

Spectroscopic Investigation on Liquid-exfoliated Hexagonal Boron Nitride Nano Particles

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ABSTRACT

Although hexagonal boron nitride and graphene in two-dimensional materials have similar structures, there are great differences in their electronic structures. hBN has a huge energy gap (~ 6 eV) and can be regarded as a semiconductor or insulator, while graphene can be used as a conductor because of its zero-energy gap. Because of their high degree of lattice matching, they often overlap each other and are used as conductive layer and insulating layer in the material process of electronic components. In this study, we tried to prepare nano-sized hexagonal boron nitride particles by a relatively simple method "liquid-assisted ball milling and ultrasonic exfoliating" to solve the high-cost problem of the industrialization of hBN. We prepared hBN nanoparticles using zirconium milling balls, water-proof sonication and ultrasonic crusher, then studied the essential changes to their electronic structures and sizes through Atomic Force Microscope and various spectroscopic methods such as PL, PLE, absorption and Raman spectrum. It helps us to find ways to control the electronic structure and energy gap of hBN, which would help the development of advanced semiconductor manufacturing applications and advanced quantum light sources.

Introduction

Background

In 2004, physicists Andre Geim and Konstantin Novoselov of Manchester University, England, used adhesive tape to peel off monolayer graphene from graphite and their special physical and electronic characteristics surprised the scientific community. Graphene is a planar two-dimensional material with hexagonal honeycomb structure composed of carbon atoms, and only has a single atom thickness. Its electronic band structure shows that Dirac points are formed at six corners, and its electronic transmission behavior shows that its resistivity is lower than that of good metal conductors such as silver and copper, and it has high electron mobility. Its excellent performance also brings about the research and development of different kinds of two-dimensional layered materials. Both of them won the Nobel Prize in Physics in 2010, and they also started a boom in research and application of graphene and two-dimensional materials.

Because the dimension of the material is limited to two dimensions and the thickness is limited to several nanometer scales, the surface properties of the material are quite different from those of bulk materials. Two-dimensional materials have special rigidity, flexibility, transparency, optical properties, thermal conductivity, mechanics and high carrier mobility. Because of their advantages of light weight, low energy consumption and miniaturization of components, they have great potential in electronics, optics, optoelectronics, electron spin, battery materials, quantum information and biomedicine. Two-dimensional materials push the application and development of nanotechnology to atomic level and widely penetrate into various fields of applied science and technology, which may bring revolutionary changes to science and technology industry.

Hexagonal Boron Nitride (hBN), which is similar to graphite structure, has attracted considerable attention in the past twenty years because of its photoelectric applications. It has been successfully proved to be a promising luminescent material for deep ultraviolet and single photon light sources [1,2]. HBN is a wide bandgap material (~6 eV) and bulk hBN is an indirect bandgap semiconductor with a bandgap of 5.955 eV [3]. Although the long-standing debate about the bandgap properties of hBN blocks has been resolved, the properties of unusually high light emission efficiency remain to be studied. Since its lattice coefficient is similar to graphene, the two-dimensional structure of hBN has attracted widespread interest. It has been successfully used to produce hBN films with wafer grade sizes using Chemical Vapor Deposition. Theoretical studies have shown that monolayer hBN has a direct band gap at the K-point and becomes an indirect band gap when it is not a monolayer.[4] In addition, due to the strong sonic auxiliary effect, even for indirect band gaps, it is predicted that high-efficiency ultraviolet light emission is expected.

Two-dimensional materials have high potential application value, which may bring great innovation to future industries, great revolution to various fields of science and technology, and influence the international competition mode of science and technology. Two-dimensional materials have not been widely used in domestic industry, because academic circles have limited mastery of manufacturing technologies suitable for industry. Academic research and industry must actively cooperate and invest in R&D and identify the research results suitable for the industry to take over in order to have the opportunity to further occupy resources.

Motivation

The main research direction of the professor in the past year was the glossy properties of graphene [5], and many data have also found that graphene has a wide range of potential applications due to its single-atom thickness, so there are many related properties that have been studied. Considering the similar structural properties of hexagonal boron nitride and graphene and the possibility of binding applications, it is intended to study the glossing and other properties of hexagonal boron nitride, as well as the influence of single-atom thickness characteristics on its properties, and how it can be applied in today's scientific and technological industries.

The energy gap of hexagonal boron nitride is very large, which can be bulk or semi-conductor, which is different from graphene in the application of semi-conductor field. Its conversion efficiency of light energy is higher than that of graphene, which can increase the application possibility of related products and improve the efficiency of existing products. However, due to the complexity and high cost of equipment processes such as chemistry, the threshold of hexagonal boron nitride has not yet been realized. This study believes that the transformation and optimization of equipment and the difference between the performance of the finished products and the previous situation are effective research directions to change this situation.

Research Purpose

After referring to many related literatures [6-8], it is found that most of the experiments to study nano-scale hexagonal boron nitride (hBN) choose to buy ready-made samples. This method is not only expensive, but also the quality of samples may change with different manufacturers, resulting in inaccurate data, which will affect the related research on the application of the experimental results. This study tries to find a more efficient and low-cost preparation method by combining ball grinding method with ultrasonic stripping method, and to explore whether hexagonal boron nitride samples with good quality can be prepared by this method, and to study that change of its optical characteristics.

Literature Discussion

Introduction of Different Preparation Methods of Hexagonal Boron Nitride [9]

In recent years, how to detach and function hBN has become the focus of attention and research by many scientists, who have also done a lot of research and experimentation in this area. With the requirements of environmental protection and energy conservation development, the traditional high-energy-consuming preparation method has gradually been eliminated by people, and the clean and low-energy consumption method has attracted the attention of researchers. At present, the more widely used preparation methods are divided into physical methods and chemical methods, physical methods include ball grinding method, ultrasonic decomposition method, plasmon engraving method, chemical method has CVD direct synthesis method, solvent thermal synthesis method, chemical extraction method and so on. This study refers to various methods to design the preparation process to be carried out.

Mechanical Stripping Method

It is commonly used to prepare low-layer or monolayer nanomaterials, through a physical action to strip the material layer by layer, and finally stripped of the resulting nano-level material. This method is highly respected because the experimental method is simple, easy to operate, and the technical requirements are low; However, in addition to the B-N covalent key, hexagonal boron nitride also contains the characteristics of ion bonds, resulting in the interaction between adjacent boron nitride layers and layers, which makes the extraction difficulty of hBN increase and also makes its modification face great challenges.

Chemical Vapor Deposition (CVD)

This method is the method of preparing hexagonal boron nitride nanoflakes, with the most complete sheet structure and the most uniform size distribution. The hexagonal boron nitride obtained by this method can be well controlled and the number of layers and the size and morphology are relatively uniform; However, the high process difficulty of the method, the experimental temperature, gas flow rate, environmental factors, etc. are all restricted, and the disadvantages of large raw material consumption and high cost make it difficult for this method to be mass-produced.

Chemical method

Among various preparation methods, this method is the most direct method to prepare hexagonal boron nitride, which is prepared by chemical reaction between boron-containing compounds and nitrogen-containing compounds. The number of layers of hexagonal boron nitride can be controlled by controlling the ratio of boron-containing chemicals to nitrogen-containing compounds and their reaction conditions. Compared with other methods, this method is also difficult for mass production.

Solvothermal Synthesis Method

Usually, a solvent is used as a reaction medium, so that insoluble substances are dissolved in the solvent through high-pressure and high-temperature reaction; However, the purity of hexagonal boron nitride obtained by this method is not high, impurities are excessive, and it is not easy to remove. It has the advantages of simple operation, few uncontrollable factors and large-scale production.

Ultrasonic method

At present, ultrasound is divided into ordinary liquid ultrasound method and mixing ultrasound method. Liquid ultrasonic power is low, the reaction is mild, there is no restriction on the solvent, and can be used on a large scale, the obtained hexagonal boron nitride nanosheet, the sheet layer is complete, the defect is less, and it is regarded as the best method by the scientific research community; However, the number of nanosheet layers obtained is larger, and

the ultrasound time is longer. Mixing ultrasound is also known as pulverized ultrasound, the use of stronger ultrasound to strip away the hexagonal boron nitride, the method can obtain a thin layer of nanosheets, can also make the hexagonal boron nitride is functionalized, the disadvantage is easy to introduce impurities, the resulting nano sheet is less complete, and should not use organic solvents. It is more appropriate to use water as a solvent to prevent pollution of the environment.

Ball Grinding Method

This method is a new method in recent years and has been favored by the majority of researchers. This method is most likely to functionalize hexagonal boron nitride and obtain a thinner layer of nanosheets. It is through a physical action of the hexagonal boron nitride layer by layer stripping, this method is simple and easy to operate, and has low requirements for the environment. The hexagonal boron nitride is placed in a sealed ball grinding tank and inert gas can be introduced for protection. The number of layers of nanosheets can be controlled by adjusting the ball grinding time.

Spectral Results of Previous Laboratory Studies on Monolayer, Multilayer and Block Material hBN [10]

Refer to the spectroscopic measurement results of hexagonal boron nitride prepared by the relevant research.

Photoluminescence Measurement Results

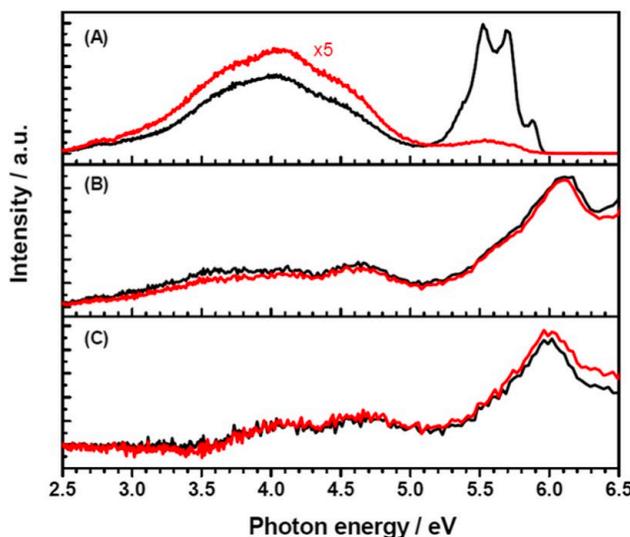


Fig. 1. Photoluminescence (PL) spectra of (A) bulk hBN powder, (B) monolayer hBN/MgF₂, and (C) multilayer hBN/MgF₂ excited at 180 nm at 10 (black) and 298 (red) K. The block hBN powder peaked at about 5.5 eV and 5.7 eV, while the monolayer hBN and multilayer hBN peaked at about 6.1 eV and 6.0 eV, respectively.

Photoluminescence Excitation Measurement Results

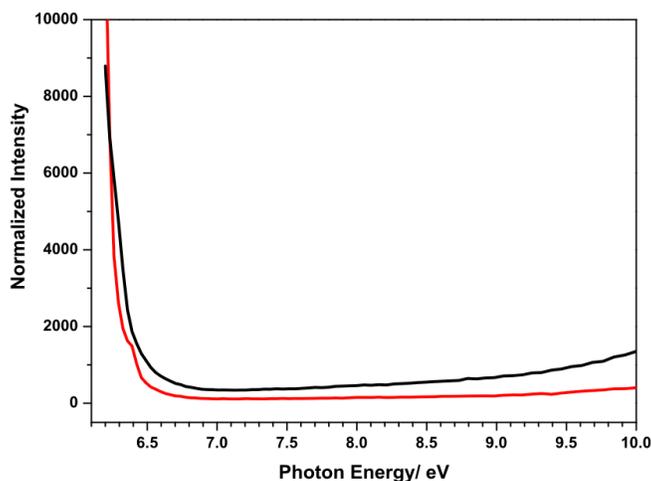


Fig. 2. PLE spectra of monolayer hBN (red) and multilayer (black) hBN recorded at 10 K. Both monolayer and multilayer hBN films show a high degree of coincidence between the emission wavelength position and the effective excitation wavelength position, which further shows that both monolayer and multilayer hBN films have quite high quantum luminous efficiency.

Measurement Results of Absorption Spectrum

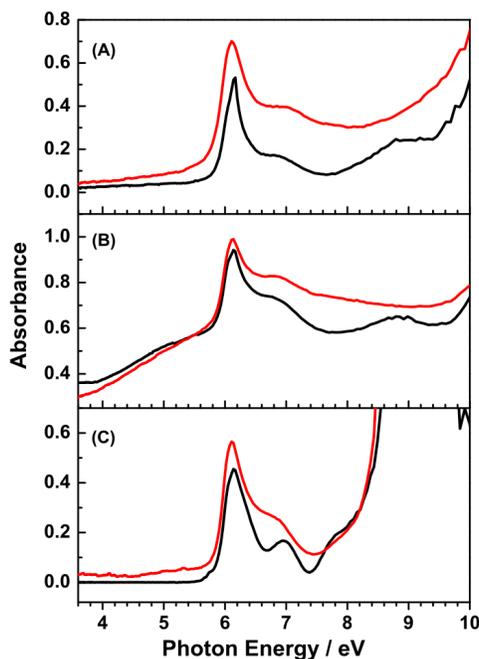


Fig. 3. Absorption spectra of monolayer (black) and multilayer (red) hBN on (A) MgF₂, (B) LiF, and (C) quartz substrates at 10 K. The absorption spectrum measurement results show that there is an absorption peak at about 6.1 eV and an absorption shoulder belt at 6.8 eV on magnesium fluoride, lithium fluoride or quartz substrates. The comparison of the data shows that the influence of different substrates on the electronic structure of hBN near the energy gap is negligible.

Measurement Results of Atomic Force Microscope

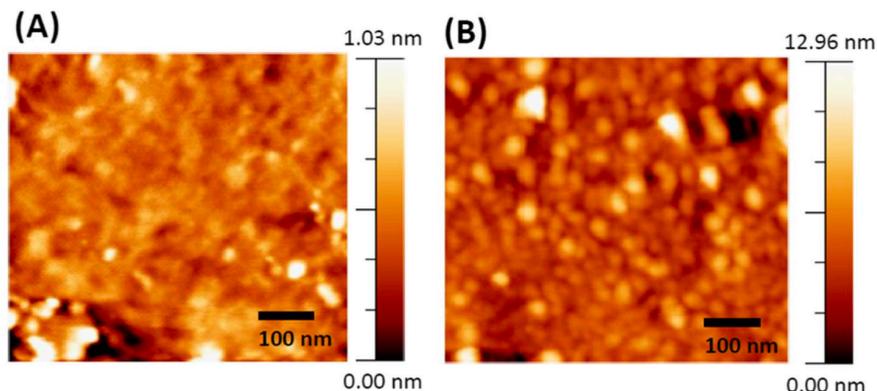


Fig. 4. AFM images of the (A) monolayer hBN and (B) multilayer hBN samples. The thickness of a monolayer sample is 1.03 nm, which is much smaller than the thickness of 12.96 nm for a multilayer sample. Observations can be observed that the color of the monolayer hexagonal boron nitride is lighter, that is, the surface is smoother; In contrast, multilayer hBN ground is darker in color and has a rougher surface.

Raman Spectrum Measurement Results

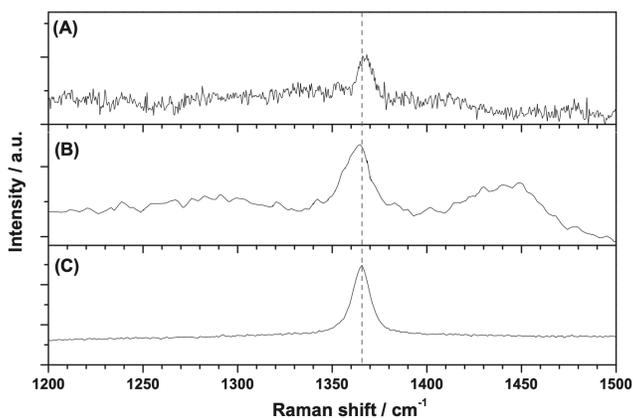


Fig. 5. Raman spectra of (A) monolayer hBN/SiO₂, (B) multilayer hBN/SiO₂, and (C) bulk hBN powder at 298 K. The Raman shift peak is about 1365 cm⁻¹. It can be seen that the number of layers and morphology of hBN have no great influence on Raman shift, only the spectral line intensity increases obviously.

Method

Using synchrotron radiation for spectral research

The Use and Status of Spectrum

In this study, hexagonal boron nitride was prepared in a simple way, and its luminescent properties were studied, that is, the spectrum analysis. Because the energy gap of a material determines its luminescent properties, we can measure the energy gap by measuring, observing and analyzing the spectrum.

Because the energy band and optical properties of the material can be seen from the spectrum, we can confirm the application range of the material by measuring the spectrum, for example, what wavelength range can hexagonal boron nitride be used as a luminescent material. If the material with this luminous range is needed in engineering, hexagonal boron nitride can be selected as the material by the research results of spectrum.

Principle of Energy Gap

After the establishment of quantum mechanics in the early 20th century, the energy level theory was developed and widely used in the microscopic world of matter. The energy levels of atoms and molecules are discontinuous, and when the two energy levels transition, only the energy of the energy difference between the two energy levels associated with this transition can be absorbed or released. When solid is considered, it is composed of a large number of atoms, and the density of energy levels increases, which makes the distribution of energy levels change from discontinuous to continuous, but discontinuous conditions can also be observed for non-conductive materials. The observed results do not correspond to one energy level, but to multiple "energy bands", that is, the energy of electrons can be distributed in a range.

The energy difference between energy bands is called Energy gap or Bandgap, and the electrons between energy gaps cannot exist stably, so the region is called Forbidden band. In the atomic model, the valence electrons in the outer layer usually have higher energy than those in the other inner layers, and they are also the easiest to break away from the atomic bonds. Inside the solid, the valence electrons provided by each atom will form the energy band with the highest energy when the absolute temperature is zero, which is called the Valence band. If an electron in a valence band gets more energy than the energy gap, it has the opportunity to jump to the Conduction band with higher energy. The electrons in the conduction band have enough energy to move freely inside the solid without being bound by atoms, which also makes the solid conductive. When an electron transitions to the conduction band, it will leave a "hole" in the valence band. The hole can move freely between atoms, so it also has the function of conducting electricity.

In this experiment, the correlative literature found that changing the thickness of the material affects the energy gap, which in turn changes the wavelength of the excitation light. The same material, the thicker the material, the stronger the excitation light intensity due to the greater the number of photons absorbed; Different materials, their energy gaps are different, the energy of the excitation light is also different, so the wavelength is also different.

The particularity of synchronous radiation light source

Synchronous radiation light sources can provide a wide range of electromagnetic waves (light) covering an infrared to X-ray range compared to other light sources. Through the specific design of the beam line to provide a specific range of photonic energy for researchers to use. General commercial instruments for spectral measurement often to laser light source or xenon lamp as the light source, although the laser can provide high power narrow frequency single wavelength laser light output, but the spectrum scanning range is not as good as the synchronous radiation light source can adjust the photon energy range of a large number of times. In addition, synchronously radiated light can provide shorter wavelengths (high energy) of photons ($\lambda < 200$, nm), which is difficult for other light sources to achieve. Because high-energy photons are absorbed by nitrogen and oxygen molecules in the atmosphere, scientists are difficult

to experiment with light sources in this band in the atmosphere, so they must operate under vacuum. Therefore, synchronous radiation light accelerators including beam lines and related experimental stations must be maintained under ultra-high vacuum when operating. In addition, since the synchronous radiation light source is a broadband light source, after selecting the wavelength through a single optical instrument, it is still necessary to place a specific filter to avoid damage to the test sample caused by the glare of the high harmonic term.

In general, the advantages of synchronous radiation light sources over other light sources are: they can provide a wide range of photon energy for use, provide high-intensity vacuum ultraviolet and X-rays, and have the characteristics of small spot and high degree of homology, so that many cutting-edge advanced experiments can only be carried out with synchronous radiation light, which is the unique value of synchronous radiation light sources.

Preparation of hexagonal boron nitride

Transfer the CVD monolayer hBN humidity to a transparent optical substrate

Experimental equipment and samples: boron nitride sample, CaF₂ substrate, Quartz (SiO₂) substrate, Acetone, de-ionized water, Needles Tubing. Wet the cotton sheet under the boron nitride sample with a syringe and wait for the sample to float from the cotton sheet. After floating, take off the sample and soak it in deionized water to wait for two hours. Pick up the sample with the substrate. This step has special skills and is quite difficult. Both hands should hold tweezers to help each other in order to avoid bubbles and wrinkles during fishing, and try to keep the sample in the center of the substrate. After picking up, mark the sample position with a strange pen. As moisture on the sample must be avoided during measurement, put the sample in the oven for about 30 minutes and adjust the temperature to about 70 degrees. After drying, the polymethyl methacrylate (PMMA) is stripped from the sample with acetone. (In order to protect the new sample itself, there is another layer of PMMA on the sample, so after fixing the sample, remove PMMA with acetone). Dry again for about 10 minutes, then put it in the storage box and mark the relevant information of the sample.

Ball Grinding and Ultrasonic Stripping to prepare hBN nanoparticles

Because samples with different parameters have been made, the following experimental materials and steps are taken as examples of the main samples successfully measured by spectrum.

Experimental equipment and samples: hexagonal boron nitride powder purchased from Sigma-Aldrich, with a particle size about 1 μm , Isopropanol (IPA) is purchased from Honeywell (Honeywell 17829, Ball mill, Ultrasonic wave processor, Ultrasonic crusher (750 W), Centrifuge, Base MgF₂ (1 inch round, 2 mm thick), Ball Grinding (zirconium), Ball Grinding tank. Take 150 g of ball mill balls with diameter of 3 mm and 5 mm and put them in a ball mill tank, then take 0.1 g of original hexagonal boron nitride powder and 30 mL of isopropyl alcohol, mix them and put them in a ball mill tank. Place the ball grinding tank on the ball mill and grind the ball at 582 rpm for 3 hours.

Ultrasonically treat the sample for 30 minutes. Tap water must be poured to make the water level higher than the liquid level of the ultrasonic treatment object. Treat the mixture with an ultrasonic crusher for 10 minutes, then centrifuge at 8000 rpm for 10 minutes. Take out the centrifuged upper layer mixture with a dropper, drop it on the substrate, and dry it automatically. If only one drop of the centrifuged mixture is dropped on the substrate, it is difficult to measure its spectrum, but its thickness can be measured by atomic microscope. After this study, the mixture of 10 drops, 20 drops and 30 drops were dropped on the substrate to measure its spectrum.

Measurement of photoluminescence spectrum, fluorescence excitation spectrum and absorption spectrum

The Principle of Photoluminescence (PL)

Photoluminescence can be divided into fluorescence and phosphorescence according to delay time. Photoluminescence (PL) can detect the optical properties, energy level structure and carrier transition behavior of materials in a non-destructive way. By analyzing the photoluminescence data, we can know the important information such as the type of doped impurities, the size of energy gap, the composition of compounds, or the size, carrier transmission path and life cycle of nano-quantum dots in nanomaterials. The analysis of photoluminescence (PL) spectrum can be used to study the inner layer interface of heterostructure, which is very difficult for general physical or electrical measurement methods, and the results of PL can be used as the basis for judging the structure, composition and quality of materials, which is a key measurement technology in the development of materials.

Luminescence is a phenomenon that the physical system produces electromagnetic radiation due to excessive thermal radiation or white-hot. For luminescent materials, when the energy of the incident photon equals or exceeds the energy gap, valence band electrons will be excited to cross the energy gap and reach the conduction band. Then, when the semiconductor returns from the excited state to the ground state, radiation will be generated. These phenomena can effectively reflect the phenomenon of energy bands or impurities in semiconductors.

The luminescence process typically includes three steps: (1) electron excitation, (2) thermal balance through phonons, and (3) recombination of electron holes to emit energy in the form of light. Electron-hole pairs generated by incident light will recombine after heat balance distribution and then generate photons. Impurities and defects will form various energy levels in the energy gap and the corresponding energy will be radiated by the radiative recombination process or absorbed by the non-radiative recombination process.

Fluorescence involves a system excited by electromagnetic radiation, which belongs to optical luminescence technology. When the incident light (electromagnetic radiation) shines on the specimen, the electrons are raised to the excited state, which is a typical energy band transition process. When an excited electron returns to its initial energy state, a photon will be produced, and several phonons may be excited at the same time. When continuous wave light excites fluorescence, luminescence can be regarded as a steady-state phenomenon, and the influence of excitation source will lead to continuous luminescence of samples. Generally speaking, the material's Absorption of incident light wavelength is related to the wavelength of effective Photoluminescence Excitation (PLE).

When electrons are released to a lower energy state (recombination), there are different processes, which can be divided into radiation processes (such as photoluminescence) and non-radiation processes (phonon emission, defect trapping, Auger effect). Before luminescence, the higher the energy of excited photons, the more excited phonons. However, if the excitation energy is less than the energy difference between the ground state and the first excited state, the luminescence phenomenon may not be seen, and the energy will be dissipated in the form of thermal energy. The reason is that the process of material absorbing light can be regarded as the transition of electrons from valence band to conduction band, while the radiation process is that electrons move from the lowest point of energy in conduction band to the highest point of valence band. The free carriers associated with conduction band and valence band are electrons and holes, while photoluminescence can be regarded as the radiation recombination of conduction band electrons and valence holes in semiconductors.

The process of light emission after the material is excited is as follows: after electrons in valence band absorb photons, they are excited into conduction band. The excited photons may be radiated by phonons, releasing some energy to the lower energy state in the conduction band. After the electrons in the conduction band are released back to the valence band, photons are released.

Principle of absorption spectrum

Photoluminescence excitation (PLE) spectrum is usually matched with photoluminescence spectrum. The photoluminescence spectrum is the energy gap in the semiconductor, or the characteristic band emitted by the recombination process. The excitation spectrum is the spectral analysis of the effective excitation wavelength for a specific band energy of the photoluminescence spectrum. By measuring the fluorescence excitation spectrum, the excited state related to the luminescence band can be detected and the transition route can be determined.

During the measurement of fluorescence spectrum, the specific emitted light energy is detected, and the excitation light energy is modulated, which is similar to the measurement method of absorption spectrum. If the emission band of a sample is at 500 nm, the fluorescence excitation spectrum measurement can obtain the absorption light intensity when it emits a specific wavelength, while the absorption spectrum measurement can obtain all the absorption bands of the sample in this emission band.

Before the measurement, the light with a specific wavelength is usually separated by a single light meter, and the PL is measured and analyzed, and then the PL is measured for its peak value. In the process, the incident white light can be split by scanning monochromator.

Principle of absorption spectrum

The absorption spectrum is to calculate the amount of incident radiation absorbed by the substance in a certain frequency range in the process of the substance to be measured ascending to the excited state, which is mainly determined by the molecular structure of the substance. Absorption occurs in the conversion between two quantum states, and if the frequency of radiation matches the energy difference between the two quantum states of a molecule, it is easier to be absorbed.

A spectrum usually consists of many spectral lines, which are drawn by the transition frequency and absorption intensity of absorbed photons. The frequency and relative intensity of the spectral line depend on the electronic and molecular structure of the sample. The frequency is also affected by the interaction between the molecules of the sample, the phase state, and various environmental factors, such as temperature, pressure, electromagnetic field, etc.

In the absorption spectrum, the function value corresponding to each wavelength is the absorbance of light. When a beam of light irradiates a sample, part of the light will be absorbed by the sample, while the rest will pass through the sample. Let the incident ray intensity I_0 of the original light be I , then the transmittance T (Transmittance) of the light is I/I_0 , and the absorbance A is $A = -\log(T) = -\log(I/I_0)$. The absorbance A is a real number greater than or equal to zero, which generally falls between 0 and 2. When the absorbance is 0, it means no absorption at all, and when it is 2, it means that 99% of the light is absorbed when it passes through.

By measuring and analyzing the absorption spectrum of a substance, we can use its specificity to distinguish one substance from other substances in the mixture or confirm unknown samples and check whether there is some special substance in the samples. In addition, the absorption spectrum can also quantitatively reflect the quantity of substances, measure the absorption coefficient of substances, etc., and has a wide range of applications.

Overview of beam line and experimental station setting

The synchrotron light source at the front end emits synchrotron radiation, which is guided and split by the High Flux beam line and then irradiated on the sample, and then detected and data collected by instruments such as the back end experimental station. There are two layers of slit at the exit of HF, which control the incident light intensity, all of which are manually adjusted; There is a diffraction grating between them to split the light, which can be controlled by a computer.

There are detection systems on the side and right back of the cavity where the sample is placed, which can measure the photoluminescence spectrum and absorption spectrum respectively. When measuring the fluorescence excitation spectrum, the light emitted from the sample is split by a single light meter IHR320, and then amplified by a photomultiplier and converted into a current signal, which is detected by a photon counter and transmitted to a computer. When measuring the absorption spectrum, it is only detected by the photomultiplier tube, and the value is

transmitted to the computer. The monochromator and photomultiplier tube are covered with black cloth to prevent indoor light from entering the instrument and affecting the experimental results.

In the measurement of absorption spectrum, sodium salicylate is placed between the photomultiplier tube and the sample because the detection range of the photomultiplier tube is limited to the light with wavelength longer than 200 nm. After sodium salicylate absorbs ultraviolet light, it can emit the sensitive visible light of the photomultiplier tube, and indirectly detect the light with the wavelength shorter than 200 nm. In addition, adjusting the lens can focus the divergent light at the slit to increase the light collection efficiency and enhance the signal collection.

When measuring the fluorite excitation spectrum, because the detection object is the emission of the sample after the excitation, its intensity is weaker than when directly measuring the excitation light source, so the gainer of the photomultiplier tube needs to provide a larger voltage. When measuring the fluorite excitation spectrum, the voltage provided by the regulator of the photomultiplier tube is 1700 volts; When measuring the absorption spectrum, it is 880 volts.

Light and Slit Settings

There are two slits and a light kit at the light source, which is the first spectroscopic mechanism for spectring the synchronous radiation light source; After the sample, there is an instrument iHR320, which contains a slit, a gloss and a mirror to speciate and collect the light emitted by the sample.

When measuring the fluff spectrum of light excitation, the size of the two narrow stitches at the light source is set to 300 microns and 5000 microns, and the light between the two uses 450 grooves/mm for the spectroscopy of the synchronous radiation source in the 110~350 nm region; When measuring the fluorite spectrum, the two crops at the light source are set to be 300 microns and 1000 microns.

When performing PL spectroscopy, the slit of iHR320 is set to be smaller due to the desire to measure the spectroscopy; When performing PLE spectroscopy, the slit at High Flux is set. This practice is to improve the resolution of the wavelength of the excitation light.

Filter and sample chamber settings

A filter is set up in front of the sample to block high-energy (high-harmonization) photons to avoid damage caused by high-energy photon irradiation and avoid the measurement effect caused by multiple-frequency light. Depending on the range of wavelengths that can be measured by the substance, decide on the type of filter to use. This experiment sets up a CaF₂ filter to filter out light with a wavelength below 125 nm.

Screw the sample on the sample holder and fix the sample holder in the vacuum chamber. Record the coordinates of the sample for adjustment in the experiment. Then adjust the sample angle. When measuring the excitation fluorescence spectrum, it is necessary to set the sample facing direction to form an angle of 45 degrees with the incident light of synchrotron radiation and the right PMT; When measuring the absorption spectrum, the sample must be set to face the incident light of synchrotron radiation.

It is necessary to set the sample surface direction at an angle of 45 degrees with the incident light and PMT in order to measure the excitation light. The method is: adjust the second slit of HF to 200 microns and make the beam line emit visible light. The angle of the sample can be confirmed by using the angle observation hole on the wall of the chamber, which is 45 degrees with the incident light. If the light directly enters the observation hole after reflection, it means that the angle of the sample at that time is 22.5 degrees. You can adjust the sample to an angle of about 45 degrees by using the principle of incidence and reflection angle and dial scale.

After the sample is set, perform vacuum extraction and reduce the air pressure to 10⁻⁷ torr. In addition, depending on the experimental requirements, the low-temperature system can be started to cool the sample, and the spectrum of the sample at low temperature can be measured.

Signal confirmation

Adjust the focusing mirror in front of iHR320 monochromator and adjust the focusing mirror to the position with the strongest signal by two adjustment buttons: up and down, left and right coordinates. After confirming that the slit and grating values at HF light source are correct, the measurement can be started.

Operation steps

When the fluorescence spectrum is excited by measuring light, the wavelength of incident light is fixed, and the intensity of each wavelength of luminescence is detected; When measuring fluorescence excitation spectrum or absorption spectrum, change the wavelength of scanning excitation light and detect the fixed emission wavelength position.

Measuring substrate: before measuring the fluorescence excitation spectrum and absorption spectrum, since the sample must be placed on the substrate, the absorption and emission spectrum of the substrate itself must be measured separately and compared with the spectrum of the sample to distinguish the spectral characteristics of the sample and the substrate.

Measuring samples by computer control: in this experiment, we will measure the spectra of samples at 300 K and 10 K respectively. After setting the measurement mode and wavelength range by computer, we will measure the photoluminescence spectrum, fluorescence excitation spectrum and absorption spectrum of three samples placed on the substrate.

Data Correction and Processing: the measured data are plotted as an atlas and analyzed. Because diffraction grating and PMT have different current signal conversion efficiencies for different wavelengths of light, after obtaining the measurement results (i.e., the graph of light intensity versus wavelength), all light intensity values must be divided by the instrument efficiency function (i.e., the graph of conversion efficiency versus wavelength) in order to avoid the influence of instrument efficiency on the experimental results and obtain the real measurement results. The measurement results show a sharp upward trend at the maximum and minimum wavelengths, which is due to the response function of the instrument itself.

Fine Adjustment of Sample Angle: in the experiment, reflecting light spectrum is used to capture and emit light. In this way, besides receiving the light from the sample, the stray light from the synchrotron radiation source itself will also be collected. Therefore, the sample is deflected several degrees in the direction of the incident light to adjust the angle to screen out the stray light. According to the past measurement experience, the angle between the sample plane and the incident light clip ($45^\circ \pm 8^\circ$) can properly suppress the scattered stray light and obtain an acceptable signal strength.

Atomic force microscope measurement

Overview of Atomic Force Microscope

Atomic Force Microscope (AFM) is one of the representative instruments of Scanning Probe Microscope. AFM is widely used to explore the measurement of physical properties at micro-scale, which is directly beneficial to the development of nanotechnology. Its atomic resolution ability can be applied to the surface detection of various materials, and it can operate in vacuum, gas or liquid environment. At present, it has a wide range of applications, including surface topography measurement, roughness analysis and biomedical sample detection.

When the spatial resolution to be detected is on the order of nanometer scale, the optical microscope can't meet this requirement, because the wavelength of the detection light to be achieved must be at least twice as short as the resolution, that is, visible light is used as the detection wavelength, and the maximum spatial optical resolution is

only 200 nm. When detecting nanomaterials, if the size of the material is less than 200 nm, the optical microscope cannot be directly used as a detection tool, so other properties of the material should be used to understand its characteristics. Atomic force microscope (AFM) can be used to measure the microscopic physical properties of nanometer scale, which can effectively solve this problem.

Atomic microscope consists of probe, offset detector, scanner, feedback circuit and computer control system. Generally, the probe consists of a cantilever beam composed of Si or Si₃N₄ (silicon nitride) and a needle tip, and the diameter of the needle tip is between 20 and 100 nm. Piezoelectric ceramic scanner has the ability of vertical fine tuning and feedback circuit, so that the interaction between the probe and the sample remains fixed during scanning.

Measurement principle of atomic force microscope

Interaction between needle tip and sample: van der Waals force and electronic Coulomb force. Based on the relationship between the distance between the needle tip and the test piece and the force between them, the probe cantilever beam generates a fine displacement to measure the surface structure, and the most commonly used way to detect the distance change is beam deflection technology.

Deflection of light: the purpose is to measure the probe offset. The Light is emitted by the diode laser and focused on the back of the tip of the crossbar (coated with a metal film with high reflectivity, usually gold), and the laser light is reflected to a highly sensitive position detector.

Recording images: the computer controls the X-axis and Y-axis drivers to scan the sample, while the probe will shift up and down, and the differential signal will change accordingly. The feedback circuit controls the Z-axis driver to adjust the distance between the probe and the sample. The distance is fine-tuned, or other signals are sent to the computer, and recorded as a function of X-axis and Y-axis, which is AFM image.

Force and probe: the probe is composed of a needle tip attached to the front end of a cross bar. When the probe tip contacts the sample surface, because the elastic coefficient of the cross bar is equivalent to the acting force between atoms, the acting force between the atoms at the probe tip and the atoms on the sample surface will make the cross bar move in the vertical force direction. The force sources include the coulomb repulsion between the Van der Waals force Tsutomu force of the probe and the surface and the outer electrons of the probe and the surface.

Classification of atomic force microscope

Contact AFM: as the earliest developed operation mode, the force between the probe and the sample is the repulsive force between atoms. Because repulsive force is very sensitive to distance, contact AFM is easy to obtain images with atomic resolution. When the probe with cantilever touches and lightly presses the surface, the reaction force deflects the cantilever of the probe, and the deflection represents the reaction force. When scanning the surface, a three-dimensional surface structure is drawn by maintaining the same deflection. The disadvantage of contact scanning is that it is easy to damage samples, especially soft materials.

Non-contact AFM: to solve the problem that contact AFM may damage the sample, the long-distance attraction between atoms is used to operate by van der Waals force. When AFM operates in the atmosphere, a layer of water is often adsorbed on the surface of the specimen. Therefore, when discussing the interaction between the probe and the specimen, the phenomenon of capillary holes between the probe and the water film on the surface of the specimen must be considered. Non-contact operation in vacuum environment, its resolution can reach atomic level, which is the best operation mode in AFM.

Intermittent Contact (tapping) AFM: the principle of improving the non-contact type is to make the distance between the probe and the sample closer, increase the amplitude, and make the probe contact the sample when oscillating to the trough. The fluctuation of the surface of the sample causes the amplitude change and a high-resolution image can be obtained by using a similar non-contact feedback control method.

Operation steps

Electronic Signal Confirmation: turn on and off the machine once every time. Insert the opaque card, check the values and continue to see if they meet the requirements.

Laser calibration: the laser is irradiated on the cantilever. Dim the light of the observation window and adjust the light with two knobs on the right side of the machine so that the light spot is about one third of the length from the top of the probe; Adjust the base position with the knob on the left side of the machine and cooperate with the red dot on the computer screen.

Find the resonance frequency of the probe: check that the set point is between 0.8 and 0.9.

Lower the needle: click approach to make the probe close to the sample surface.

Confirm the force curve: stop after 2 seconds and check the slope of the force chart. If the slope surface is jagged, the reason may be that the sample is not properly adhered to the substrate, or the sample surface is too rough.

Start scanning: scan to get the image after checking everything.

Raman Spectroscopy Measurement

Raman Spectroscopy Measurement principle

Raman spectroscopy is a kind of vibration spectroscopy, and its principle is to use a laser source with a fixed wavelength to excite the sample. When the excitation light interacts with the sample molecule, if the photon collides with the molecule to produce energy exchange and the frequency of the excitation light is changed, this change is called Raman shift.

Raman shift value does not change with laser wavelength, so it can be used to understand molecular bonding and structure, or molecular environment. For example, the impurities in the sample will change the bonding due to stress and tension and react in Raman shift. In addition, the deformation of compounds in different states, such as melting and crystallization caused by heating or external force, can also be known by Raman spectroscopy. Actually, it is applied to the change of graphite structure in the charging and discharging process of lithium batteries and the analysis of foreign matters in gem identification, etc.

When light strikes molecules and interacts with the electron cloud and excitation light in the molecules, Raman effect will occur. For spontaneous Raman effect, photons excite molecules from the ground state to a virtual energy state. After the excited state molecule emits a photon, it returns to a rotating or vibrating state different from the ground state. The energy difference between the state and the ground state will make the frequency of released photons different from the wavelength of excitation light. If the energy of the molecule in the final vibration state is higher than that in the initial state, the excited photon frequency is lower, and this frequency change is called Stokes shift ; ; If the energy of the molecule in the final vibration state is lower than that in the initial state, the excited photon frequency will be higher, and this frequency change is called Anti-Stokes shift.

Raman Spectroscopy and infrared spectrum belong to vibration spectrum, and they are complementary. When the sample belongs to the structure with strong dipole moment, it has strong IR absorption for infrared light; on the contrary, if the structure with weak dipole moment, Raman scattering technique can be used for analysis. Vibration spectroscopy is widely used in the field of chemistry, because chemical bonds and molecular symmetry have their special spectral information, which can be used as an important spectral feature to identify molecules.

Raman Instrument Setup and Operation Steps

Raman scattering spectrometer includes optical microscope, laser light source, spectrometer, Charged-Coupled Device or photomultiplier tube.

Use a laser light source with a fixed wavelength to excite the sample and make it have Raman effect. Filter the Rayleigh scattering light with a filter. After splitting the light with grating in the monochromator, absorb it with photoelectric coupling element or photomultiplier tube. Perform computer atlas analysis.

Research Analysis and Results

Image Analysis by Atomic Force Microscope (AFM)

The following image scanning object is a sample prepared by mixing 0.1 g of hBN powder with a particle size of about 1 μm with 30 mL of IPA, ball milling at 582 rpm for 3 hours, ultrasonic treatment in water isolation for 30 minutes, treatment with a cell crusher for 10 minutes, and centrifugal treatment at 8000 rpm, and then giving different parameters (the number of times of dropping hBN-IPA mixture on the substrate MgF_2 with a dropper). It was measured by atomic force microscope. Through AFM image analysis, the roughness and thickness of the sample can be known.

Compared with AFM images in related studies, the thickness of the smallest sample (a drop of mixture on the substrate) prepared in this study is between 5~8 nm, which is just between the thickness of multilayer and monolayer samples in the literature. The following two figures are images of the same sample (several drops of mixture on the substrate) measured at different scales (Fig. 6 and Fig. 7).

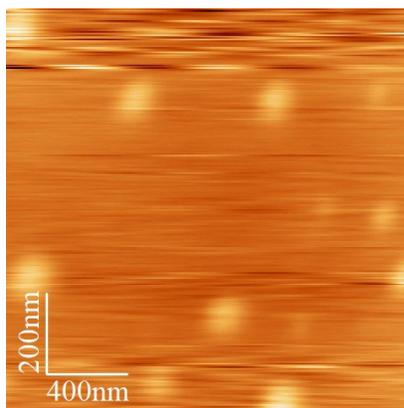


Fig. 6. One of the results of atomic force microscope measurement of the sample prepared by dropping several drops of mixture.

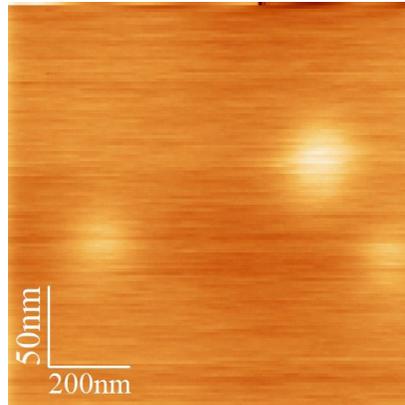


Fig. 7. The second measurement result of atomic force microscope of the sample prepared by dropping several drops of mixture.

The following four figures show the thickness image of the cross section of the same sample (several drops of mixture on the substrate) at different scales and the cutting line diagram of the cross section (Fig. 8 and Fig. 9).

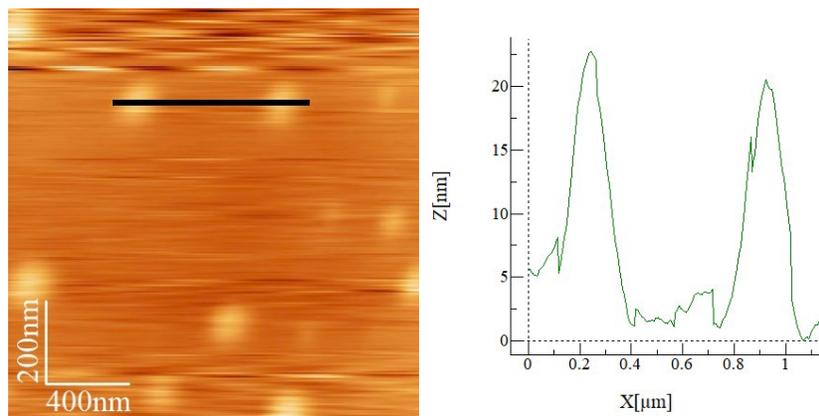


Fig. 8. One of the section thickness image and section cutting line diagram of the sample prepared by dropping several drops of mixture.

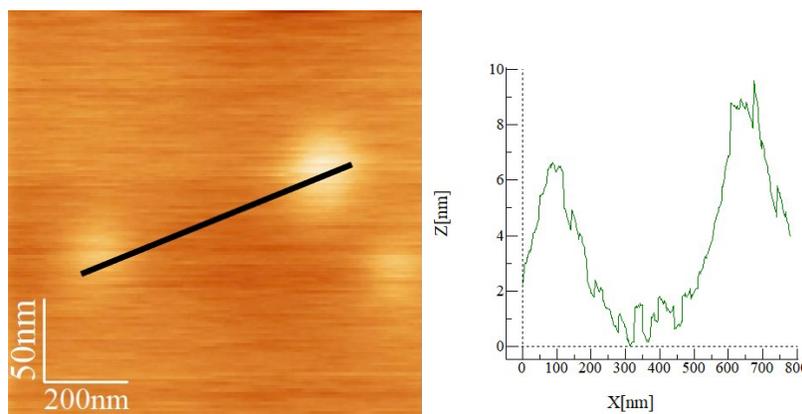


Fig. 9. Profile thickness image and profile cutting line diagram 2 of the sample prepared by dropping several drops of mixture.

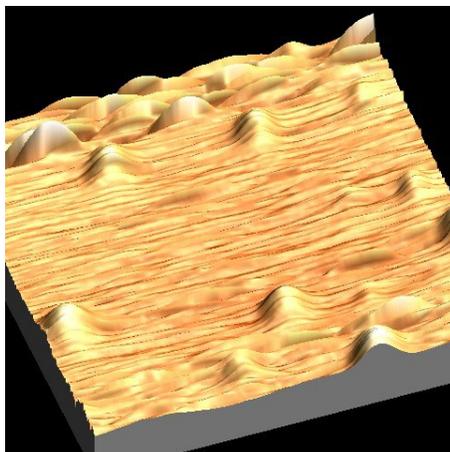


Fig. 10. Three-dimensional map of sample surface

Raman Spectroscopic Analysis

The figure below shows Raman spectroscopic analysis. The measurement object is a sample prepared by mixing 0.1 g of hBN powder with a particle size of about 1 μm with 30 mL of IPA, ball grinding at 582rpm for 3 hours, ultrasonic treatment with water insulation for 30 minutes, and treatment with a cell crusher for 10 minutes. After centrifugal treatment at 8000rpm, different parameters (the number of times of dropping hBN-IPA mixture on substrate MgF_2 with dropper) are given. Raman analysis can be used to check whether the sample is completely attached and whether there are impurities on it.

The Raman Spectroscopic of the sample prepared in this study (as shown in Fig. 11) has a spectral line at 1364cm^{-1} and the Raman spectroscopic of hexagonal boron nitride measured in related studies also has a spectral line at about 1364cm^{-1} , which proves that the hexagonal boron nitride sample prepared in this study is attached to the substrate and there is no obvious impurity on the sample.

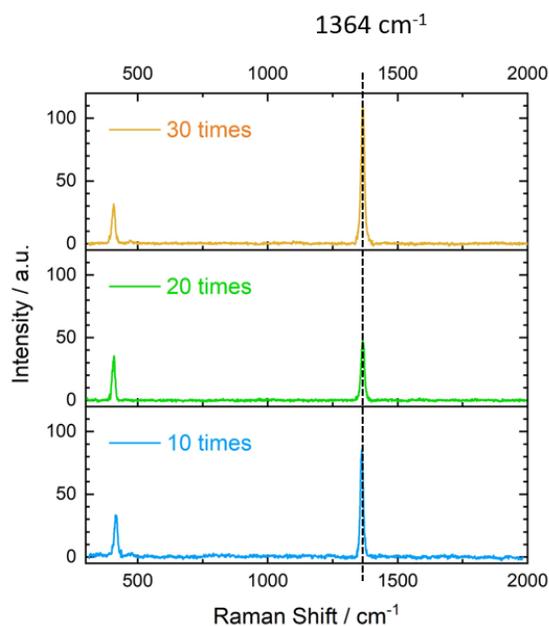


Fig. 11. Raman Spectroscopic measurement results of samples prepared in this study.

Analysis of Photoluminescence (PL)

Fig. 12 shows the photoexcitation fluorescence spectra of samples prepared by mixing 0.1 g of hBN powder with a particle size of about 1 μm with 30 mL of IPA, ball milling at 582rpm for 3 hours, ultrasonic treatment in isolation of water for 30 minutes, treatment with a cell crusher for 10 minutes, and centrifugal treatment at 8000rpm, and then giving different parameters (the number of times of dropping hBN-IPA mixture on the substrate MgF_2 with a dropper).

Observe the measurement results of this study (as shown in Fig. 12). When the sample is irradiated with a light source with a wavelength of 200 nm, there are several broad bands of light emission between the wavelengths of 350 and 500 nm. According to experience, it is speculated that it should be the light emission of the substrate MgF_2 . In addition, the excitation light of the sample has a peak at 218 nm, which should be the indirect energy gap of hBN. It is reported in the literature that the peak of photoluminescence spectrum of monolayer hexagonal boron nitride film is about 203 nm, while that of multilayer hexagonal boron nitride film is about 207 nm. While the single crystal hBN emits light at 215 nm. In addition, the broad band at 304 nm is the luminescence caused by the substitution of N vacancy in hBN structure by C impurity [11,12].

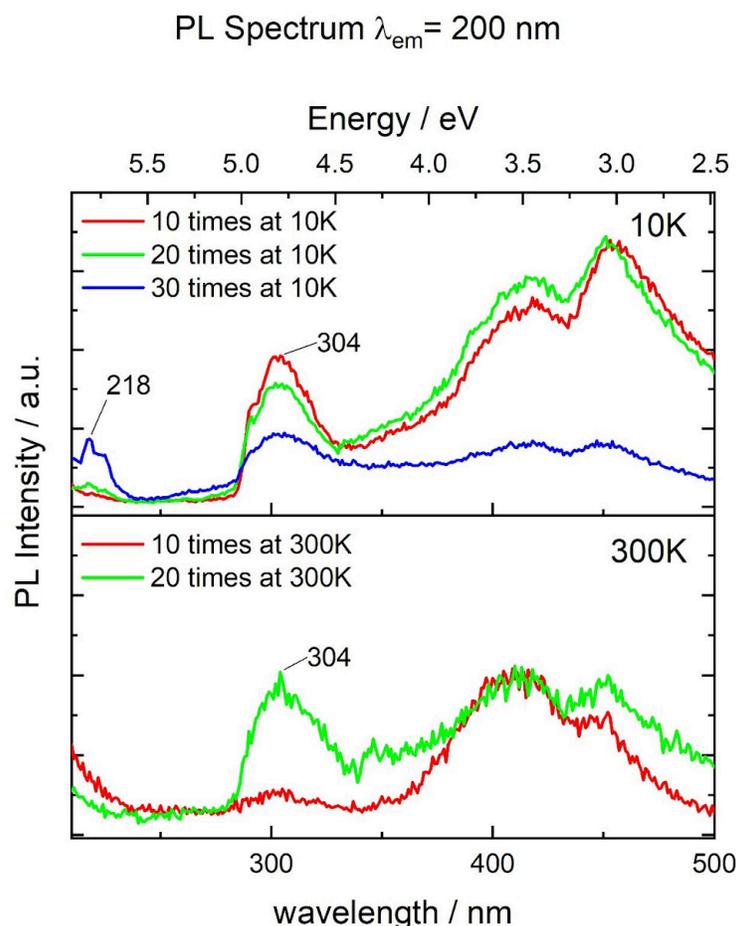


Fig. 12. Measurement results of photoluminescence spectra of samples prepared in this study.

Photoluminescence Excitation (PLE) Analysis

The following spectrum measurement object is a sample prepared by mixing 0.1 g of hBN powder with a particle size of about 1 μm with 30 mL of IPA, ball grinding at 582 rpm for 3 hours, ultrasonic treatment in isolation of water for

30 minutes, treatment with a cell crusher for 10 minutes, centrifugal treatment at 8000 rpm, and giving different parameters (the number of times of dropping hBN-IPA mixture on the substrate MgF₂ with a dropper). The Photoluminescence Emission Spectrum was measured and analyzed.

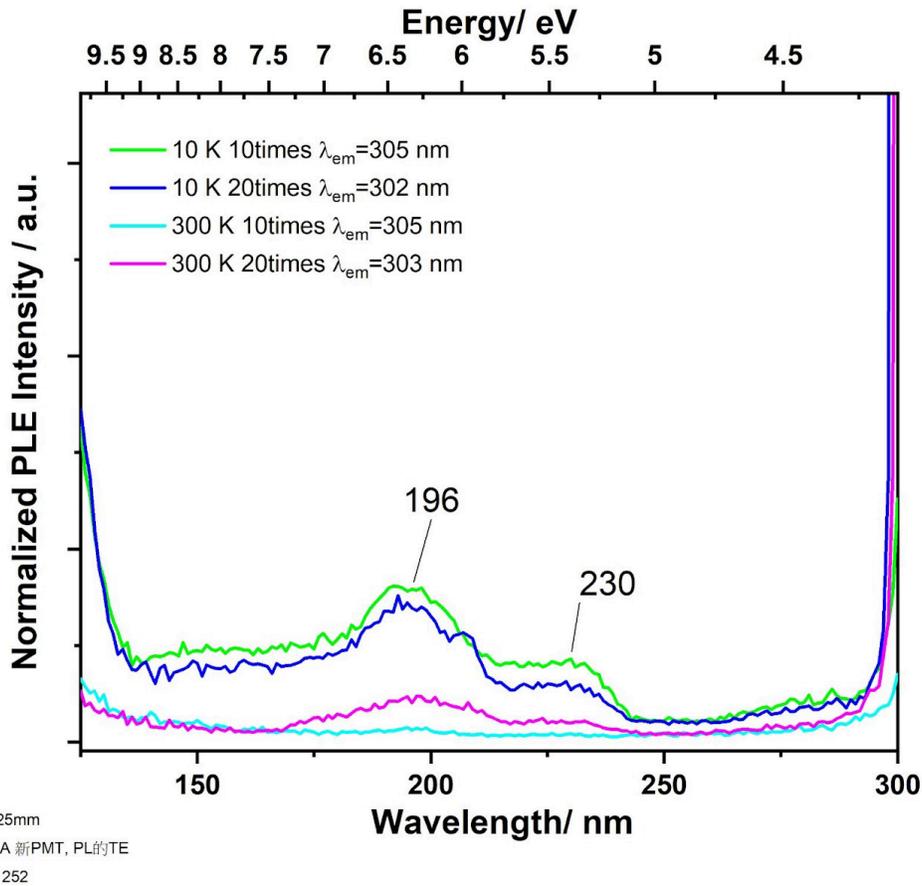


Fig. 13. Measurement results of fluorescence excitation spectra of samples prepared in this study.

Analysis of Absorption Spectra

Fig. 14 The measured sample is a sample prepared by mixing 0.1 g of hBN powder with a particle size of about 1 μm with 30 mL of IPA, ball milling at 582 rpm for 3 hours, ultrasonic treatment in isolation of water for 30 minutes, treatment with a cell crusher for 10 minutes, and centrifugal treatment at 8000 rpm, and then giving different parameters (the number of times of dropping hBN-IPA mixture on the substrate MgF₂ with a dropper). The absorption spectrum was measured and analyzed.

The absorption spectrum measured in this study (as shown in Fig. 14) shows that the main peak has a blue shift compared with the reference. The wavelength is blue shifted from about 203 nm to about 196 nm. It is supposed that the absorption band with the original wavelength at 180 nm redshifts and then overlaps with the absorption band at 203 nm.

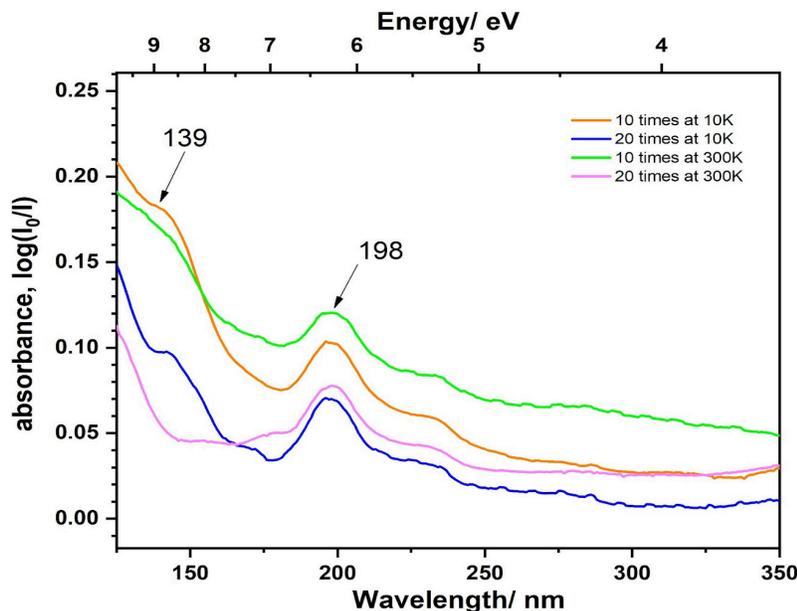


Fig. 14. Measurement Results of Absorption Spectra of samples prepared in this study

Research Conclusions and Suggestions

In this study, the samples prepared by dropping 10, 20 and 30 drops of mixture on the substrate have similar peak values of photoluminescence emission spectrum (PLE) and absorption spectrum at 196 nm and 198 nm, respectively, which means that the absorption efficiency in the measurement range is high, that is, most of the absorbed energy is used for light emission, while less is lost by heat energy. However, the measured peak value of PLE spectrum is different from the value in the reference study, which means that the optical properties of the sample are different. It is speculated that the reason is that the thickness, particle size and shape of the sample itself have some influence on the electronic structure.

In addition, the photoluminescence (PL) of the above samples were measured by light with wavelength of 200 nm, and there were peaks at 304 nm and 218 nm, and the peak at 304 nm was stronger. The Photoluminescence Excitation (PLE) was measured at 304 nm, and there was a peak at 196 nm, which was near the wavelength of the original excitation light of 200 nm. The PL results were successfully confirmed. When the sample prepared in this study was excited with light of about 200 nm, the light of about 304 nm could be excited. Therefore, based on the information obtained from the above absorption spectra and fluorescence spectra, it can be speculated that the transition of the most important exciton may be from $\pi \rightarrow \pi^*$ at the point K or M in the electronic structure, then delayed to the defect state of VN through phonon assistance, and then to the defect state of CN in the form of ultraviolet radiation, while a few of them directly emit deep ultraviolet light from $\pi^* \rightarrow \pi$ with phonon assistance.

Compared with monolayer or multilayer high-quality CVD hBN thin films, the photoluminescence spectrum of this sample shows that the luminescence intensity at low energy (~ 3 eV) is almost close to that at high energy (~ 5.7 eV), which is a phenomenon not observed in thin film samples. The luminescence of this low-energy band can be assigned to the luminescence phenomenon caused by defects in hBN structure. Therefore, it can be inferred that hBN nanoparticles made in this experiment produced too many structural defects in the preparation process through ball grinding and ultrasonic stripping, and thus the exciton excited luminescence focused on defect luminescence. Although the preparation method adopted in this experiment can't prepare high-quality defect-free hBN for the development of deep ultraviolet light-emitting sources, the combination of ball milling and ultrasonic stripping can efficiently

produce a wide range of vacancy defects in hBN structure. If oxygen or carbon atoms can be properly introduced to replace the vacancy in the future, it will be possible to prepare narrow-frequency ultraviolet single-quantum light-emitting source carriers, thus replacing the low efficiency dilemma faced by CVD method at present.

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