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Exfoliation and Analysis of Large-area, Air-Sensitive Two-Dimensional Materials

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TITLE:

Exfoliation and Analysis of Large-area, Air-Sensitive Two-Dimensional Materials

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KEYWORDS:

Two-dimensional materials, black phosphorus, chromium triiodide, oxidation, hydration, air sensitivity

SUMMARY:

A method for exfoliating large thin flakes of air sensitive two-dimensional materials and safely transporting them for analysis outside of a glovebox is presented.

ABSTRACT:

We describe methods for producing and analyzing large, thin flakes of air-sensitive two-dimensional materials. Thin flakes of layered or van der Waals crystals are produced using mechanical exfoliation, in which layers are peeled off a bulk crystal using adhesive tape. This method produces high-quality flakes, but they are often small and can be hard to find, particularly for materials with relatively high cleavage energies such as black phosphorus. By heating the substrate and the tape, two-dimensional material adhesion to the substrate is promoted, and the flake yield can be increased by up to a factor of ten. After exfoliation, it is necessary to image or otherwise analyze these flakes but some two-dimensional materials are sensitive to oxygen or water and will degrade when exposed air. We have designed and tested a hermetic transfer cell to temporarily maintain the inert environment of a glovebox so that air-sensitive flakes can be imaged and analyzed with minimal degradation. The compact design of the transfer cell is such that optical analysis of sensitive materials can be performed outside of a glovebox without specialized equipment or modifications to existing equipment.

INTRODUCTION:

Various layered materials that can be exfoliated down to a single atomic layer have generated interest across a broad range of fields. However, investigation and application of many of these materials is complicated by the fact that they are unstable in air and quickly oxidize or hydrate when exposed. For example; black phosphorus is a semiconductor with a tunable direct band gap, high mobility and anisotropic optical and electrical properties[1-5] but is unstable in air and will deteriorate in less than an hour[6,7] due to interactions with oxygen[8]. CrI_3 has been recently shown to exhibit two-dimensional ferromagnetism[9-11] but, when exposed to air, it degrades almost instantly[11].

Devices made from these materials can be protected from air by working in a glovebox and encapsulating them in a chemically inert material such as hexagonal boron nitride[12,13]. However, when developing these devices, it is often necessary to identify and analyze the flakes before encapsulation. This analysis requires either removing the sample from the inert environment of the glovebox or putting the analysis equipment in the glovebox. Removing the sample, even for a short time, risks damage via oxidation or hydration, while placing the necessary equipment inside a glovebox can be costly and cumbersome. To remedy this, we designed a hermetic transfer cell that safely encloses a sample, keeping it in an inert environment, so that it can be removed from the glovebox. While in the transfer cell, a sample sits 0.3 mm below a glass window to allow easy identification of flakes under a microscope as well as the use of optical analysis techniques such as photoluminescence or Raman spectroscopy.

Some two-dimensional materials, in addition to being air sensitive, are also difficult to exfoliate into thin flakes with the typical mechanical exfoliation method because a relatively high cleavage energy, relatively weak in-plane bonds, or both. Other methods, such as CVD growth[14,15], liquid exfoliation[16], or gold mediated exfoliation[17,18] have been developed for producing thin layers but may result in less than pristine flakes and only work for certain materials. Although exfoliation of graphene at elevated temperatures has been known to produce large flakes for at least a decade[19], this technique has been quantitatively characterized recently for both graphene and $Bi_2Sr_2CaCu_2O_x$ flakes[20]. Here, we demonstrate that hot exfoliation improves exfoliation yield also for black phosphorus, a material that is notoriously difficult to exfoliate. This technique, together with a hermetic transfer cell, facilitates the exfoliation and analysis of air sensitive, two-dimensional materials.

PROTOCOL:

1. Hot exfoliation of 2-D materials

NOTE: This procedure is done inside a glovebox.

1.1. Tape Preparation

1.1.1. Cut a length of tape (see **Table of Materials**) that is ≈5–10 cm long and ≈2 cm wide. Place it, sticky side up, on the working area. Fold the ends of the tape for easier handling.

1.1.2. Using tweezers, deposit the desired material approximately one-quarter of the way down the length of the tape by repeatedly pressing the material into the tape.

1.1.3. Further distribute the material by folding the tape in half, sticking it to itself, and pulling it apart so that the material covers an area of at least 1 cm^2. Depending on the material, repeat this multiple times: 1-2 times for black phosphorus, or several times for graphite or hexagonal boron nitride.

1.2. Sample preparation

1.2.1. Using the desired method, such as a carbide-tipped scribe, cleave an oxidized silicon wafer or other desired substrate into chips suitable for the experiment, ≤1 cm wide. Clean the chips by sonicating for 2 min in acetone, followed by isopropanol (IPA), at relatively low power (we used 12 W). Blow the chips dry with N_2.

1.2.2. Using the prepared tape, firmly press the deposited material onto the substrate. Apply firm pressure with a thumb or gently press with tweezers so the material contacts the chip as much as possible

1.2.3. Place the tape with substrate (substrate side down) on a hotplate at 120 °C for 2 min.

1.2.4. Allow the substrate to cool to RT and carefully remove it from the tape. Soak in acetone for 20 min to remove tape residue. Rinse with IPA for 30 s and dry the substrate with nitrogen. Depending on the material, further options for cleaning may be available, such as a forming gas anneal.

2. Hermetic transfer cell construction, operation, and maintenance

2.1. Construction

2.1.1. Construct the cell (**Figure 2**) out of the desired material (we used aluminum). It is 30 mm in diameter and 17.6 mm tall when closed. Fabrication drawings are available at http://churchill-lab.com/useful-things.

2.1.2. Make the base 16.2 mm tall with a raised sample platform that is threaded with ¾ - 10 threads with a vent cut into the threads. Where the cap meets the base, make an inset for an O-ring (see **Table of Materials**).

2.1.3. Make the cap 8.6 mm tall with matching female threads through the center.

2.1.4. Recess the cap by 0.2 mm to accommodate a 24 mm diameter x 0.1 mm thick coverglass window (here, borosilicate glass).

2.1.5 Apply a small amount of vacuum grease to the all sides of the O-ring and drop it into the

base inset.

2.1.6. Before affixing the window to the cap of the cell, clean the cap in acetone and IPA to remove any oil or debris left by the machining process.

2.1.7. Attach the window to the cell cap using epoxy. Thoroughly mix the epoxy according to the manufacturer's specifications. Here, parts A and B are combined in a 1:1.8 ratio by weight.

2.1.8. Apply a small amount of epoxy to the recessed area on the cap and spread it around as evenly as possible.

2.1.9. Set a 0.1 mm thick, 24 mm diameter coverglass (borosilicate glass in this case) into the recess and gently press it into the epoxy. Ensure the window is level with the top of the cap and there that there are no bubbles in the epoxy.

2.1.10. Wipe up any extra epoxy so that nothing protrudes from the surface of the cap. Allow the epoxy to cure for the manufacturer prescribed time at room temperature.

2.2. Operation

NOTE: This procedure is done inside a glovebox.

2.2.1. Using the desired method, affix a prepared sample to the cell base (double sided tape, glue, etc.). The cell is designed to accommodate samples up to 1 cm wide and 0.7 mm thick, including the adhesive.

2.2.2. Firmly screw the cap onto the base. This makes a seal between the cap and base by compressing the O-ring. Make sure that the pressure inside the transfer cell does not exceed 3 mbar above the ambient pressure.

2.2.3. Check that the sample sits just below the window. The sample can now be safely removed from the glovebox.

2.3. Window repair

2.3.1. Using tweezers, remove any broken glass that is not firmly affixed to the epoxy. Break up what glass remains (using a carbide-tipped scribe or other method) so that the epoxy beneath is exposed.

CAUTION: Wear gloves and eye protection when removing broken glass.

2.3.2. Soak the cap in a 50:50 mix of acetone and trichloroethylene (TCE) for 1-2 h or until the epoxy softens and begins to separate from the cap. Rinse in IPA for 30 s.

2.3.3. Peel off any loose epoxy and scrape the remaining epoxy from the surface with a razor blade. Take care not to damage the surface of the cap. Repeat the previous step if necessary.

2.3.5. Scrub the recessed area with acetone until the surface is clean of any epoxy residue. The cell window can now be replaced following the aforementioned steps.

3. Example uses of the transfer cell

3.1. Optical analysis

3.1.1 For flake imaging, place the transfer cell under the microscope. The cell can be used with any conventional microscope. When focusing, be careful not to crash the objective into the fragile widow.

3.1.2. Proceed with desired method for finding material flakes.

3.2. Polarized Raman spectroscopy

3.2.1. For polarization-resolved Raman spectroscopy, align a laser spot to a flake of interest. In this case we use 633 nm wavelength and 50 μW power and a 100x objective lens. For black phosphorus, low laser power is required to prevent damage to the flake.

4.2.2. Using a half-wave plate, vary the polarization angle.

REPRESENTATIVE RESULTS:

The goal of exfoliating two-dimensional materials is to isolate atomically thin layers. During the exfoliation process, flakes separate from the bulk crystal, leaving behind flakes of varying thicknesses, with a small probability for some flakes to be monolayers. By increasing the density and size of all exfoliated flakes, hot exfoliation increases the density and lateral size of thin flakes. This is accomplished by increasing the material area that makes close contact with the substrate. While in contact, gasses trapped between the material and the substrate expand during heating and are pushed out from under flakes. The removal of trapped gas allows more of the material to come into close contact with the substrate, thus increasing the amount of exfoliated flakes (**Figure 1A,B**) as clearly explained in Ref 20. Exfoliations of black phosphorus were performed using the typical mechanical exfoliation and hot exfoliation technique on silicon chips with 90 nm thick SiO_2. By measuring the total area of deposited material on a 1 cm x 1 cm silicon chip, it can be seen (**Figure 1C**) that hot exfoliation deposits 6-10 times more material. We note that in our experience other materials can be picked up from HF-cleaned substrates using polycarbonate following hot exfoliation, including graphene, hexagonal boron nitride, black phosphorus, $MnPSe_3$, and WSe_2. We used a 10:1 HF:water solution to clean the SiO_2 substrates over a 15 s period. Note, 10% HF etches SiO_2 at a rate of 23 nm/min[21] , so this process etches our substrates by 6 nm.

We now consider the effectiveness of the hermetic transfer cell (**Figure 3A**) in maintaining an

inert atmosphere when removed from a glovebox. CrI_3 is particularly sensitive to hydration and degrades within seconds when exposed to air (**Figure 3D**). Inside a transfer cell, however, an exfoliated CrI_3 sample remained unchanged for 15 hours (**Figure 3B**) and only began to show signs of degradation (blisters) after 24 hours (**Figure 3C**). While damage on a scale too small observe optically likely occurs on a shorter timescale, these results demonstrate that the hermetic transfer cell described here slows the sample degradation rate by at least three orders of magnitude (hours inside the cell compared with seconds outside).

To demonstrate use of the transfer cell for optical analysis of air-sensitive materials, we performed polarization-resolved Raman spectroscopy on a relatively thick (> 50 nm) flake of black phosphorus (**Figure 4A**). The spectra were acquired using 50 μW laser excitation at 632.8 nm with a 100x objective lens. A half-wave plate was used to rotate the polarization of the excitation beam. In **Figure 4B**, three Raman peaks can be observed in BP at around 466, 438 and 361 cm^{-1}, corresponding to A_g^2, B_{2g} and A_g^1 vibration modes respectively, regardless of the polarization, which agrees well with previous observations in bulk BP crystals for excitation and collection along the z-axis.[5,22] The peak positions do not vary with polarization angle. However, the relative intensities of these three modes change significantly with incident light polarization. The vibration mode A_g^2, which has the strongest intensity variation with the excitation laser polarization, as shown in **Figure 4B,C**, is associated with the atomic motion along the armchair direction. Therefore, as previously reported[5], this vibration mode provides an effective method to determine the armchair direction of the BP crystal and hence the crystal orientation. In **Figure 4C**, the Raman intensity shows two maxima within one full rotation, located at 26.5° and 206.5° with respect to the X and Y axes defined in the microscope images, and we conclude that the armchair direction of the BP is oriented at 26.5° for this flake. Similar optical spectroscopy methods can be used to determine crystal orientation and other properties, such as layer number or optical band gap, for other air-sensitive 2-D materials.

FIGURE AND TABLE LEGENDS:

Figure 1: Distribution of material on an oxidized silicon chip. (**A**) Typical sample of black phosphorus exfoliated at room temperature. (**B**) Typical sample of black phosphorus exfoliated at 120 °C. (**C**) Histogram of exfoliated black phosphorus area using room temperature(cold) and hot exfoliation.

Figure 2: Transfer cell. (**A**) Picture of a hermetic transfer cell showing separate cap and base. (**B**) Schematic drawing of transfer. A vent (green) is cut into the threads. Note that the bottom of the base is tapped and threaded for mounting.

Figure 3: Transfer cell suppression of flake degradation. (**A**) Fresh CrI_3 in a transfer cell (**B**) CrI_3 in a cell after 15 h. (**C**) CrI_3 in a cell after 24 h Hydration blisters can be seen at this point. (**D**) CrI_3 in air after 24 h in transfer cell and 30 s in air. Large areas of hydrated CrI_3 have collected at the edges of the flake.

Figure 4: Crystalline orientation identification. (**A**) Optical micrograph of thick flakes of exfoliated BP. (**B**) Polarization-resolved Raman spectroscopy of a thick BP flake. (**C**) Polar plot of

Raman intensity averaged over the spectral range in (**B**) as a function of linear excitation polarization angle (plot origin is zero intensity). The fit is a sine function plus a constant. The dashed line indicates the armchair direction.

DISCUSSION:

Hot exfoliation retains the ability of typical mechanical exfoliation to produce pristine thin flakes while also avoiding many downfalls of alternatives. Like typical mechanical exfoliation, this technique is not limited to a small subset of materials. Hot exfoliation can be applied to any material that can be exfoliated using room-temperature mechanical exfoliation as long as the material tolerates heating to 120 °C for 2 min in an inert atmosphere. We also note that it has been shown[20] that the heating time and temperature (above 100 °C) do not make any noticeable difference in flake density. Along with increased contact, average flake size can also be improved by increasing the bond strength between the substrate and the flakes. One way to do this would be by treating the substrate with O_2 plasma but this would also make the flakes hard or impossible to pick up for use in devices requiring heterostructure fabrication[20].

The transfer cell can be constructed from any suitable metal. We used aluminum because it is easy to machine but it should be noted that TCE (used to remove epoxy) is corrosive to aluminum when unstabilized, heated, or mixed with water. Stainless steel would be more durable and less reactive with TCE. However, we have not seen any corrosive effects using this method at RT. For imaging and analysis with high numerical aperture objectives, construction of the transfer cell is such that, when closed, the bottom of the window is 0.8 mm above the top of the base. With a 0.5 mm thick substrate and 0.1 mm thick adhesive, the sample sits 0.3 mm below the top of the transfer cell. This proximity allows for imaging and analysis with high magnification and relatively short working distance objectives. Exfoliated material can be clearly seen at 5, 20, 50 times magnification allowing for easy identification of thin flakes. At higher magnifications, spherical aberrations caused by the window significantly degrades the image quality. Provided that the sample substrate is less than 0.7 mm thick, there is no risk of over tightening the cell. When the cap is screwed down, excess gas is expelled through the vent in the threads. During construction, the precise location of the vent is not important, but it is important that it is not obstructed by the sample, vacuum grease or anything else. The vent prevents the fragile 0.1 mm thick window from breaking due to overpressure when the cap is screwed down. The window can only withstand pressure changes of a few mbar.

The coverglass window used for the transfer cells is made of borosilicate glass but for optical analysis at wavelengths other than visible to near-infrared, other window materials may be use. For the best imaging, care should be taken when installing the glass window. If not seated properly, the distance between the sample and window could be larger than expected. Especially for small working distance objectives, this could cause the objective to crash into and break the window. Also, some epoxies will cure faster at higher temperatures, but because metals and glass have different thermal expansion coefficients, the widow will deform after cooling back to room temperature. The epoxy should be cured at the same temperature at which it will be used (i.e., if the cell will be used at room temperature), the epoxy should also be cured at room temperature.

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DISCLOSURES:

The authors have nothing to disclose.

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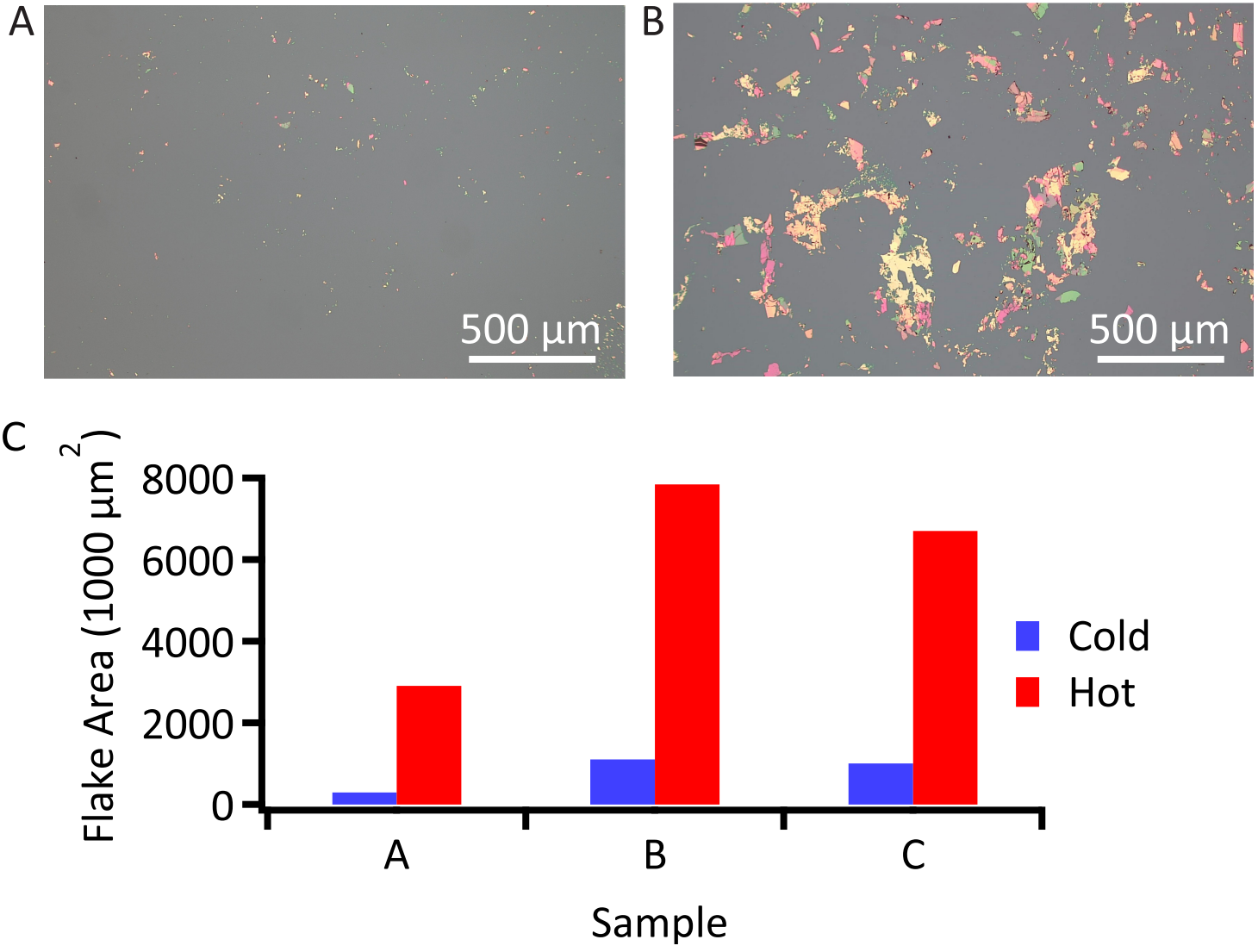
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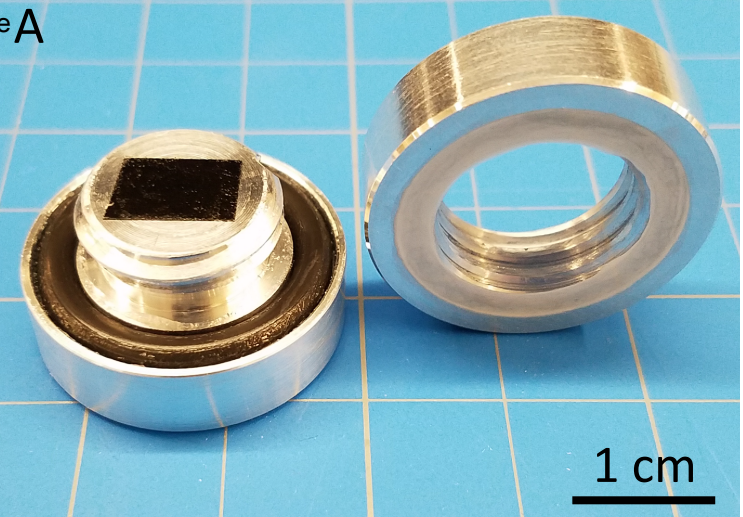
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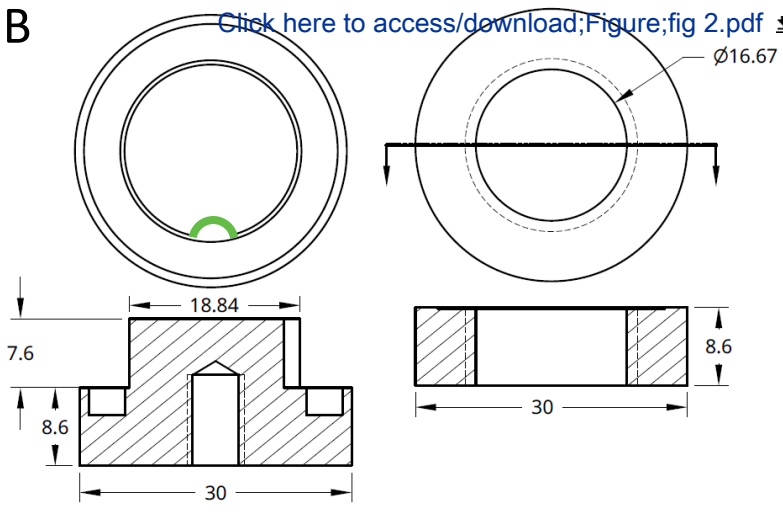
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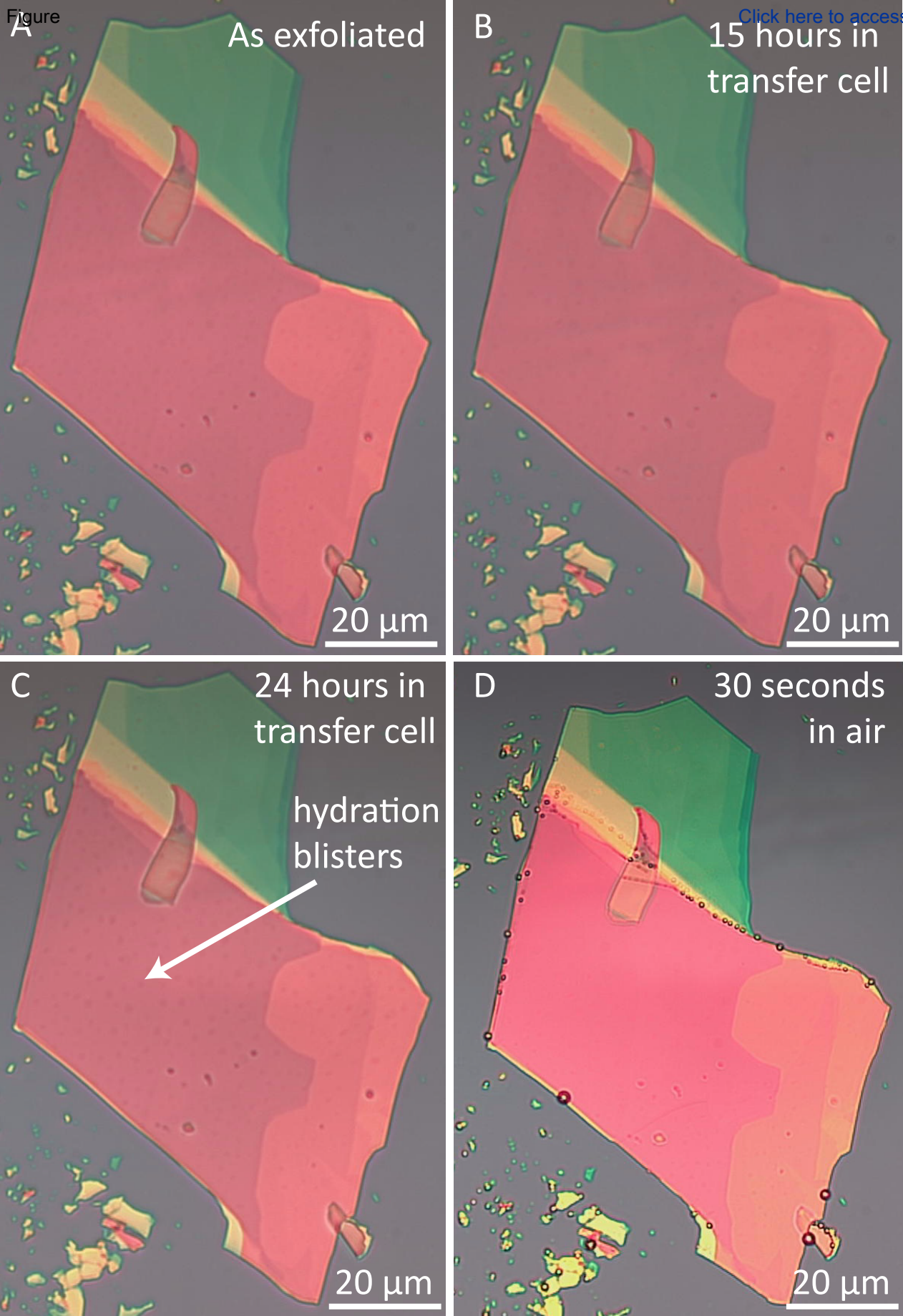

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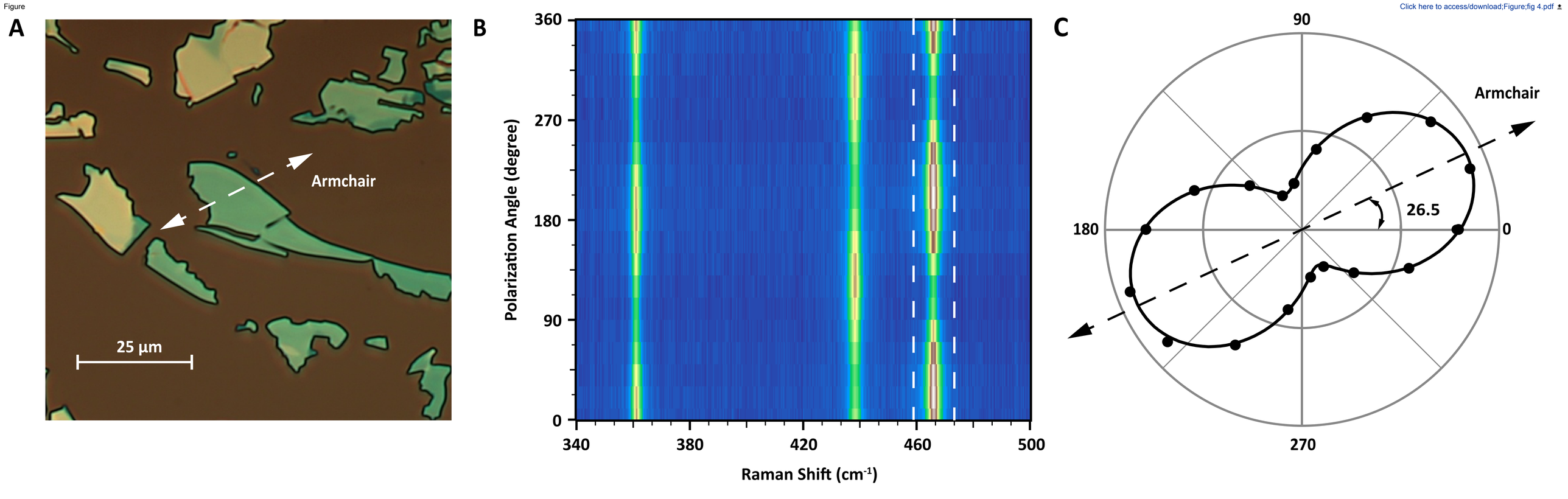

Table of Materials

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Name of Material/ Equipment	Company	Catalog Number
Ablestik 286 epoxy	Loctite	256 6 OZ TUBE KIT
Acetone	EDM Millipore Corporation	67-64-1
Circular coverglass, 24 mm dia, 0 thickness	Agar Scientific	AGL46R22-0
Dicing tape	Ultron systems	1009R
High-Vacuum grease	Dow Corning	1597418
Isopropanol	VWR Chemicals	BDH20880.400
Silicon wafer, 300 nm oxide	University Wafer	E0851.01
Silicon wafer, 90 nm oxide	Nova Electronic Materials	HS39626-OX

Comments/Description
air-tight epoxy
window glass
exfoliation tape
O-ring grease
flake substrate
flake substrate

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Institution:	University of Arkansas
Article Title:	Exfoliation and Analysis of Large-Area, Air-Sensitive Two-Dimensional Materials
Signature:	
Date:	June 28, 2018

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October 23, 2018

To: Review Editor, JoVE

Dear Dr. Steindel,

We would like to submit a revision of our manuscript "Exfoliation and Analysis of Large-area, Air-Sensitive Two-Dimensional Materials" by Josh P. Thompson, M. Hasan Doha, Peter Murphy, Jin Hu, and Hugh O. H. Churchill for publication in *JoVE*.

We have addressed the comments and concerns raised by the reviewers, as well as the editorial comments, and we hope you will find the improved manuscript and video suitable for publication in *JoVE*. Below you will find responses to the editorial comments and to each of the reviewers' comments, along with a description of changes made to the manuscript and the video.

Sincerely,

Hugh Churchill

Response to Editorial Comments

Changes to the manuscript:

2. Keywords: Please provide at least 6 keywords or phrases.

We have added an additional key-phrase to bring the total to 6.

3. Figure 2: Please provide exact measurements of the cap and base if possible.

Measurements are not included in the figure for clarity. A link to the full design is included in line 124.

4. Figure 3: Please include a scale bar for all images taken with a microscope to provide context to the magnification used. Define the scale in the appropriate figure Legend.

The figure is updated to include a scale bar.

6. Please revise the protocol (2.1.1-2.1.4, etc.) to contain only action items that direct the reader to do something (e.g., "Do this," "Ensure that," etc.). The actions should be described in the imperative tense in complete sentences wherever possible. Avoid usage of phrases such as "could be," "should be," and "would be" throughout the Protocol. Any text that cannot be written in the imperative tense may be added as a "Note." Please include all safety procedures and use of hoods, etc. However, notes should be used sparingly and actions should be described in the imperative tense wherever possible.

Protocol 2.1 has been rewritten in the imperative.

7. Please add more details to your protocol steps. There should be enough detail in each step to supplement the actions seen in the video so that viewers can easily replicate the protocol. Please ensure you answer the "how" question, i.e., how is the step performed? Alternatively, add references to published material specifying how to perform the protocol action. Some examples:

1.1.1: Please specify the type of the tape used in this step.

We used Ultron Systems dicing tape and have modified the manuscript accordingly.

1.1.2: What is used to handle and deposit the desired material?

We used tweezers to deposit material on the tape and have modified the manuscript accordingly.

1.2.1: What is used to cleave? Please mention sonication parameters (power and time).

Any cleaving method will work, and we mention one such method (carbide-tipped scribe) and have modified the manuscript accordingly. We have also specified the sonication power and time in the manuscript.

2.1.5: Please specify the size and material of the window used in this step.

This step has been changed to 2.1.9 and the window details are included.

2.3.1: Please revise this sentence to be clear.

This step has been rewritten and more detail has been added.

8. The Protocol should contain only action items that direct the reader to do something. Please move the discussion about the protocol to the Discussion.

Details is Protocol steps 2.1.5 (now 2.1.9), 2.1.6 (now 2.1.10), 2.2.2, 2.3.2, 2.4.2, 2.1.4 have been moved to the Discussion.

9. Please revise to explain the Representative Results in the context of the technique you have described, e.g., how do these results show the technique, suggestions about how to analyze the outcome, etc. The paragraph text should refer to all of the figures. However for figures showing the experimental set-up, please reference them in the Protocol. Data from

both successful and sub-optimal experiments can be included. Please more relevant information from Discussion to Representative Results.
10. As we are a methods journal, please revise the Discussion to explicitly cover the following in detail in 3-6 paragraphs with citations:
a) Critical steps within the protocol
b) Any modifications and troubleshooting of the technique
c) Any limitations of the technique
d) The significance with respect to existing methods
e) Any future applications of the technique

The Representative Results and Discussion have been significantly revised to address these issues.

11. Please provide journal names for references 6, 7, 10 and 11, etc.

Those journal names have been added.

Changes to the video:

1. Please increase the homogeneity between the written protocol and the narration in the video. It would be best if the narration is a word for word from the written protocol text.

Both the video and the manuscript have been modified to match closely.

2. Please use the same headings/subheadings for the written manuscript and the video. For instance, the heading is "1. Hot Exfoliation" in the written manuscript but "1. Hot Exfoliation of Two-Dimensional Materials" in the video.

Protocols 1, 2, and 3 in the manuscript have been changed to match the video.

3. The details in the video are not the same as the details in the written manuscript. Please cross-reference the video narration with the protocol text. Some examples:
00:29: "Fold ends for easier handling" is shown in the video but not mentioned in the written protocol.

This step is now in the protocol, Line 87.

00:48: The video says "covers an area of about 1 cm2" while the written protocol indicates "slightly larger 1 cm2".

Both the video and manuscript now say "at least 1 cm^2".

00:59: The video says "about 1 cm on the side" while the written protocol indicates "≤ 1 cm wide".

The video now says "less than 1 cm on a side".

01:09: The details mentioned here (i.e., apply pressure with your thumb…, tweezers can be used…) are not stated in the written protocol.

Section 1.2.2 Now includes these details.

01:26: The detail in the written protocol (substrate side down) is not mentioned in the video.

This detail is now included.

01:54: "Dry the substrate …" is not in the written protocol.

This has been included in manuscript, line 16.

02:42-03:08, 06:14-07:06: Such steps/details in the video are not in the written protocol.

Protocol 2.4.3-2.4.4 have been added.

4. Step 2.1 of the protocol in the video is hard to follow along with step 2.1 of the written protocol.

The manuscript and video have been revised to be more consistent.

5. 08:17: Please change hr to h.

This has been changed at 08:00.

6. The music is competing too much with the narrator voice. The music volume should be lowered by 6-12 dB.

The music volume has been reduced by 12 dB throughout so that it doesn't interfere with the narration. Additionally, the background music volume is now constant throughout the video.

7. 0:28-1:56, 2:34-2:37, 2:58-3:15, 4:40, 5:10, 5:15 - Most of the edits in these ranges are jump cuts, which tend to have a jarring effect on the viewer. We refer specifically to the edits that are within the same shot. The edit at 0:28 is the first example of this. These should be smoothed out with crossfades instead.

The cuts are now smoothed out with crossfades.

Response to Reviewer Comments:

Reviewer 1 Comments:

Comment 1:

As claimed by the authors, heating would cause the escape of gas between materials and substrate, thus leading to better contact and higher flake yields. This statement is quite confusing because the expansion of gas usually causes further separation instead of closer

contact. Is there any pressure applied to the tape during heating procedure to push out the gas?

Gas trapped between the flake and substrate are responsible for weaker adhesion between the flake and substrate. The reviewer is correct that when the trapped gas is heated it will expand and the increased pressure will push some of that gas out from under the flake. With less trapped gas, the flake and substrate now become more adherent, particularly after the sample has cooled back to room temperature when the tape is removed. After removal of trapped gas, the flake is now closer to the substrate, and new gas is unable to enter between the flake and substrate. This mechanism is clearly explained in Ref. 20 (previously Ref. 19), and we feel it is best to allow the original report to speak for itself in this regard.

Comment 2:

In case the cell over-pressurizes when the cap is screwed down, a vent is cut into the threads to expel excess gas. Will oxygen and water vapor diffuse into the cell during venting when the cell is placed outside of a glovebox?

The vent is only cut into the internal threads. This is to allow gas flow through the threads as the cap is screwed down so venting should only occur inside a glovebox. When the cell is closed, the vent is entirely enclosed within the cell and there is no risk of diffusion through the vent. The o-ring is what seals the cell and ultimately limits the longevity of the inert interior of the cell.

Comment 3:

Line 248: "these results demonstrate that the hermetic transfer cell described here slows the sample degradation rate by at least three orders of magnitude." How to get such a precise conclusion without support of specific experiment data?

Respectfully, we believe we have demonstrated this using the data presented in Fig. 3, and we thank the reviewer for providing us an opportunity to clarify our manuscript. Figure 3 shows the condition of CrI_3 inside and outside a hermetic cell. It remains unchanged after 15 h inside a cell and only begins to show changes after 24 h. Outside the cell, the same CrI_3 flake begins to degrade within seconds. The claim comes from hours in the cell as compared to seconds outside (ratio > 10^3). This calculation is now mentioned in the manuscript.

Comment 4:

Scale bars in Figure 3 should be provided.

We thank the reviewer for pointing out this omission, which has been fixed in the revised manuscript.

Reviewer 2 comments:

Major Concerns:

This manuscript presents a hot exfoliation method for preparing several layered materials,

which is important for promote the study of 2D materials. Besides, the authors designed a transfer cell for protect some sensitive layered materials from oxidation and degradation, which can be widely used for further characterization. However, the main details and mechanism had been clearly shown in Ref. 19, this manuscript is just an extension of Ref. 19 and didn't show any advantage compared with Ref. 19. Mechanical exfoliation method is widely used in the 2D material society, but it was never deeply studied before Ref. 19 coming out. Besides, the hot exfoliation is not a new concept in this work, many layered materials were successfully exfoliated by using the method presented in Ref. 19, such as MoS2, BP, and WSe2, et al. Some detailed suggestions are listed below:

The reviewer is correct that hot exfoliation for a variety of layered materials has been demonstrated before and that the exfoliation process alone is certainly not unique to this protocol, nor do we have the intention to claim that it is. We believe the novelty of our report lies in the high flake yield of hot exfoliation *combined* with the ability to safely analyze air-sensitive 2D materials outside of an inert environment without the need of specialized equipment or expensive modifications to existing equipment. Hot exfoliation is included in the protocol because it is the best way we have found, thanks to Ref. 20, to exfoliate thin flakes, and the purpose of the transfer cell is to facilitate finding and analyzing flakes of 2D materials. Additionally, we believe that providing a video protocol of these methods, including hot exfoliation, will provide a significant help to some in the 2D material community, while also disseminating more broadly the insights and utility of the techniques analyzed in Ref. 20.

Comment 1:

Please recheck the references, some references are not cited properly. For example, line 67, "such as CVD growth", if you want to cite one CVD graphene paper among thousands reports, the authors should cite the first CVD graphene on copper (Science 324, 1312-1314 (2009)) or on some other metal substrate (Nature Materials volume7, 406-411 (2008)). These two papers were published earlier than Ref. 14, so I suggest to change Ref. 14 by the two papers. Line 219-221, O2 plasma was used for cleaning the substrate, it can enhance the exfoliation yield ratio, which has also been reported in Ref. 19 (ACS Nano. 9 (11), 10612-10620), are there any details shown in Ref. 20 that O2 plasma can help to exfoliate 2D materials?

The reviewer is correct on both points, and we have revised the manuscript accordingly. Ref. 14 has been changed to the suggested citations and Ref. 20 (*Baden-Powell, B. H. Hand-book of the economic products of the Punjab, with a combined index and glossary of technical vernacular words)* has been removed. It should have been Ref. 20 (ACS Nano. 9 (11), 10612-10620) (previously Ref. 19).

Comment 2:

The authors used BP and CrI3 to demonstrate that the new designed transfer cell can help to protect some air sensitive layered materials, some papers about the stability of BP and CrI3

are suggested to cite in this work. Previously, there are some misleading views about the degradation mechanism, especially for BP, understanding the degradation mechanism can be very helpful for designing the protecting facilities. The degradation mechanism was just clarified two years ago (Chem. Mater., 2016, 28 (22), pp 8330-8339), so I suggest to cite that work in this manuscript.

We thank the reviewer for pointing out this important reference, which has been added to the manuscript.

Comment 3:

In the Discussion part, the mechanism of hot exfoliation was not clearly explained, for example, after removing the molecules absorbed on substrate surface, the contact distance between layered materials and substrate were decreased, which is helpful to enhance the van der Waals interaction. In fact, the mechanism has clearly given in Ref. 19.

Because the discovery of the mechanism for improved yield via hot exfoliation is not new in our work, we prefer to summarize the results of Ref. 20 (previously Ref. 19) and provide a citation to the original work. Additionally, we have revised our summary statement of the mechanism for clarity.

Comment 4:

The authors mention that HF-cleaned substrate can help to exfoliate many layered materials, could the authors give more details. Normally, HF can etching SiO2 in a short time.

It is correct that a 10% solution of HF in water does etch SiO2 rather quickly (23 nm/min) and this is now mentioned in the manuscript, but we do not claim that it can help to exfoliate layered materials. In fact, it is quite the opposite. HF cleaned SiO2 reduces flake adhesion, but this can be useful when building heterostructures where it is necessary to pick up exfoliated flakes. Some layered materials, for example BP, are more difficult to pick up than others and exfoliating on HF cleaned substrates improves our chances of successfully picking up a desired flake. We mention this in the manuscript because some methods for increased material exfoliation (O2 plasma treated substrates) can also make the material very difficult to pick up. Given the significant current interest in the field of forming 2D material heterostructures via pick-up and stacking, we believe it is important to include a discussion of HF-treatment of substrates.