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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 cm2”.

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 CrI3 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 CrI3 flake begins to degrade within seconds. The claim comes from hours in the cell as compared to seconds outside (ratio > 103). 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.