. The combination of BNQD with h-BNNs inherent qualities, including excellent thermal conductivity, superior stability in chemicals, great luminescence properties, low toxicity, and good dispersibility, has made them promising candidates for use in optical electronic devices [4-6], Far-ultraviolet light-emitting devices, lubrication [5], bio-medicine [6], and Sensors application [7]. However, the usage of the few-layer Tow dimension (2D) equivalents is more complex. Because pure h-BN retains a significant amount of its crystallinity, top-down techniques, including mechanical cleavage, chemical modification, and liquid phase separation by sonication, have been favoured to exfoliate BN multilayer materials [8, 9]. A practical method for creating well-controlled h-BN nanosheets or nanoparticles with a surface activity that supports certain characteristics is pulse laser ablation in liquid (PLAL), particularly for optic applications. Meanwhile, laser exfoliation in solution (LES) provides an easy, quick, and environmentally friendly method for creating various nanomaterials by concentrating a laser beam on a powder dispersion in an aqueous solution, LES produces nanomaterials compared to bulk targets, with a more homogeneous structure on the surface and a lower size distribution [10]. The preparation of h-BN through laser exfoliation poses certain challenges that need to be addressed for efficient and reliable synthesis compared with other methods, such as chemical vapour deposition (CVD), ball milling, and plasma-enhanced chemical vapour deposition (PECVD). One of the primary issues is achieving a high yield of h-BN flakes. The process relies on precise laser energy to cleave the layered material, but it is often difficult to maintain consistent energy levels, leading to varying flake sizes and qualities. Additionally, the scalability of the laser exfoliation process remains a challenge. While small-scale experiments have shown promise, scaling up production to meet industrial demands is complex. Optimising laser parameters, substrate choice, and deposition techniques are key aspects that must be thoroughly investigated to enable large-scale, cost-effective synthesis of h-BN. Addressing these problems in preparation for h-BN by laser exfoliation will contribute to advancing the understanding and application of this remarkable material in various fields, including electronics, optics, drug delivery, and energy storage. In this study, we report and focus on the characterisation and properties of h-BNNs prepared using a new technique called exfoliation and fragmentation by laser. The physical-chemical properties of the h-BNNs were thoroughly investigated through surface characterisation, determination of morphology, analysis of structures and chemical bonds, and examination of fluorescence and optical properties. These investigations were crucial in revealing the essential characteristics of the h-BNNs. Our method offers an easy way to create nanomaterials based on Boron nitride, which has promising applications in cancer treatment and optoelectronics.

2. Theoretical Part

Synthesising h-BNNs involved laser exfoliation/fragmentation of BN particles in deionised distilled water (DDW). The resulting h-BNNs were characterised within two hours of production using the same approach as described in a previous study and shown in Fig. 1 [4, 11, 12]. To produce BN nanosheets, 20 mg of the h-BN powder with 3–4 μm size particles and 99.99 % purity acquired from Sky Spring Nanomaterials, Inc. The substance was diluted in 50 mL of DDW and subjected to prop sonication for 10 minutes. The suspension was then laser irradiated at different energies (10, 30, and 50 mJ/pulse) with an Nd: YAG laser system (central wavelength: 1064 nm, pulse duration: 2 ns, repetition rate: 1 Hz) followed by further laser fragmentation in liquid (532 nm, 50 pulses by the same laser system) to form colloids [11]. After irradiation, the solution underwent centrifugation at a speed of 4,000 rpm for five minutes to separate the boron nitride nanoparticles from the supernatant and eliminate larger

particles. Colloidal samples were applied to a glass surface and allowed to air dry. The Shimadzu, Inc. X-ray diffractometer (XRD) was used, with Cu-K α radiation at 1.5405 Å, 40 kV, and 25 mA, measuring the diffraction pattern between 20 and 80 over a 2 θ range. The UV absorption spectra of colloidal suspensions within the 200–500 nm range were measured using a Shimadzu Ultraviolet-2600 spectrophotometer. Using a Nicolet Avatar 360 spectrophotometer, Fourier Transform infrared (FTIR) spectra were collected, while fluorescence emission was measured using a Shimadzu Spectra fluorophotometer model RF-5301pc. The INSPECT F50 Field Emission Scanning Electron Microscopy (FESEM) was used to characterise the dimensions and structural characteristics of h-BNNs. The shape and size distribution of nanoparticles were investigated using high-resolution transmission electron microscopy (HRTEM) (JEOL-2100F 200 kV), and Selected Area Electron Diffraction (SAED) was used to determine the atomic structure of a crystalline sample.

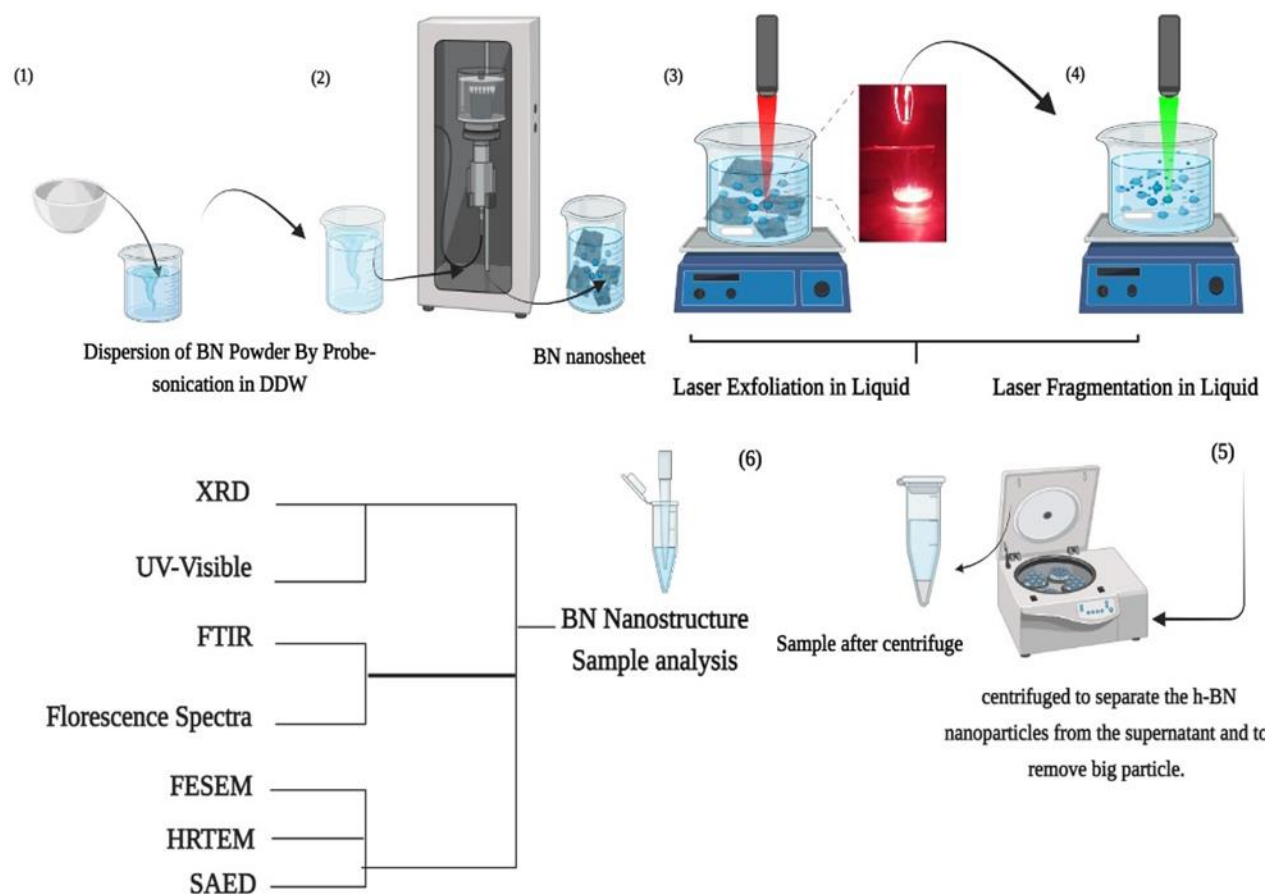


Figure 1: Depicts a schematic view of the preparation h-BNNs method.

3. Results and Discussion

3.1. X-ray Diffraction

Fig. 2 shows XRD images of the colloidal solution obtained from a pulsed Nd: YAG laser, using the first (1064 nm) and second harmonics (532 nm). The XRD patterns of the six products were compared to standard patterns of h-BN (JCPDF card number 45-0893 and JCPDS 34-0421) and previous studies [13, 14]. The absence of additional peaks indicating impurity phases in the observed pattern confirms the high purity of the synthesised material. Distinctive peaks of h-BN are observed at various diffraction angles, namely (002), (100), (101), (004), (102), (103), and (110), with the main peak at 26.7° (002) and a weak peak (210) of BN nanotube [12, 15], as shown in Tables 1 and 2.

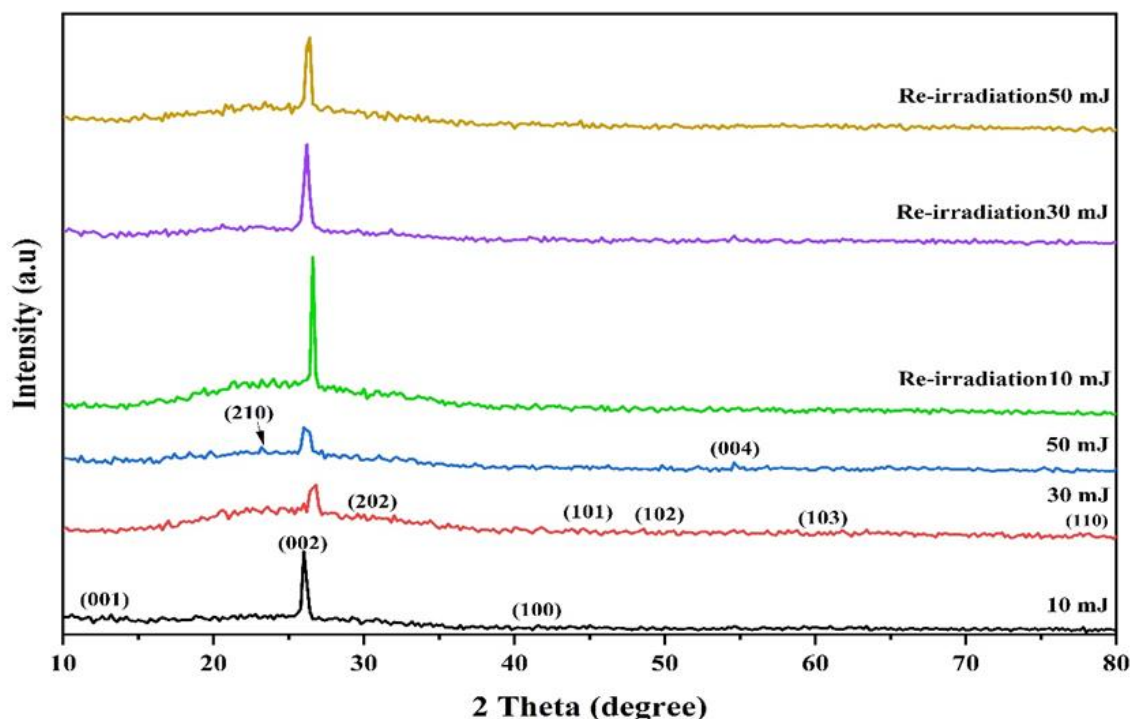


Figure 2: X-ray patterns of h-BNNs synthesised by laser exfoliation (1066 nm) and fragmentation by (532 nm) in DDW with different laser energy.

In Fig. 2, it is clear that the intensities of XRD peaks for the sample prepared using a 1064 nm laser with different energy levels (10, 30, and 50 mJ) decrease. The full width at half maximum (FWHM) of the (002) diffractions also increases, indicating a reduction in the crystalline perfection of the h-BNNs samples with increased pressure due to increasing laser energy. Various factors, such as changes in lattice parameters, microstrain, crystal size, and nanoparticle size, can cause peak shifts in XRD. Nanoparticle size significantly impacts the diffraction pattern, making it challenging to analyse nanoparticles with crystalline domains below 5 nm due to broad peaks and low signal-to-noise ratios. Furthermore, the XRD analysis indicates that there is an increase in h-BNNs content with higher laser energy, particularly after laser re-irradiation (laser fragmentation using 532 nm) at 10, 30, and 50 mJ laser energy as shown in Fig. 2. Laser re-irradiation results in a significant increase in oxygen-functional-groups content within the h-BN layer structure, which has been confirmed by FTIR analysis. This observation is consistent with the similarity between the structures of h-BN and graphene. Additionally, the shift in peaks resulting from laser-water interaction causes defects on the surface of h-BNNs. Laser ablation of boron nitride also generates other BN nanostructures such as BN nanosphere, nanosheets, nanotubes, and nanoflake that detach from BN nanosheets under high temperature and pressure conditions caused by the laser plasma plume. This finding is consistent with the FESEM results discussed in the following section. It can be observed that the three samples exhibit variations in the broadening of diffraction peaks during X-ray analysis, indicating differences in the fine structure of the synthesised nanoparticles. To determine the average grain size (D) of the samples, the Scherrer equation (Eq.(1)) [16, 17] can be utilised:

$$D = 0.9 \lambda / \beta \cos \theta \quad (1)$$

Where λ represents the X-ray wavelength, β represents the full width at half maximum (FWHM) of the diffraction peak, and θ denotes the Bragg angle. The mean grain sizes are given in Tables 1 and 2. D of h-BN (preparation at 1064nm) by Scherrer approximation leads to approximately (18 nm) by 10 mJ, (13 nm) by 30 mJ, and (18 nm) by 50 mJ in Fig 2A, but in Fig. 2B for h-BNNs synthesis after re-irradiation by 532 nm D equal to (11nm) of 10 mJ, (14 nm) of 30mJ, and (16.5 nm) of 50 MJ [18].

Table 1: Peaks analysis data for h-BNNs sample synthesis by laser exfoliation in DDW.

Parameter	Sample	2 θ	FWHM	Crystallite Size (nm)	Average (nm)	hkl
1064nm, 338pulse	10 mJ	14.2	0.473	17	18	001
		26.7	0.352	24		002
		41.6	0.656	13		100
	30 mJ	20.532	0.577	14	13	210
		26.7	0.498	16		002
		41.761	0.6	14		100
		58.274	0.9	10		103
		77.63	0.819	12		110
		15.711	0.359	23		001
		23.207	0.431	20		210
	50 mJ	26.143	0.582	14	18	002
		49.892	0.472	19		100
		54.641	0.56	16		004
		56.677	0.51	18		103
		77.477	0.578	17		110

Table 2: Peaks analysis data for h-BNNs sample synthesis by laser fragmentation in DDW.

Parameter	Sample	2 θ	FWHM	Crystallite Size (nm)	Average (nm)	hkl
532nm, 50 pulse	10 mJ	19.2	0.856	9	11	001
		23.2	1.47	5		210
		26.585	0.357	23		002
		32.049	0.956	8		001
	30 mJ	20.617	0.889	9	14	210
		26.188	0.394	21		002
		31.766	0.704	11		001
		54.625	0.567	16		004
		20.989	0.355	23	16.5	001
	50 mJ	23.503	0.645	12		210
		26.314	0.394	21		002
		44.347	0.491	17		100
		50.647	0.948	9		102
		77.818	0.592	17		110

3.2 Field Emission Scanning Electron Microscopy

The surface morphology of h-Boron nitride ultra-fine nanoparticles and nanosheets generated through two-step laser exfoliation and fragmentation in deionised distilled water was analysed using FESEM in Fig. 3 and 4. The nanoparticles' morphology was influenced by both the energy and wavelength of the laser pulse, with the h-BNNs appearing spherical and forming disk and sheet-like particles that were attached. Compared to BN powder, laser exfoliation in DDW significantly reduced the thickness of h-BNNS; FE-SEM micrographs revealed that sheet-like structures were generated and connected, with alterations in thickness observed in samples produced at various laser energy levels. As the laser's energy was increased, the surface morphology became coarser. Despite these variations, all samples exhibited tiny sheet structures that enhanced their exfoliated-like structures. Similar structures have also been traced to BN by other literature reports [18, 19].

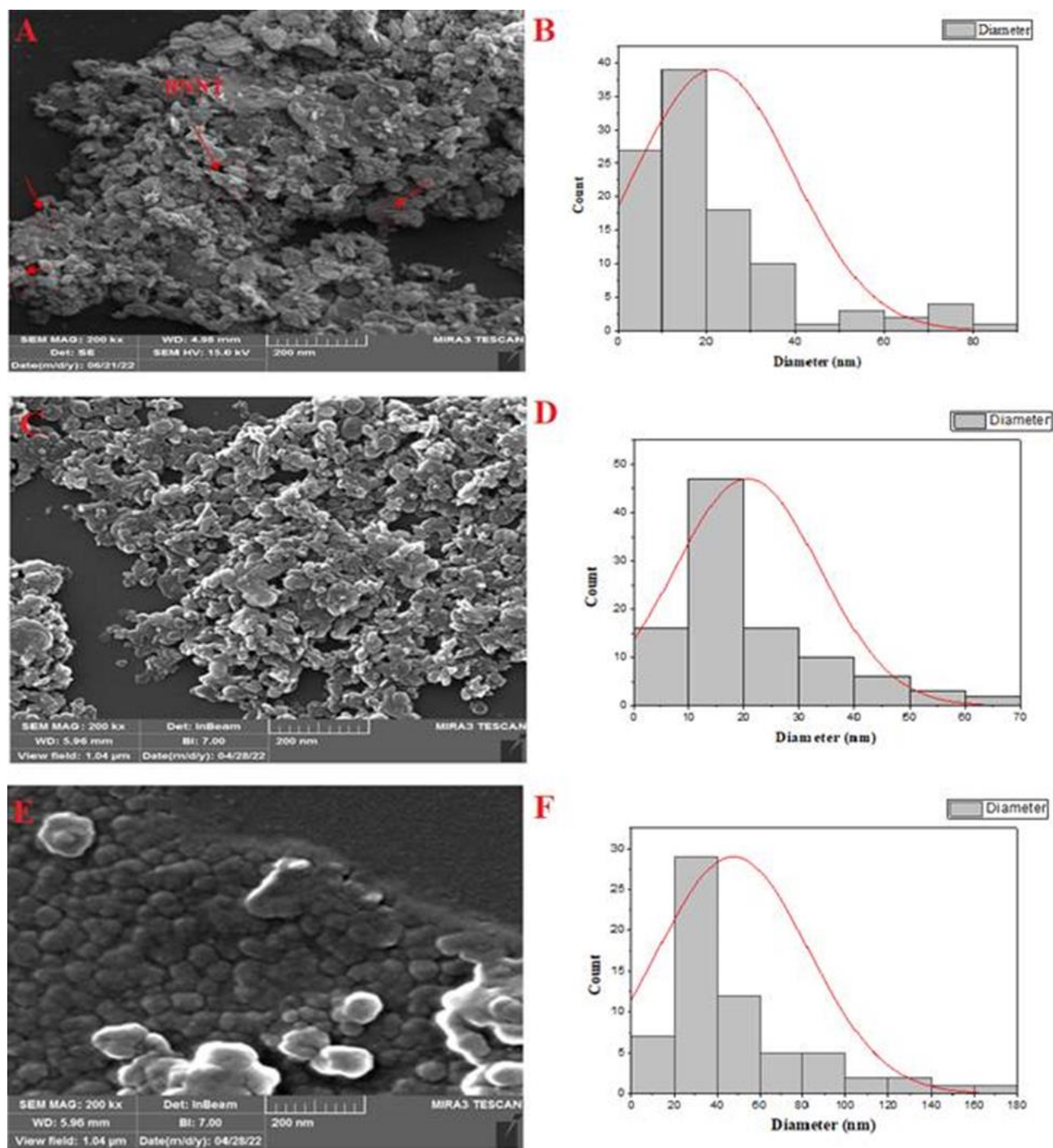


Figure 3: FESEM images of h-BNNs prepared by 1064 nm laser exfoliation in DDW at different laser energies (A (10 mJ), C (30 mJ), and E (50 mJ)), with histogram.

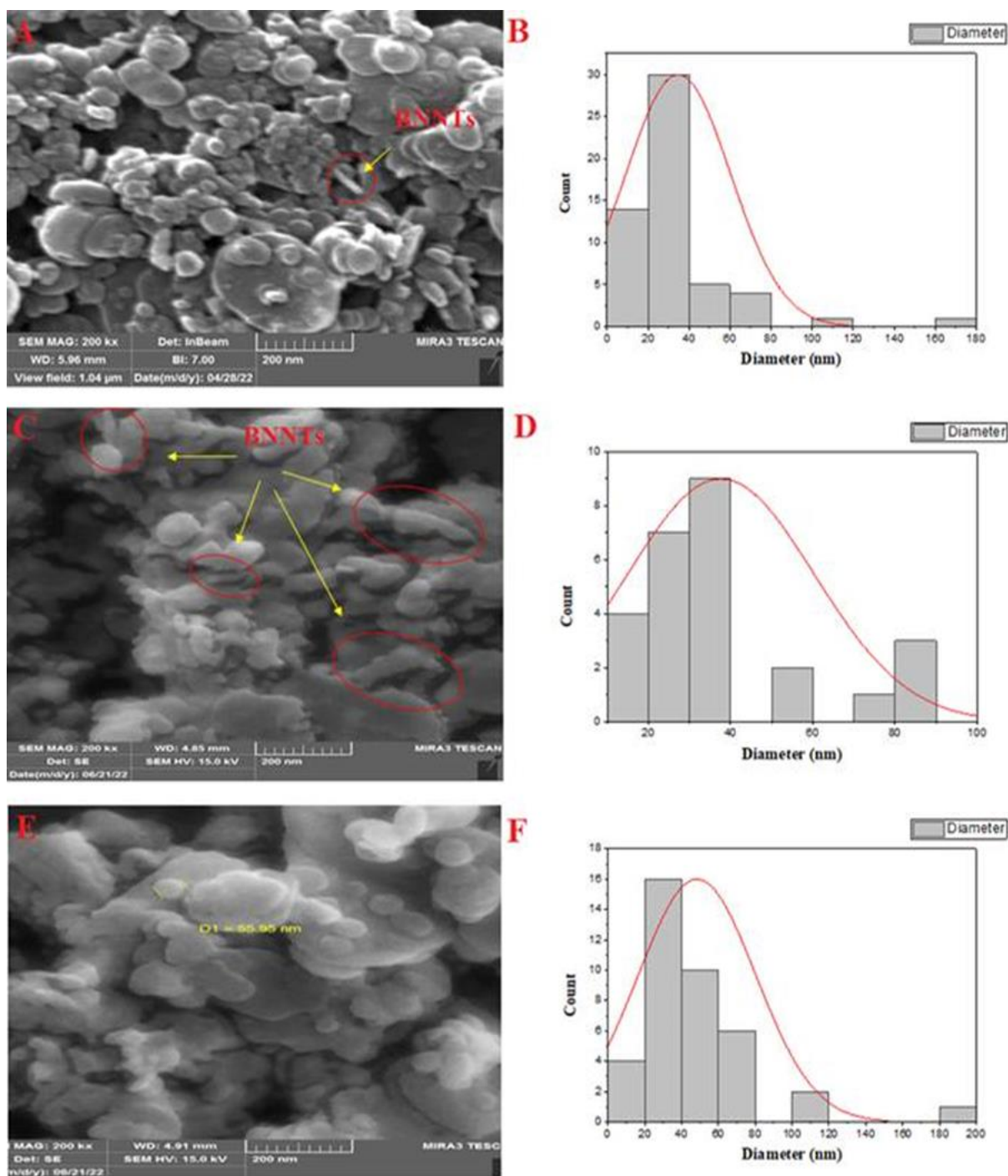


Figure 4: FESEM images of h-BNNs prepared by 532 nm laser fragmentation in deionised DDW at different laser energies (A (10 mJ), C (30 mJ), and E (50 mJ)), with histogram.

The FESEM image reveals that h- BN colloidal nanoparticles aggregate due to multiple factors. Firstly, inter-particle forces play a significant role, including the induced dipole-dipole force between charged particles at polar/non-polar liquid interfaces. This force can be either attractive or repulsive depending on the charges and surface roughness of the particles. Secondly, weak forces cause nanoparticle adhesion, resulting in (sub) micron-sized entities. The agglomeration process is governed by thermodynamics and can be influenced by laser energy. The sign of the enthalpy of interaction determines whether poorly agglomerated (repelling) or highly agglomerated (attracting) particle ensembles are formed.

3.3 High-Resolution Transmission Electron Microscopy

The creation of h-BNNS in deionised distilled water involved using various wavelengths and laser energy, with its shape being analysed through HRTEM and electron diffraction shown in Fig. 5, 6, and 7, respectively. The image of h-BNNS displayed a stacked morphology with a lateral size of a one-micrometre scale and demonstrated that the BNNSs obtained are transparent and evenly distributed. It has been observed that the particles tend to clump together, resulting in strong, significant agglomeration. As a result of this high level of aggregation, it was impossible to determine the average particle size via the TEM micrograph. Fig. 7A and B display the TEM image at low and high magnifications, respectively. The TEM image shows a wrinkled structure with edges resembling graphene and minimal agglomeration. The HRTEM image in Figure 7C shows that the structure of crystals was visible in h-BN, with a 0.21 nm d-spacing and apparent flaws. The distance separating two neighbouring B or N atoms in the basal plane of BNNS was found to be 0.21 nm, similar to the reported d-spacing of 0.22 nm. We hypothesise that defects in BNNS unclear lattice structure may have resulted from hydrolysis caused by sonication during liquid-phase exfoliation using Nd-YAG lasers (1064 and 532 nm). These exfoliated h-BNNSs can be easily dispersed in an aqueous solution to form a uniform creamy white, stable, and homogeneous dispersion. The HRTEM micrographs reveal that a wavelength of 532 nm effectively fragment h-BNNSs into ultra-nanoparticles of 3-20 nm. These nanoparticles are well-crystallised, as observed from the SAED pattern of h-BNNS displayed in Fig. 7D and E. The pattern shows the presence of two sets of hexagonal electron diffraction patterns, indicating that two BN layers are covering each other at an angle of 18°.

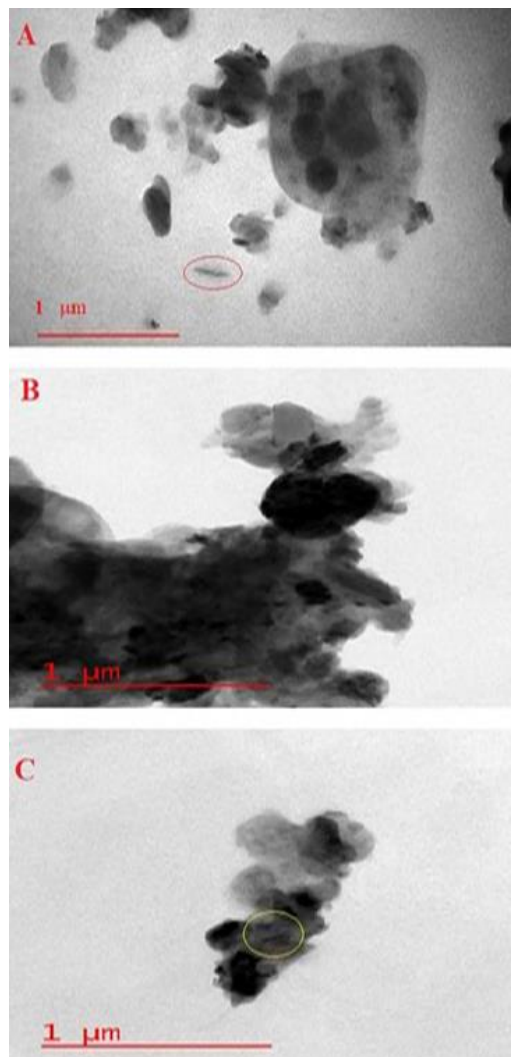


Figure 5: HRTEM images of h-BNNS prepared by 1064 nm pulsed laser exfoliation in DDW at different laser energies (A (10 mJ), B (30 mJ), and C (50 mJ)).

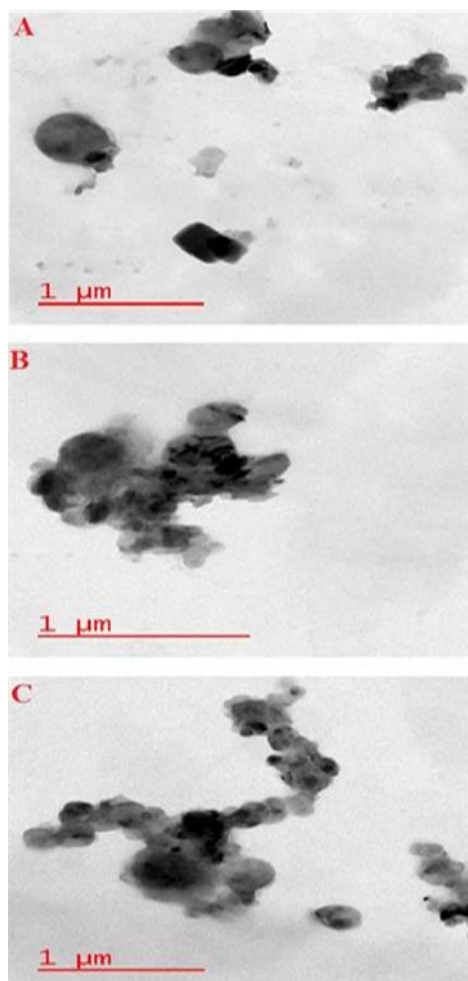


Figure 6: HRTEM images of h-BNNs prepared by 532 nm pulsed laser fragmentation in DDW at different laser energies (A (10 mJ), B (30 mJ), and C (50 mJ)).

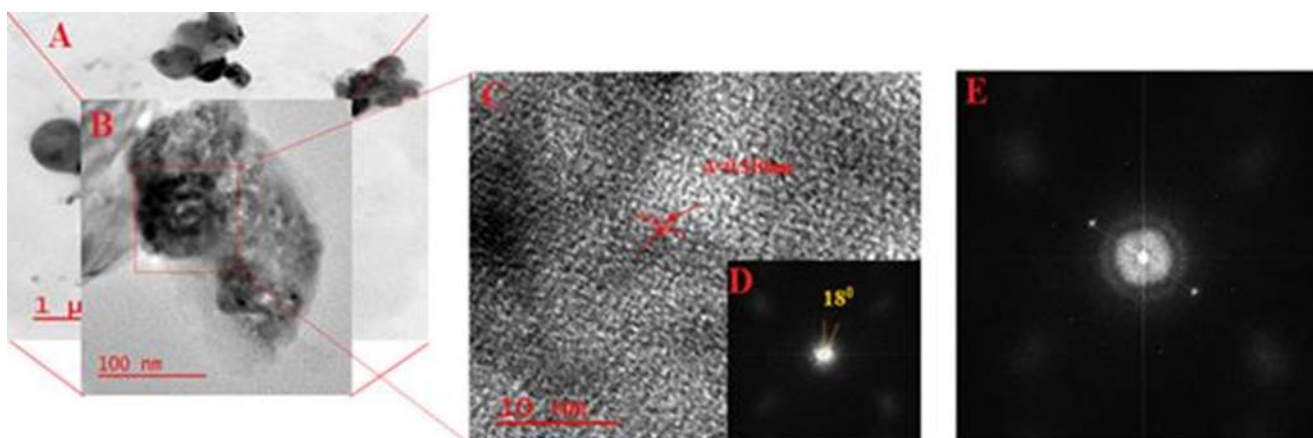


Figure 7: (A, B, and C) HRTEM images of h-BNNs of the sample prepared by laser fragmentation in DDW with 532 nm and 10 MJ (D and E) SAED pattern for h-BNNs.

3.4 Fourier Transform Infrared

FT-IR spectroscopy was used to investigate the changes in the chemical compositions of the reactants. Fig. 8 and 9 demonstrate the use of FTIR spectroscopy to elucidate the bonding nature of h-BN ultra-fine nanostructures. The two strong absorption peaks at 600-800 and 1500-1700 cm^{-1} , corresponding to in- the plane B-N-B vibration of bending and the plane B-N vibration of stretching, are consistent with the nanoparticles produced by laser

exfoliation and fragmentation in DDW. Additional absorption peaks at 800-1000 and 1300-1400 cm^{-1} are attributed to B-N-B bending and B-N bending. Peaks at 2125 and 2362 cm^{-1} are ascribed to -CH and C-O bending, respectively. The functional peaks are clearly defined and unambiguous. Water absorption on the sample causes an in-plane band at 3000-3700 cm^{-1} , corresponding to B-O-H in-plane bending. The presence of oxygen is confirmed by the strong peak at 450-550 cm^{-1} corresponding to O-B-O bending vibration. Vibrations between 1100 and 1300 cm^{-1} in boron oxynitride indicate a transition from BO^{2-} to BO^- species [19, 20, 24]. The disappearance of B-N-O and shift of the B-O-B band after increased laser energy indicate that the B-O group Ascbinds to the surface of h-BNNs. A substantial change in peak positions of h-BN is a direct indication of the covalent bonding of deionised water molecules on the surface of h-BNNs. Stabilised h-BNNs have a band around 500-700 cm^{-1} , indicating O-B-O and B-N bond formation. This confirms the existence of surface oxygen vacancies on boron nitride. The electronic band structures of prepared nanoparticles are strongly influenced by these oxygen vacancies, which will be discussed in Sect. 3.5.

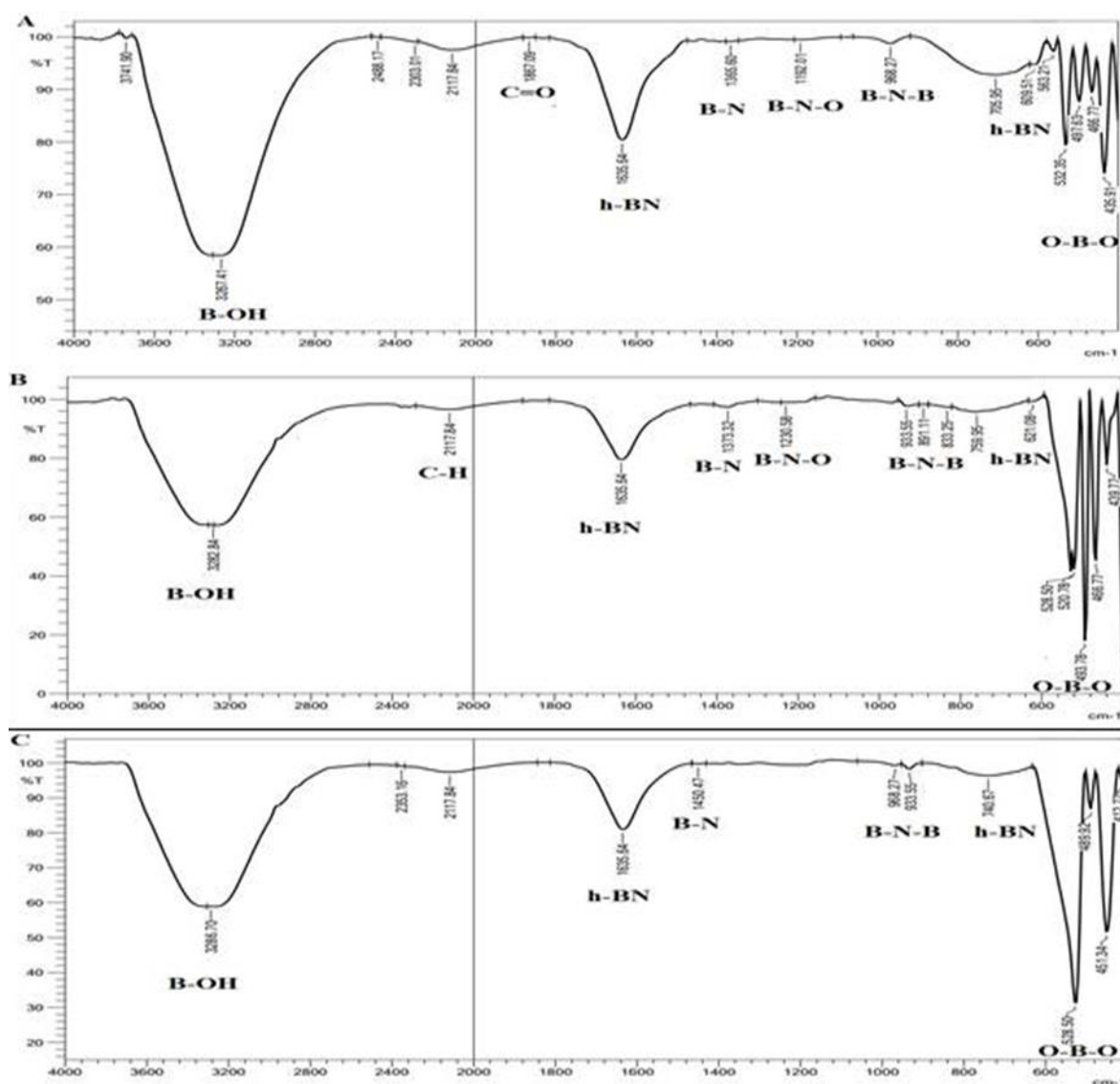


Figure 8: FTIR spectra of h-BNNs colloidal prepared by laser exfoliation by 1064 nm and different laser energy A) 10 mJ, B) 30 mJ, and C) 50 mJ.

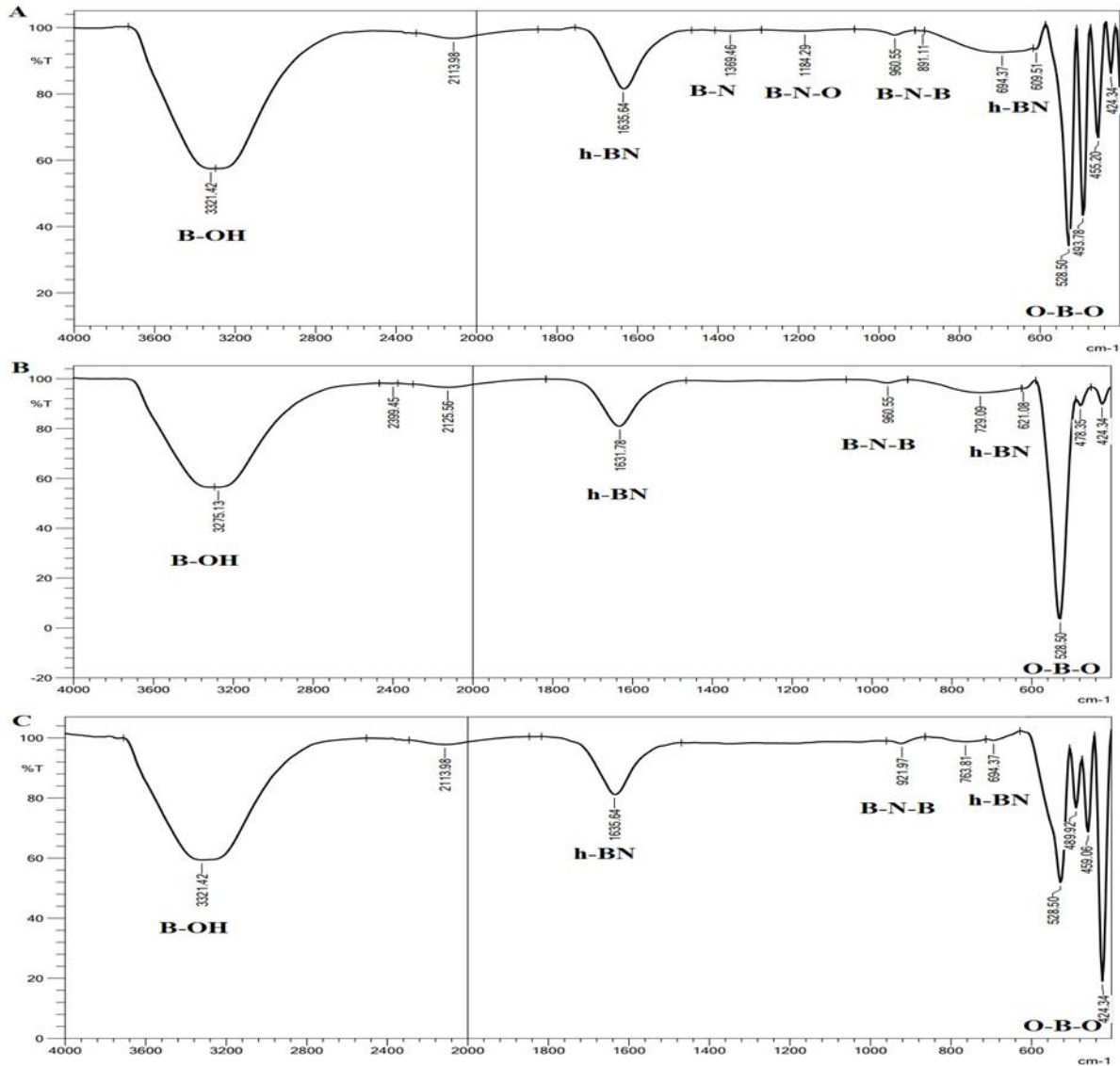


Figure 9: FTIR spectra of h-BNNs colloidal prepared by laser fragmentation by 532 nm and different laser energy A) 10 mJ, B) 30 mJ, and C) 50 mJ.

3.4 UV/Visible Analysis

Fig. 10 demonstrates how UV-visible absorption measurements were used to assess the optical properties of the h-BNNs before and after fragmentation in DDW. All absorption spectra appeared typical of h-BNNs, with consistent absorbance in the 200 to 500 nm range and a shoulder peak between 200 and 215 nm. Additionally, absorption peaks at 205, 207, 210, and 215 nm were observed, indicating the production of h-BNNs, which falls within the ultraviolet range. This absorption peak is a result of electronic transitions within the material. The extensive contact with the solvent and a slight hump at 277, 347, and 360 nm are believed to be caused by vacancy defects in the crystal structures of the nanoflakes and BNNTs synthesised [4]. The change in the size of h-BNNs, the impact of quantum confinement, size, and the synthesis of BNNTs are all responsible for the minor shift of the observed shoulder peak. Optical absorption between 390 and 500 nm is absent in the electromagnetic spectrum for h-BNNs. Nevertheless, they exhibit an absorption peak in the ultraviolet range (203-360 nm) [25, 26]. This unique characteristic makes h-BNNs, including nanotubes and nanosheets, an excellent choice for producing transparent films that effectively block ultraviolet radiation. The optical energy gap was determined using Tauc's relationship [27-30]. $\alpha h\nu = (h\nu - E_g)^{1/2}$, $r = 1/2$ (direct allowed transition)

$$(\alpha h\nu)^2 = (h\nu - E_g) \quad (2)$$

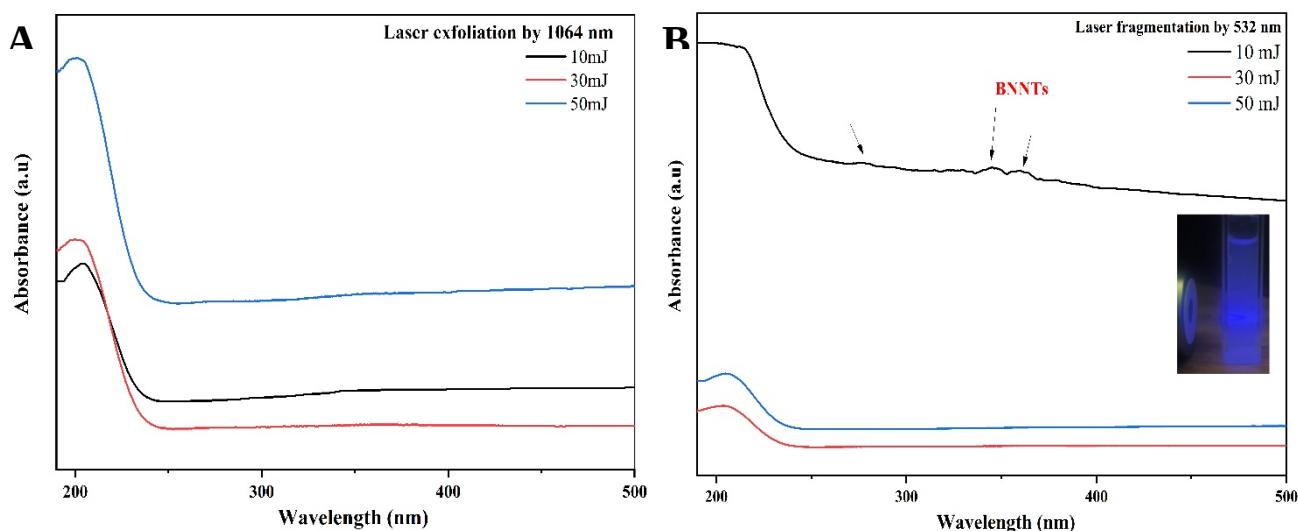


Figure 10: Optical characteristics of UV-visible absorption spectra of h-BNNs samples, prepared by A) laser exfoliation, B) laser fragmentation in liquid with different laser energy.

Fig. 11 and 12 illustrate the plot of the rising edge of the energy dispersion curve against $(\alpha E)^2$ vs E , enabling extrapolation to the energy axis. The value of E that corresponds to $(\alpha E)^2$ when it reaches 0 represents the optical band gap energy, E_g . The energy gap of a colloidal solution prepared by 1064 nm increases from 4.8 to 5.1 eV, while the energy gap of a colloidal solution prepared by 532 nm increases from 4.4 to 5 eV. However, an increase in the quantity of nanostructures in the colloidal solution corresponds to a rise in the energy gap, as confirmed by SEM investigations [27-33]. H-BNNs are typically white and become transparent due to their large band gap [23, 32, 34]. When examining the absorption spectra, it is important to note that the produced h-BNNs exhibit an absorption edge in the UV range. Furthermore, an increase in laser fluence leads to a blue shift in the absorption edge of the resulting products. This indicates that particle size reduction causes quantum confinement as laser fluence increases, leading to an increased energy band gap. The quantum confinement effect confines electrons and holes at a nanoscale level, bringing them closer together and making the coulombic interaction between them negligible. As a result, there is higher kinetic energy and an increase in the energy difference between filled and empty states, ultimately widening the semiconductor's band gap [35].

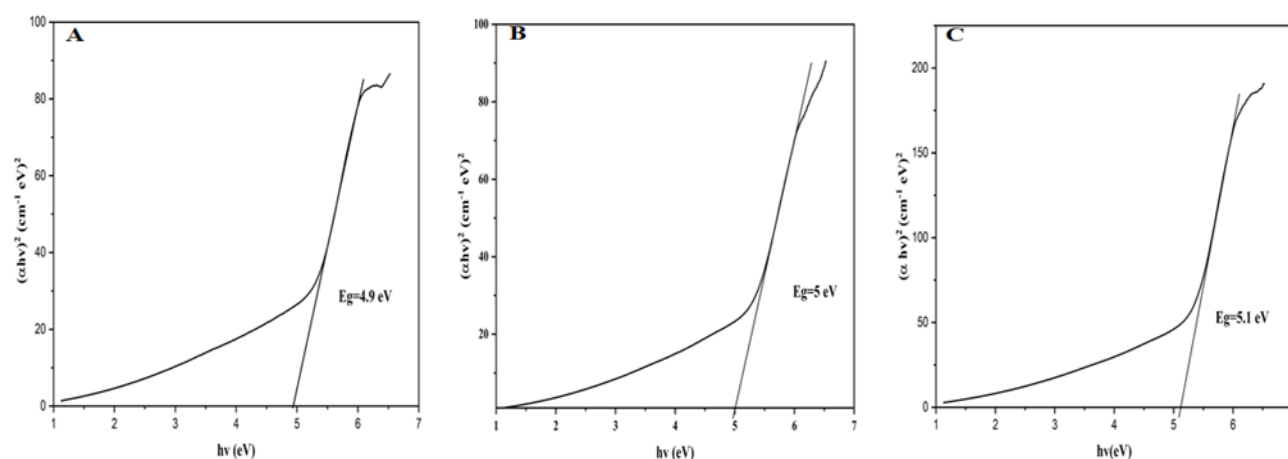


Figure 11: Optical the band gap of h-BNNs colloidal prepared by laser exfoliation by 1064 nm and different laser energy A) 10mJ, B) 30 mJ, and C) 50mJ.

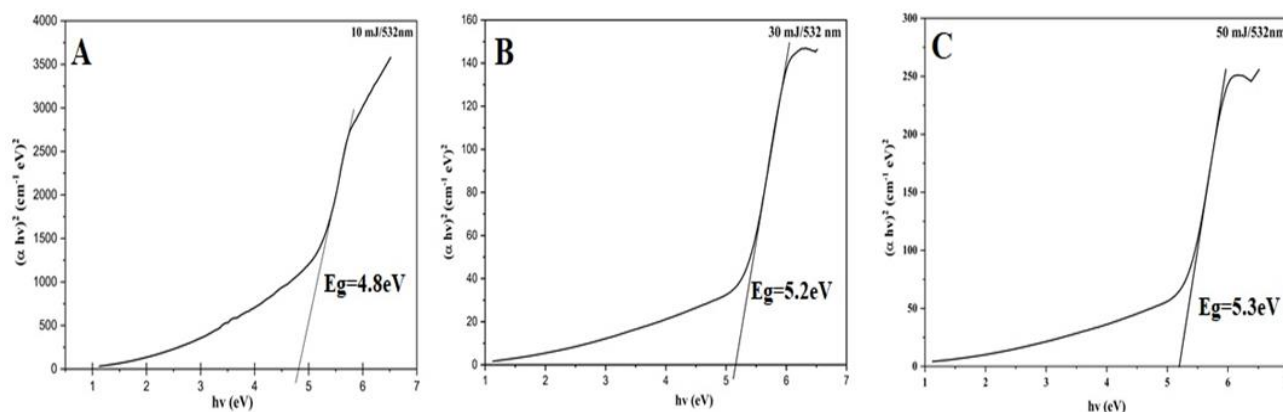


Figure 12: Optical the band gap of h- BNNs colloidal prepared by laser fragmentation by 532 nm and different laser energy A) 10mJ, B) 30 mJ, and C) 50.

3.5 Fluorescence Emission

When h-BNNs colloidal samples were created by laser exfoliation and fragmentation in DDW with two wavelengths and 10mJ, they were given an excitation wavelength of 220, 265, and 365 nm. This emission's reaction was measured in the 250–600 nm range. In Fig. 13, the observed UV emission in h-BNNs at 375 nm can be explained by its band gap of 4.8 eV, corresponding to deep ultraviolet wavelengths.

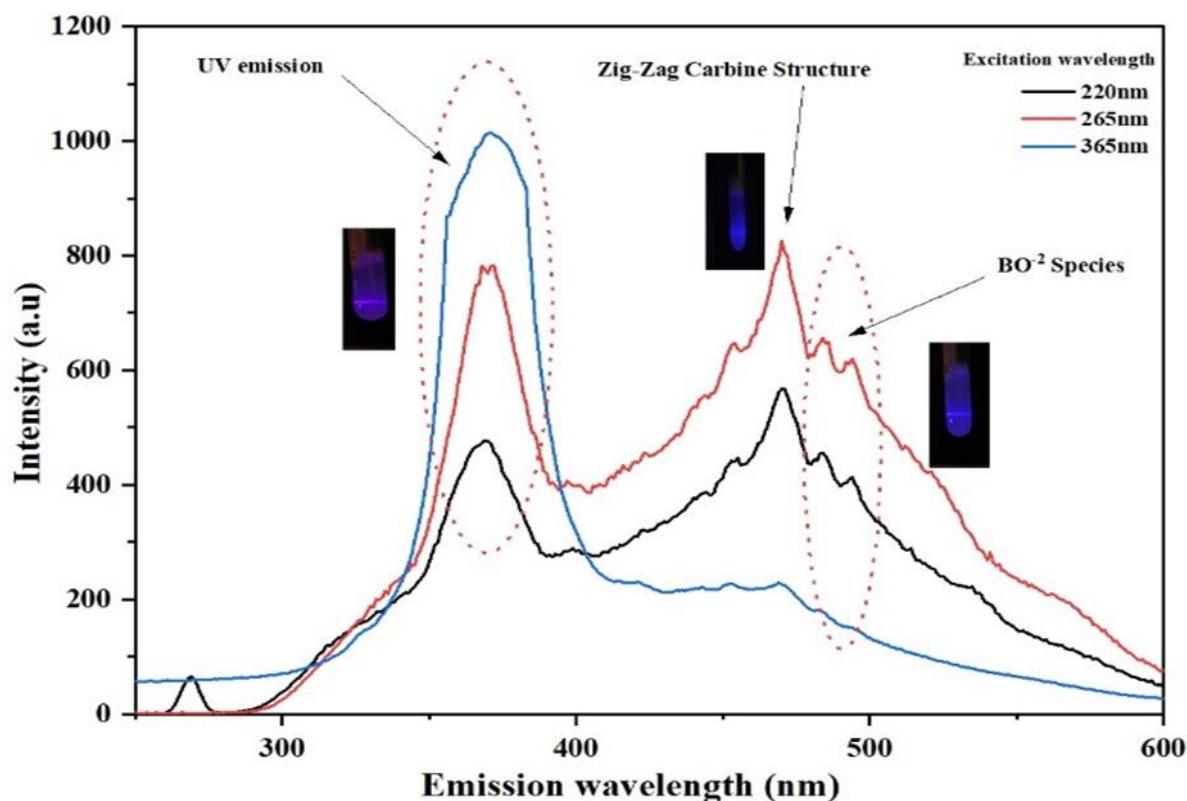


Figure 13: Fluorescence spectra of h-BNNs prepared by laser fragmentation in DDW with 532 nm and 10 mJ at an excitation of 220, 265, and 365 nm. In the inset, the luminescence of the sample is under UV light.

This emission is associated with excitonic transitions, where the Coulomb interaction binds together electron-hole pairs. When an electron is excited from the valence band to the conduction band, an exciton forms due to the generated hole. The recombination of these excitons produces photons, resulting in the observed UV emission. Additionally, UV emission can be influenced by quantum confinement effects. As the size of h-BNNs decreases,

the confinement of charge carriers causes the electronic states to become quantised. This quantum confinement alters the electronic band structure, leading to changes in energy levels and allowing for tunable UV emission. About 470–474 nm, a robust emission peak is observed from various excitation wavelengths, indicating the presence of Doping of the oxygen atom in h-BNNs. This emission peak was previously attributed to zigzag carbene structures that caused fluorescence behaviour in a white graphene-like system, resulting in quantum confinement. However, the presence of contaminants in the sample produces a hump at 485 nm, likely due to the small amount of BO₂ impurity confirmed by FTIR spectra. BO₂- species can release blue emission as an impurity in the h-BNNs structure. The nanoflake exhibits a dominant emission peak at 415 nm in the fluorescence spectra, resulting from the confinement of quantum states within the zigzag carbene structure. This emission is highly influential, as it signifies the transition from the highest occupied molecular orbital (HOMO) to the orbitals of the lowest occupied molecular orbital (LUMO). Similar to a carbene, Zigzag edges with a triplet ground state characterise this transition [36-39]. The electronic properties and photocatalytic characteristics of h-BN nanoparticles can be significantly altered by surface oxygen vacancies, resulting in modifications to their band gap. Based on our findings, it is evident that the exfoliation of Boron Nitride (BN) using laser and other methods involves unique processes and mechanisms, leading to variations in the properties and characteristics of the resulting BN nanomaterials. The disparities between laser exfoliation and other commonly used methods are summarised in Table 3.

Table 3: Comparison between exfoliation by laser exfoliation and fragmentation and other exfoliation method.

Exfoliation method	starting material	Time (hour)	Scalable parameters	Product size	Mechanism	Degree of Exfoliation	Ref.
Laser exfoliation and fragmentation in liquid (LEFL)	Powder suspension	>0.25h	Sonication time; solvent; laser energy; laser wavelength; pulse frequency; irradiation time; liquid volume;	Laser parameters can be finely tuned to control the size and thickness of the BN nanosheets produced.	Using a high-powered laser to ablate or vaporise a bulk BN material leads to the formation of a BN nanosheet or nanoparticles. The laser energy breaks the interatomic bonds within the BN structure, causing exfoliation into smaller layers.	Highly exfoliated BN nanosheets with fewer defects due to the localised energy input.	This work
Laser-assisted exfoliation	Crystal; powder suspension	<0.5 h	Solvent; laser energy; laser wavelength; pulse frequency; irradiation time; liquid volume;				[40]
Sonication	Powder suspension	>3 h	Solvent; sonication power; liquid volume; time		In mechanical exfoliation, bulk BN is mechanically sheared or peeled using adhesive tapes or other mechanical means to obtain thin layers or nanosheets.		[41]
Ball-milling	Powder; powder suspension	>10 h	Solvent; revolution speed; ball size; ball-filling ratio; volume; time	These methods may offer less precise control over the size and thickness of the BN nanosheets.		These methods may result in a wider range of exfoliation degrees, possibly increasing defects and impurities in the BN nanosheets.	[42]
Hydrothermal	Powder suspension	>1 h	Solvent; chemical species; temperature; liquid volume; time				[43]
Microwave-assisted	Powder suspension	<1 h	Solvent; microwave energy; microwave frequency; chemical species; liquid volume; time		Chemical exfoliation relies on chemical agents to break the interlayer bonding in bulk BN, forming BN nanosheets.		[44]
Direct electrochemical	Conductive crystal	<1 h	Solvent; chemical species; potential; temperature; liquid volume; time				[45]

4. Conclusions

In summary, we have developed a straightforward method for producing h-BNNs using nanosecond laser pulses and probe sonication-assisted exfoliation. Without surfactants, we successfully achieved exfoliation and fragmentation of bulk BN powder in DDW. This resulted in the generation of three distinct samples of h-BNNs. Our study primarily focused on investigating the effects of laser energy and wavelength on these nanomaterials' nanostructure, shape, and optical properties. The hexagonal structure of the nanoparticles was confirmed through X-ray diffraction (XRD) and selected area electron diffraction (SAED) tests, where the diffraction peak corresponding to pure h-BN was observed at 26.7° (002). The crystallite size was determined to be in the range of 11-18 nm.

Interestingly, we observed various nanostructures, including disk-like, spherical, rod-like, and sheet-like shapes, which could be attributed to variations in laser energy and wavelength during synthesis. Moreover, the optical band gap energy (E_g) was measured to be between 4.9-5.1 eV for samples synthesised using a 1064 nm laser and between 4.8-5.3 eV for samples synthesised using a 532 nm laser. Furthermore, the fluorescence spectra exhibited three distinct peaks at wavelengths of 375 nm, 470 nm, and 485 nm, indicating the presence of fluorescent emissions in the h-BNNs samples. Laser exfoliation of BN offers advantages in terms of precision and reduced defects but may have limitations in scalability and energy efficiency.

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Conflict of Interest

The authors declare that they have no conflict of interest.

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