EXFOLIATION OF TWO-DIMENSIONAL MATERIALS

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EXFOLIATION OF TWO-DIMENSIONAL MATERIALS

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Thesis

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ABSTRACT

Layered crystals, also called two-dimensional materials, are those which form strong chemical bonds in-plane but have weak interaction out-of-plane. It means they can be exfoliated into nanosheets that less than one nanometer thick. As layered materials, transition metal dichalcogenides (TMDs) like molybdenum disulfide (MoS$_2$) have attracted many interests due to their outstanding electronic properties. Recently, we have developed a new simple method for the exfoliation of TMDs by using Na/K alloy through liquid-phase. We have synthesize few-layer MoS$_2$, molybdenum diselenide (MoSe$_2$), tungsten disulfide (WS$_2$), tungsten diselenide (WSe$_2$) four compounds. Characterization of the exfoliated materials was done by X-Ray Diffraction (XRD), Raman Spectroscopy, Transmission Electron Microscopy (TEM). We also tested these exfoliated materials for the lithium-ion batteries.

Also, we used this two-solvent interface trapping method to exfoliation molybdenum disulfide (MoS$_2$) and hex-boron nitride (h-BN). For this method we expect to make some large-scale thin film by exfoliated materials. Characterization of the exfoliated materials was done by Raman Spectroscopy, Transition Electron Microscopy (TEM), Scanning Electron Microscopy (SEM).
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CHAPTER I
INTRODUCTION AND BACKGROUND

1.1 Two-Dimensional Materials

Layered materials are those crystals which form strong in-plane chemical bonds but weak out-of-plane van der Waals interaction. These kind of materials can allow people to exfoliate into so-called nanosheets which are less than one nanometer thick. Exfoliation is defined as the process that changes the pristine bulky materials to nano-scale thin films. After exfoliation, the nanosheets will not retain all the original properties from the pristine bulky crystal. However, some new properties will occur that are very different from the bulky one which makes the nanosheets so unique for applications.

There are many kinds of layered materials. One of the simplest and most common are the graphene\cite{1,2} and hexagonal boron nitride\cite{3}. Transition metal halides (such as TiCl$_2$), transition metal oxides (such as MoO$_3$, TiO$_2$)\cite{4,5} and metal double hydroxides[such as Mg$_6$Al$_2$(OH)$_{16}$]\cite{6} also represent diverse layered structures. What's more, clays, layered silicons and other layered minerals are the members of the layered materials family\cite{7,8}. And nowadays one of the most popular layered materials are the transition metal dichalcogenides(such as MoS$_2$, WS$_2$)\cite{9,10}.

Transition metal dichalcogenides have attracted many research interests in the post graphene layered material era due to their unique electrochemical and mechanical
properties\textsuperscript{[10]}. These properties make us think that transition metal dichalcogenides can be excited starting material for exfoliation. After exfoliation, the accessible surface area of the material will dramatically increase, so it can be used as surface-active or catalytic chemicals. Recently, another effect of exfoliation has been reported that the band gap of the transition metal dichalcogenide will change after the exfoliation, this allows electronic response to be chosen at will\textsuperscript{[11]}.

1.2 Ion Intercalation Exfoliation

As for the exfoliation of layered materials, graphene exfoliated by mechanical force such as scotch tape was reported at first\textsuperscript{[11]}. These mechanical forces can obtain high-quality graphene which has outstanding properties, however, low yield and production rate limited their applications. After some great research works, people developed some exfoliation methods that were done in the solution which can give us large quantities, high-quality and sizable few layer or monolayer materials.

The earliest liquid-phase method of exfoliation is the chemical oxidation of graphite\textsuperscript{[12]}. Natural graphite was treated with oxidizers such as sulfuric acid and potassium permanganate. These oxidation will add hydroxyl and epoxide groups to the basal plane of graphite which makes the graphite become hydrophilic. Then water intercalation or ultrasonication can be used to yield large scale monolayer graphene oxide which is stable in solution. Afterwards the thin graphene oxide can be easily reduced chemically in the liquid-phase but will be no longer stable and aggregate unless polymer or surfactant stabilizers are present. However, although graphene oxide can be reduced to
graphene easily, the structural defects will remain and cause low quality which will narrow its application.

Recently, a new method has been developed as to exfoliate layered materials that is to use ultrasonic waves in solvent\textsuperscript{[13]}. These kind of powerful ultrasonic beam can generate cavitation bubbles that can collapse into high-energy jets which can break the van der Waals interaction between the layers of the materials so as to produce single layer materials. Graphite, hexagonal boron nitride, transition metal dichalcogenides and some of transition metal oxides can be exfoliated by this method. On the other hand, due to the power of the ultrasonic waves, the size of single layer flakes is relatively small and cannot be controlled.

Another liquid-phase method of exfoliation of layered materials is called intercalation. Because of the weak van-der-waals interaction between the layers, layered materials can strongly absorb the small molecules into the space between layers. This introduced another method of exfoliation of layered materials called intercalation, which has been widely applied in the exfoliation of graphite and transition metal dichalcogenides\textsuperscript{[14,15]}. The intercalation of molecules will enlarge the space between sheets and weaken the interlayer adhesion so as to reduce the energy of exfoliation. Some intercalation species such as IBr\textsuperscript{[14]} can transfer the charge to the layers resulting the reducing of interlayer binding. Further treatment such as low-power ultrasonication or thermal shock will be applied to exfoliate the intercalated layered materials. Intercalation can give high quality materials but have some drawbacks such as sensitivity to the ambient conditions\textsuperscript{[16]}.
For the transition metal oxides and clays, ion exchange has become a developed method of exfoliation\textsuperscript{[5]}. Since these kind of layered materials contain some exchangeable interlayer of cationic ions. Those ions can be exchanged for protons by soaking in acidic solutions. The protons can be exchanged for bulk organic ions leading to substantial swelling. Then low-power ultrasonication is applied to exfoliate the materials into nanosheets.

Among the methods that have been developed to exfoliate layered materials\textsuperscript{[17,18,19,20]}, mechanical exfoliation are most common. After that, wet chemistry exfoliation also has been emerged a lot like ultrasonication in different solution\textsuperscript{[21]}, lithium ion intercalation\textsuperscript{[22]}. Recently, Zheng et al.\textsuperscript{[23]} reported a high yield exfoliation using sodium naphthalenide. However, although long-time ultrasonication can produce good quality nanosheets, the size of nanosheets is relatively small. Compared to the lithium ion, sodium and potassium ion is more reactive and effective. Inspired by Genorio et al.\textsuperscript{[24]}, we are using Na/K alloy to exfoliation transition metal dichalcogenide.
1.3 Interface Trapping Exfoliation

Recently Adamson et al.\textsuperscript{[26]} introduced a novel method to exfoliate two-dimensional materials by applying this so-called interface trapping method. Laterally macroscopic, transparent and conductive films from pristine graphite flakes can be produced by this method with well-controlled thickness. The affinity of two-dimensional materials to the interface of the co-solvent systems plays a very important role during the exfoliation process. Unlike many other exfoliation methods, the interface trapping method is being processed in a pure co-solvent systems so the two-dimensional materials won’t be affected by other chemicals. And also, this process is very simple, easy to handle and has a very low cost. Inspired by this method, we tried to apply it on the MoS$_2$ and h-BN to see whether we can produce some macroscopic films of these two-dimensional materials and apply the few-layered MoS$_2$ on the field effect transistor fabrication.
1.4 Scheme of exfoliation

Figure 1.2 Scheme of ion intercalation exfoliation.
CHAPTER II
EXPERIMENTAL SECTION

2.1 Materials

All materials were used as received without further purification. For each material, the supplier and powder particle sizes were as follows: MoS$_2$ (Sigma Aldrich, ~6 μm), WS$_2$ (Alfa Aesar), WSe$_2$ (Alfa Aesar, -10 μm) and MoSe$_2$ (Alfa Aesar, -325 Mesh), h-BN(Graphene Market). Anhydrous THF was distilled over Na and stored in glovebox. All solvents were >98% pure.

2.2 Instrumentations and Instrumental Techniques

Spincoater (Laurell, WS-650MZ-23NPP), AFM (MultiMode$^\text{TM}$), SEM (JOEL, JSM-7401F), TEM (JEOL, JSM-1230, operated at 120 kV), Raman Spectroscopy (HORIBA, LabRAM HR), Tip Sonicator (Branson Digital Sonifier), Ultrasonic Cleaner (GB-2500B).

2.3 Synthesis

The synthesis section concludes three parts. First one is the ion intercalation exfoliation of TMDs while the second is the co-exfoliation of MoS$_2$/NG hybrid. The first
two parts of synthesis procedures are similar. The third part is the interface trapping exfoliation of MoS$_2$ and h-BN

2.3.1 Exfoliation of TMDs.

The procedure was modified from the one introduced by Genorio et al$^{[24]}$. Take MoS$_2$ as a typical example, a sample of 800 mg MoS$_2$ was added to a 1-neck 300 mL flask containing a magnetic stir bar. Then the vessel was transferred into the glovebox filled with Ar (O$_2<0.5$ ppm, H$_2$O<0.5 ppm). In the glove box, 100mL anhydrous THF wasinjected into the flask with syringe, followed by 2mL Na/K alloy. The flask containing the suspension was then sealed with a septum and transferred out of the glovebox where the suspension was dispersed by a 10 min ultrasonication to yield a dark suspension. After ultrasonication, the reaction mixture was vigorously stirred at ambient temperature for 3 d and during these 3 d, the suspension was ultrasonciated 20min each day. The reaction suspension was then quenched by the addition of the 8.1 mL 1-iodoheptane through a syringe and left to stir at ambient for another 1 d. 20 mL methanol was then added to quench excess Na/K alloy, and the mixture was ultrasonicicated at room temperature for 30 min. For workup, the reaction mixture was filtered over a 0.45 μm pore size PTFE membrane. The filter cake was successively washed with THF (100 mL), i-PrOH (100mL), H$_2$O (100 mL), i-PrOH (100 mL), THF (100 mL) and Et$_2$O (10 mL) and finally dried in vacuum oven for 24 h. The product was denoted as eMoS$_2$. Partial eMoS$_2$ (100 mg) after desiccation was annealed in tube furnace under Ar atmosphere at 400 for 1 h.
For MoSe₂, WS₂, WSe₂, the same method (same mass of a series of chemicals and experimental procedure) was also applied to these three compound, and the product was denoted as eMoSe₂, eWS₂ and eWSe₂, respectively.

2.3.2 Co-exfoliation of MoS₂/NG

Take MoS₂/NG (wt% 1:1) as an example, a sample of 400 mg MoS₂ and 400 mg natural graphite (~10 mesh) was added to a 1-neck 300mL flask containing a magnetic stir bar. Then the vessel was transferred into the glovebox filled with Ar (O₂<0.5 ppm, H₂O<0.5 ppm). In the glove box, 100 mL anhydrous THF was injected into the flask, followed by 2 mL Na/K alloy with syringe. The flask containing the suspension was then sealed with a septum and transferred out of the glovebox. The suspension was dispersed by a 10 min ultrasonication to yield a homogeneous suspension. After ultrasonication, the reaction mixture was vigorously stirred at ambient temperature for 3 d and during these 3 d, the suspension was ultrasonciated 20 min each day. Methanol (40 mL) was then added to quench excess Na/K alloy, and the mixture was ultrasonicated at room temperature for 40 min. For workup, the reaction mixture was filtered over a 0.45 μm pore size PTFE membrane. The filter cake was successively washed with THF (100 mL), i-PrOH (100 mL), H₂O (100 mL), i-PrOH (100 mL), THF (100 mL) and Et₂O (10 mL) and finally dried in vacuum oven for 24 h. After drying, the mixture was then annealed in the tube furnace at 400 °C for 4 h in argon stream to obtain the black fluffy powder denoted as eMoS₂/NG (wt% 1:1) (exfoliated MoS₂/natural graphite).
2.3.3 Interface trapping exfoliation of MoS$_2$ and h-BN

Take MoS$_2$ as an example, 2 mg of bulk MoS$_2$ was first put into a 20 ml glass scintillation vial. Then, 7 ml of $n$-heptane was added in to the vial and system was briefly bath sonicated for 10 s in order to break up large particles of the two-dimensional materials. After the bath sonication, the vial which contained two-dimensional materials and $n$-heptane was tip sonicated for 15 min at 30% amplitude (pulse on 20 s, pulse off 40 s) to exfoliate those two-dimensional materials and disperse it to the heptane layer. After tip sonication, 7 ml of water was add to the vial, and the co-solvent system was bath sonicated again for 10 s to let the materials move to the interface of the two solvent. Then, the co-solvent system was tip sonicated again for 15 min at 30% amplitude (pulse on 20 s, pulse off 40 s) with the tip right above the co-solvent interface to further exfoliate those two-dimensional materials. After the final sonication, the system was shaken to create the emulsion spheres, and the exfoliated two-dimensional materials climbed on the wall of the glass vial.

2.3.4 Characterization preparation

The morphology and lateral dimension of the TMDs was observed with AFM and TEM. The crystal structure was characterized by XRD, Raman microscopy, where the sample powder was covered on the carbon tape. A drop of a NMP solution containing the redispersed 2D nanomaterials was placed on a lacey carbon copper grid for TEM. TGA on was carried out with a ramping speed of 10/min under N$_2$ atmosphere.
The morphology of the MoS$_2$ and h-BN exfoliated by interface trapping method was observed with SEM and TEM. The crystal structure was characterized by Raman spectroscopy with the sample covered on a clean silicon wafer. A clean silicon wafer which has been pre-treated with acetone or a Ted Pella Inc. 400 mesh Cu grid was directly dipped into the interface of the co-solvent systems to let the exfoliated two-dimensional materials climb on it and then dried in oven for SEM or TEM.
CHAPTER III
RESULT AND DISCUSSION

3.1 Raman Spectroscopy of Ion Intercalation Exfoliation Products

Raman spectroscopy was utilized to further characterize the crystal structure of TMDs. Figure 3.1 shows the raman spectra of pristine, exfoliated and annealing after exfoliated TMDs. From the spectra, we can see the signature peak of pristine MoS$_2$ which is at ~383 and 406 cm$^{-1}$, which are corresponding to the in-plane and out-of-plane vibration modes in 2H-MoS$_2$\cite{27,28}. The new peak at around 204 and 356 cm$^{-1}$ plus the absence of original peak at around 383 and 406 cm$^{-1}$ is similar to what has been reported by Zheng et al\cite{23}. but different from that by Eda et al\cite{15}. It is probably due to the different ion intercalation. And it also confirmed the ion intercalation of Na$^+$ and K$^+$. The reason of the appearance of the new peaks is unknown but compared to the other three spectra, we can find that these new peaks only showed up in the spectra of MoS$_2$ and MoSe$_2$, but not in WS$_2$ and WSe$_2$. So we can tell that these peaks are corresponding to Mo. And it is obviously that the 2H-MoS$_2$ can be restored after annealing\cite{15,23}. We can find an interest thing that the new peaks still exist even after annealing at 400, although the mode was partially reactivated. And the cases of MoSe$_2$, WS$_2$ and WSe$_2$ are similar compared to MoS$_2$. 

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Figure 3.2 shows the co-exfoliation of the MoS$_2$/NG hybrid, which two regions were clearly identified. From the spectra we can clearly see the D peak around 1350 cm$^{-1}$ and G peak around 1560 cm$^{-1}$ that confirmed the existence of graphene, and two signature peaks at around 383 and 406 cm$^{-1}$ which belong to the 2H-MoS$_2$. 

(a)
Figure 3.1 Raman spectra of (a) pristine MoS$_2$, eMoS$_2$, eMoS$_2$-annealed and standard 2H-MoS$_2$, (b) pristine MoSe$_2$, eMoSe$_2$, eMoSe$_2$-annealed and standard 2H-MoSe$_2$, (c) Pristine WS$_2$, eWS$_2$, eWS$_2$-annealed, 2H-WS$_2$, (d) Pristine WSe$_2$, eWSe$_2$, eWSe$_2$-annealed, 2H-WSe$_2$.

Figure 3.2 Raman spectra of eMoS$_2$/NG hybrid (wt% 1:1) before and after annealing.
3.2 XRD of Ion Intercalation Exfoliation Products

Figure 3.3(a) shows the XRD patterns of the pristine MoS$_2$ powder, exfoliated MoS$_2$ and exfoliated MoS$_2$ after annealing. We can identified the pristine MoS$_2$ powder as 2H-MoS$_2$, the crystal structure disappeared after the exfoliation due to the intercalation of Na$^+$ and K$^+$, followed by alkyl chain after quenching. We can observe the d-spacing enlarge after exfoliation due to the (002) peak (JCPDS: 65-0160) broadened and shifted downwards according to the Bragg’s Law$^{23}$. It should be noted that crystal structure of the exfoliated MoS$_2$ recovered partially that we can find from the spectra. And the new peak around 2$\theta$ = 26 is still unknown and under investigation. It is probably originated from the carbon after annealing at 400. The situations are similar for those patterns of (b) MoSe$_2$, (c) WS$_2$ and (d) WSe$_2$. We can observe the broadened and shifted (002) peak downwards after exfoliation from the spectra of all the products
Figure 3.3 XRD patterns of (a) pristine MoS$_2$, eMoS$_2$, eMoS$_2$-annealed and standard 2H-MoS$_2$. (b) pristine MoSe$_2$, eMoSe$_2$, eMoSe$_2$-annealed and standard 2H-MoSe$_2$, (c) Pristine WS$_2$, eWS$_2$, eWS$_2$-annealed, 2H WS$_2$, (d) Pristine WSe$_2$, eWSe$_2$, eWSe$_2$-annealed, 2H-WSe$_2$.

Figure 3.4 shows the XRD patterns of the hybrid before and after annealing, the single component which is MoS$_2$ and natural graphite, before and after annealing. From the spectra, we can observe that for the single component, the (002) peak of MoS$_2$ which is around $2\theta = 14$, reappeared after annealing due to the restack, while for natural graphite, the crystallinity dropped dramatically even after annealing. And it is noted that for the MoS$_2$/NG hybrid, the crystallinity is much lower than that of the physical mixed MoS$_2$/NG. For the hybrid of MoS$_2$/NG, we can find from the spectra that after annealing, the (002) peak is still absent while other characteristic peaks reappeared compared to the
annealing MoS$_2$ patterns. We can tell that MoS$_2$ can be prevented from restocking with the existence of natural graphite. But the mechanism of this phenomenon is still under investigation. One probable reason is that we can noticed that the size of graphite and MoS2 is around 10 $\mu$m sub-millimeter, so it means the MoS$_2$ sheets is actually dispersed in exfoliated graphene matrix, which keep the MoS$_2$ sheets away from each other to prevent restacking.

Figure 3.4 XRD patterns of eNG, eMoS$_2$, eMoS$_2$/NG (wt% 1:1) hybrid and MoS$_2$/NG (wt% 1:1) mixture from vibrating mill.
3.3 TGA of Ion Intercalation Exfoliation Products

TGA was utilized to further estimate the content of alkyl chain in the TMDs. Figure 3.5 shows the TGA spectra of the four exfoliated TMDs. According to TGA, the content of alkyl chain in MoS$_2$, MoSe$_2$, WS$_2$, WSe$_2$ is 9%, 25%, 10%, 16%, respectively. It is interesting that we can see the eMoS$_2$ started tp drop at 150, as well as the eWS$_2$. For those compounds which contains Se, the drops start at 350. So we can tell that the stability of alkyl chain in these TMDs is different. Further research may be applied.
(b)

(c)
Figure 3.5  TGA measurements of (a) MoS$_2$, (b) MoSe$_2$, (c) WS$_2$, and (d) WSe$_2$

3.4 TEM of Ion Intercalation Exfoliation Products

To see the effect of exfoliation directly, TEM was utilized. Figure 3.6 shows the TEM images of exfoliated TMDs. It is obvious that these bulk materials have been exfoliated into few-layer nanosheets. And the sheets were folded which showed the distortion after the exfoliation.
Figure 3.6 TEM image of few-layer (a) MoS$_2$, (b) MoSe$_2$, (c) WS$_2$ and (d) WSe$_2$.

3.5 SEM of Ion Intercalation Exfoliation Products

SEM was utilized to study the morphology of co-exfoliated MoS$_2$/NG hybrid. Figure 3.7 shows the SEM image of eMoS$_2$/NG hybrid (wt% 1:1) after annealing. From the image we can see some large dark pieces which are corresponding to graphene and some relatively small pieces which are MoS$_2$. It can be find that the MoS$_2$ pieces are attaching
to the graphene homogeneously from the EDAX mapping. And also we know that the Na and K is not completely washed away from the EDAX, it may be trapped between MoS$_2$ or graphene. Other elements identified by EDAX like O is probably due to a series of oxygen-contained solvents during the washing process.
Figure 3.7 SEM of MoS$_2$/NG hybrid (wt% 1:1) and the corresponding EDAX mapping
Raman spectroscopy is routinely utilized to characterize crystal structure of thin two-dimensional materials. Figure 3.8 shows the raman spectra of pristine and exfoliated MoS$_2$ in the range of 300-500 cm$^{-1}$.

Two sharp peaks which around 380 cm$^{-1}$ and 400 cm$^{-1}$ can be observed whether can be allocated to the two signature peaks of MoS$_2$. It has been reported that the shift of $E_{2g}^{1}$ (~383 cm$^{-1}$) and $A_{1g}$ (~402 cm$^{-1}$) peak occur when reducing the number of layers of the two-dimensional materials$^{[29,30,31]}$. The red shift of those two peaks can be easily observed on the raman spectra which shows the MoS$_2$ has been successfully exfoliated. An intensity decrease can also be aware on the raman spectra which also confirmed that the distance between layers of the two-dimensional materials has been increased a lot that means the MoS$_2$ has been exfoliated.
Figure 3.9  Raman Spectroscopy of pristine & exfoliated h-BN exfoliated by interface trapping method

Figure 3.9 shows the raman spectroscopy of pristine and exfoliated h-BN which exfoliated by interface trapping method in the range of 1300 cm\(^{-1}\) - 1500 cm\(^{-1}\). We can clearly observe the peak located in 1370 cm\(^{-1}\) which is the signature peak of h-BN. It is obviously that the intensity of the only one peak decreased significantly which confirmed the well-exfoliated result of h-BN.
3.7 SEM of Interface Trapping Exfoliation Products

To investigate the morphology of the two-dimensional materials, SEM was utilized. Figure 3.10 shows the SEM images of MoS$_2$ exfoliated by interface trapping method. We can observe some relatively large in micrometer scale, thin MoS$_2$ sheets on the SEM image. However, we can also see some small or thick pieces of MoS$_2$ on the SEM image which tell us that the exfoliation is not thoroughly and the large power of tip sonication can break the materials into small pieces.
Figure 3.11 shows the SEM image of h-BN exfoliated by interface trapping method.

We can find some large sheets of h-BN which in micrometer scale on the image and also we can observe many thin sheets that tell us the h-BN was well-exfoliated. However compared to the MoS$_2$, we also see some small pieces on the image which shows that tip sonication can break them into very small pieces.
Figure 3.12 show the TEM image of MoS$_2$ and h-BN which exfoliated by interface trapping method. Figure 3.12(a) the exfoliated h-BN, we can observe many large scale in micrometer range and few-layered thin sheets on the image, which confirmed the well-exfoliated result. Figure 3.12(b) shows the exfoliated MoS$_2$, we can observe some isolated few-layered thin nanosheets stacked together. Compared to h-BN, we can find that MoS$_2$ nanosheets are isolated, which is different from the film-like h-BN.
Figure 3.12 TEM image of (a) h-BN and (b) MoS$_2$ exfoliated by interface trapping method
CHAPTER IV
CONCLUSION AND PROSPECT

A series of exfoliation of transitional metal dichalcogenides (TMDs) was performed and the product were characterized by XRD, Raman Spectroscopy, SEM, TEM, AFM, FT-IR and TGA. The yield of such a method was not as high as reported\(^23\). However, this method was facile and practical, if it is further optimized. Actually, this exfoliation and co-exfoliation can be more efficient if the duration time can be shortened. It is possible in this case, since exfoliation using n-butyl lithium was accelerated upon heating. Although such an experiment was not carried out yet, it’s quite interesting to improve the efficiency of exfoliation.

For the interface trapping exfoliation, a series of MoS\(_2\) and h-BN was performed and the final product was characterized by Raman spectroscopy, SEM, TEM. Compared to some similar works\(^26\), we can find that h-BN can be well-exfoliated, whether MoS\(_2\) didn’t reach our expectation. h-BN can be exfoliated into few-layered sheets and has a relatively large scale, but MoS\(_2\) is not as good as h-BN. This is probably due to the similar physical properties between graphene and h-BN which they have similar surface tension that plays a very important roll in the process. It can be said that if the co-solvent system chosen is further optimized for MoS\(_2\), we can get some exfoliated results as good as h-BN. Due to the large power of tip sonicator, the absence of it can be further applied to the exfoliation to get large scale exfoliation result.


