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## A system for the deterministic transfer of 2D materials under inert environmental conditions

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## PAPER

## A system for the deterministic transfer of 2D materials under inert environmental conditions

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Supplementary material for this article is available [online](#)

### Abstract

The isolation of air-sensitive two-dimensional (2D) materials and the race to achieve a better control of the interfaces in van der Waals heterostructures has pushed the scientific community towards the development of experimental setups that allow to exfoliate and transfer 2D materials under inert atmospheric conditions. These systems are typically based on over pressurized N<sub>2</sub> of Ar gloveboxes that require the use of very thick gloves to operate within the chamber or the implementation of several motorized micro-manipulators. Here, we set up a deterministic transfer system for 2D materials within a gloveless anaerobic chamber. Unlike other setups based on over-pressurized gloveboxes, in our system the operator can manipulate the 2D materials within the chamber with bare hands. This experimental setup allows us to exfoliate 2D materials and to deterministically place them at a desired location with accuracy in a controlled O<sub>2</sub>-free and very low humidity (<2% RH) atmosphere. We illustrate the potential of this system to work with air-sensitive 2D materials by comparing the stability of black phosphorus and perovskite flakes inside and outside the anaerobic chamber.

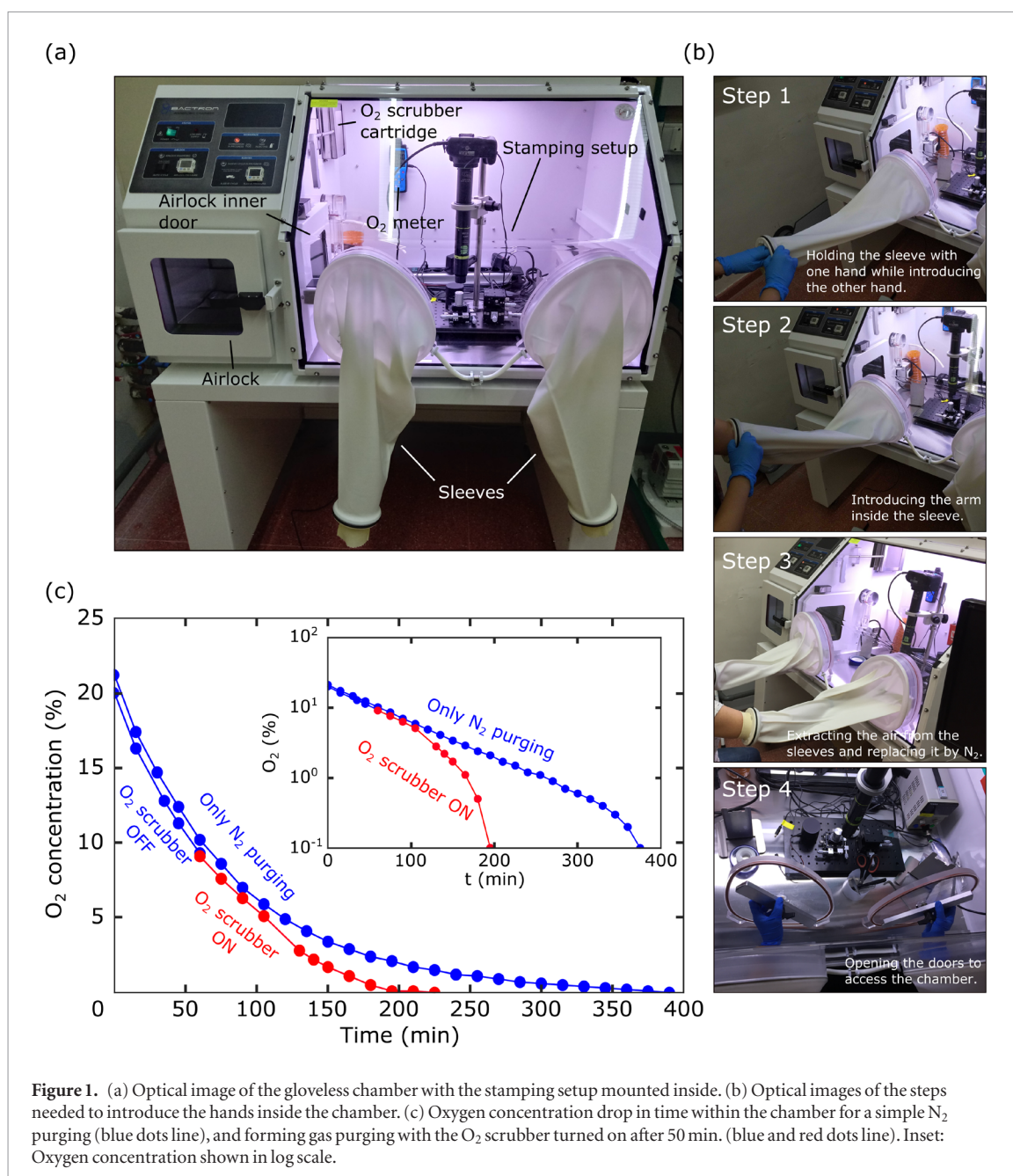
The deterministic transfer methods, that allow for the placement of 2D materials onto a user defined specific location with an unprecedented degree of accuracy and reliability, are at the origin of the large success of two-dimensional (2D) materials research [1–6]. This control over the position of the transferred flakes has been exploited to fabricate devices with rather complex architectures as well as to assemble artificial stacks of dissimilar 2D materials to build-up the so-called van der Waals heterostructures [7–10]. In particular, deterministic placement methods have enabled the fabrication of 2D-based samples fully-encapsulated between insulating layers of hexagonal boron nitride (hBN), exhibiting record-high electronic performance that allowed for the observation of intriguing physical phenomena [4, 6]. Nonetheless, there are two main challenges of this line of research: (1) how to achieve a better control of the interfaces [11–13], (2) how to

handle air-sensitive 2D materials [14, 15]. Indeed, the continuous race to increase the performances of 2D devices and the isolation of novel unstable 2D materials under atmospheric exposure, have pushed towards the development of experimental setups where the transfer process can be carried out under controlled environmental conditions [14, 16, 17]. Although several research groups have implemented their own systems based on N<sub>2</sub> or Ar glove-boxes, the literature is lacking of comprehensive technical articles providing enough details for reproducing such systems by other groups. Moreover, these glove-box-based systems can be difficult to operate as delicate manual operation (e.g. mechanical exfoliation, handling small substrates with tweezers, ...) have to be carried out while wearing thick gloves. In order to overcome this handicap, some systems are fully motorized and thus do not require any manual operation within the glovebox,

**Table 1.** List of all the setup components, which includes the part numbers and the prices.

Component	Description	Part number	Distributor	Price
Chamber <sup>a</sup>	Bactronez 12.5 CU.FT.I 354 L, anaerobic chamber, 300 plate capacity	BAAEZ22	Bactron-Sheldon manufacturing	14 700.00 €
Optomechanical component	Breadboard, ferromagnetic steel	1BS-2040-015	Standa	130.00 €
	Post 3/4" dia stainless posts, vertical post 18"	39-353	Edmund optics	57.00 €
	Mounting Post Base, Ø2.48" × 0.40" thick	PB1	Thorlabs	22.44 €
Zoom lens	Focusing, coarse/fine movement, 50 mm diameter thru hole, rack and pinion	54-792	Edmund optics	355.00 €
	EOS camera adapter	89-862	Edmund optics	75.00 €
	3.0× mini-camera tube	89-877	Edmund optics	725.00 €
	7× zoom module, manual	89-878	Edmund optics	750.00 €
	Lower module w/in-line illumination	89-888	Edmund optics	275.00 €
	4.0× lower lens	89-903	Edmund optics	275.00 €
	Fiber optic light guide adapter	89-919	Edmund optics	125.00 €
	Fiber optic light guide adapter to 10 mm	89-920	Edmund optics	55.00 €
Illumination	Bench power supply, linear, adjustable, 1 output, 0 V, 30 V, 0 A, 5 A	72-2690	Farnell	71.34 €
	LED, white, through hole, T-3 (10 mm), 20 mA, 3.5 V, 8 cd	VAOL-10GWY4	Farnell	0.47 €
	Quartz Tungsten-Halogen Lamp	QTH10	Thorlabs	157.58 €
Oxygen meter	Oxygen detector	AR8100	Smart sensor	81.10 €
Stages	Manual XY linear stage	MAXY-B60L-13	Optics focus solutions	72.10 €
	Manual XYZ stage	MAXYZ-60L	Optics focus solutions	164.00 €
	Square neodymium magnets N52 10 × 10 × 4 mm	Amazon shop	Magnetastico	18.99 €
	Ø1.40" manual mini-series rotation stage, metric	MSRP01/M	Thorlabs	66.53 €
Camera	Canon EOS 1300D—18 Mp (3" screen, Full HD, NFC, WiFi)		Canon	324.00 €
	Power supply for Canon EOS 1300D-ca. 3 m, (ACK-E10)	916606	Subtel	14.95 €
	Memory card	SDSDUNC-032G-GZFIN	SanDisk	9.99 €
	Mini HDMI to HDMI cable		AmazonBasics	6.00 €
Screen	TV 32" Led HD	K32DLM7H	TD systems	139.00 €
TOTAL				18 670.49 €

<sup>a</sup> Note that the Bactronez anaerobic chamber includes: sleeves, elastic rubber sealing rings, sleeve compartment doors, integrated dry vacuum pump for the sleeve and the interlock purging, external lights, two sets of oxygen scrubber catalysts.



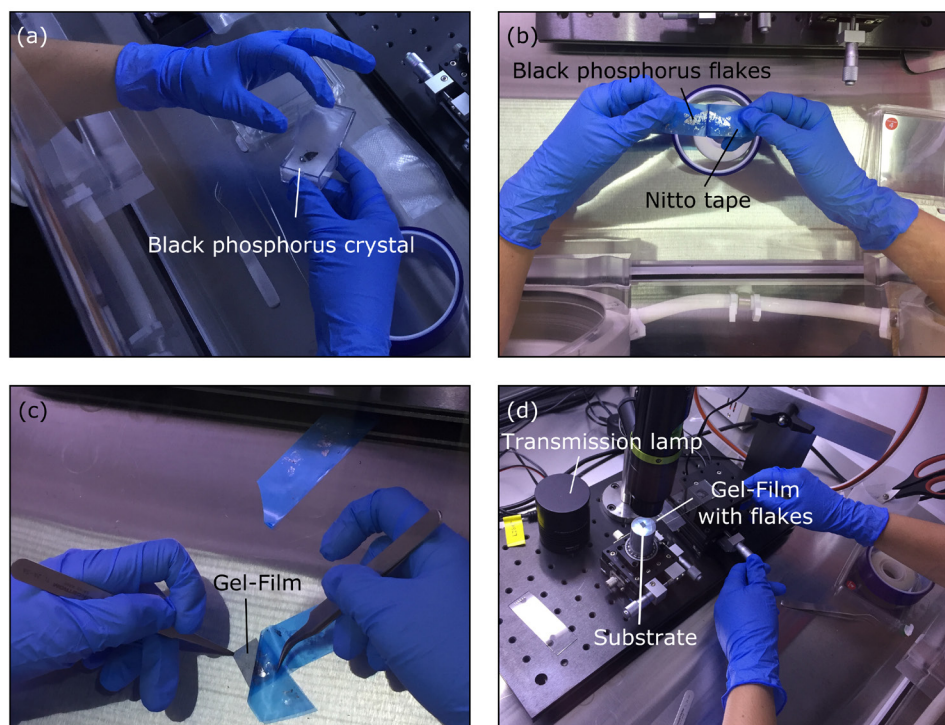
increasing substantially their cost and complexity of implementation [18].

Here, we present an alternative concept of deterministic transfer setup operated in inert conditions that is based on a gloveless anaerobic chamber. The user can operate inside the chamber using his/her bare hands without the need of thick glove-box gloves, making the transfer process virtually as easy as that carried out in air (outside the anaerobic chamber). Importantly, in the manuscript we provide all the details needed to facilitate the implementation of this system by other research groups.

Table 1 summarizes the different components needed to assemble our experimental system; whose cost is under the 20000 €. We address the reader to the supp. info. ([stacks.iop.org/TDM/7/025034/mmedia](https://stacks.iop.org/TDM/7/025034/mmedia)) for pictures of the different steps during the setup assembly process and for more details about the setup construction.

We build our transfer system within a gloveless anaerobic chamber (Bactronez 12.5). In order to access the interior part of the chamber, the system has two sealed doors connected to two plastic sleeves equipped with an elastic rubber sealing ring at their free end. The operator inserts his/her bare arms in the sleeves until feeling tight the rubber sealing ring around the arms like shown in figure 1(b). Then, the sleeves are pumped down and purged with N<sub>2</sub> three times. After this process, the operator can open the two sealed doors without altering the environmental conditions inside the chamber. The system is equipped with a scrubber cartridge with Pd coated pellets (which act as a catalyst) that actively remove O<sub>2</sub> from the chamber through the reaction  $2\text{H}_2 + \text{O}_2 \xrightarrow{\text{Pd}} 2\text{H}_2\text{O}$  [19] when the system is purged with forming gas (N<sub>2</sub> + 5% H<sub>2</sub>) mixture. The H<sub>2</sub>O generated during the O<sub>2</sub> capture reaction is condensed in a big silica gel reservoir. We show in fig-





**Figure 2.** (a) Manipulation of the box with the bulk black phosphorus inside the chamber. (b) Mechanical exfoliation with Nitto tape by hand in the chamber. (c) Black phosphorus flakes being transferred onto the Gel-Film stamp after exfoliation with Nitto tape. (d) Handling the micrometer XYZ stage to deterministically transfer a flake.

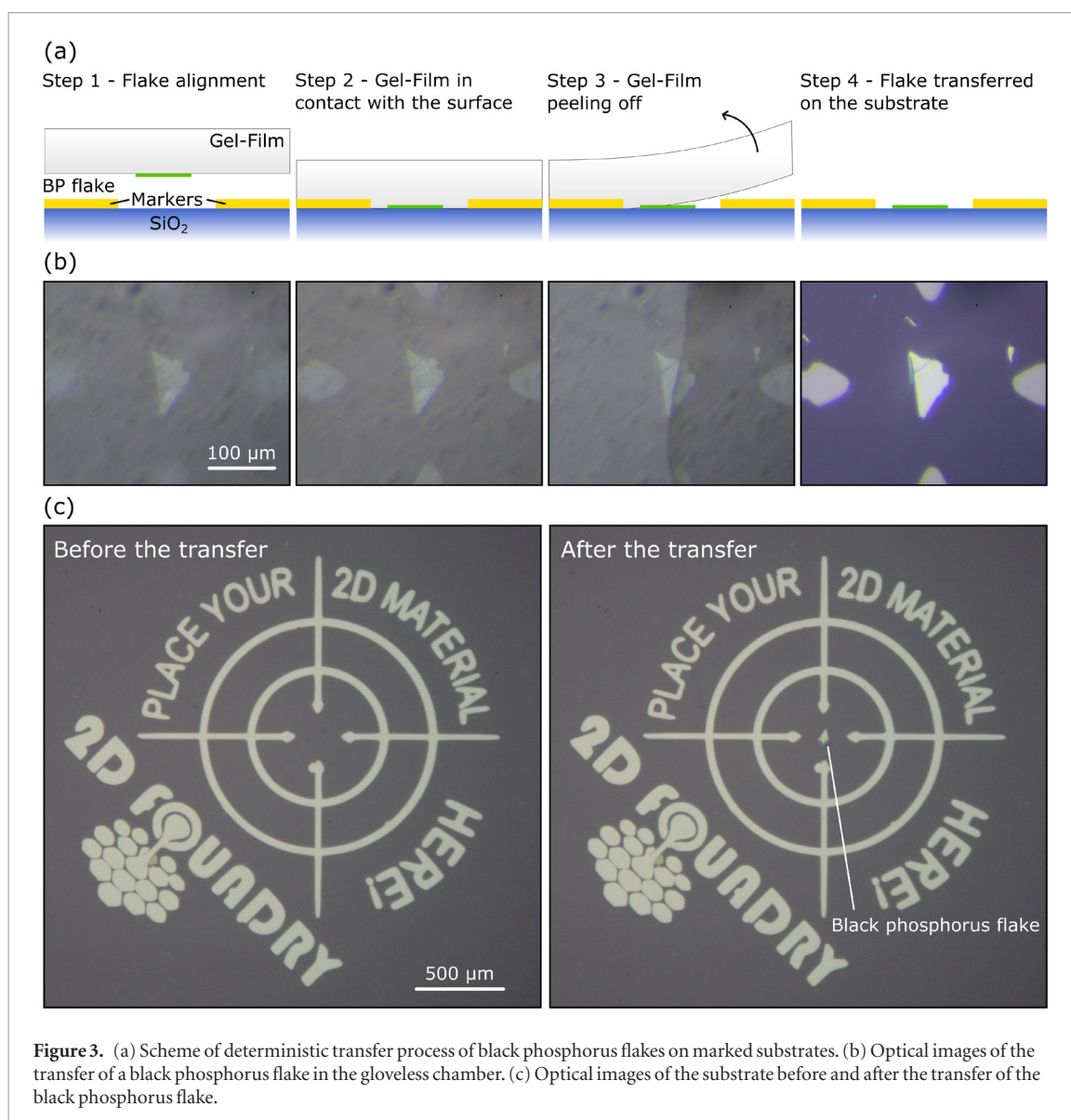
ure 1(c) a comparison of the  $O_2$  concentration evolution when the chamber is simply purged with  $N_2$  ( $O_2$  scrubber system OFF) and when the catalytic  $O_2$  capture is employed ( $O_2$  scrubber system ON). We found that the  $O_2$  scrubber speeds up the  $O_2$  concentration drop by a factor of 5 with respect to the simple  $N_2$  purge. In fact, these kind of gloveless anaerobic chambers with active  $O_2$  removal have proven to be very effective to generate environmental conditions with very low  $O_2$  levels (in the 10 ppm range) [20].

Figure 2 shows how the operator is preparing a Gel-Film (WF  $\times 4$  6.0 mil, by Gel-Pak<sup>®</sup>) stamp with mechanically exfoliated black phosphorus. These pictures illustrate how the operator is able to easily carry out all the required delicate manual tasks (handling of tweezers, cutting, peeling, etc) as he/she does not need to wear thick glove-box gloves. Briefly, a bulk piece of black phosphorus (HQ Graphene) is exfoliated using Nitto SPV224 tape. The tape containing the exfoliated black phosphorus flakes is gently pressed against the surface of a rectangle piece of Gel-Film substrate that will be used as viscoelastic stamp for the deterministic transfer [2]. The stamp is secured overhanging in the edge of a microscope glass slide with Scotch tape (Magic tape) and the glass slide is fixed to a XYZ micro-manipulator stage, that will be used to move the stamp, with double side tape (Scotch restickable tabs). In order to identify the flake to be transferred, we place a collimated light source (Thorlabs quartz tungsten-halogen lamp, QTH11) under the stamp allowing us to infer the thickness of the flakes from its transmittance [21].

Once the desired flake is located, the lamp is replaced by an XY-rotation stage that will be used to move the acceptor sample (also fixed to the stage with double side Scotch restickable tabs).

Figure 3 shows a sequence of optical microscopy images acquired with the transfer system zoom lens during the deterministic placement of a black phosphorus flake onto a  $SiO_2/Si$  substrate with a pre-patterned alignment crosshair. First, the flake is aligned in the center of the crosshair markers. Then, the Gel-Film stamp is lowered until establishing a gentle contact between stamp and acceptor sample. Finally, the stamp is slowly peeled off until it is completely removed, and the flake is successfully transferred in the middle of the crosshair. The possibility to place flakes at a desired location (as shown in figure 3) can be further exploited to fabricate van der Waals heterostructures by stacking different 2D materials on top of each other. Figure 4 demonstrates the capability of our inert atmosphere deterministic placement system to fabricate this kind of artificial stacks of 2D materials. The different transfer steps to fabricate a heterostructure based on a few-layer black phosphorus (BP) flake sandwiched between two flakes of hexagonal boron nitride (hBN) are shown in figure 4.

In order to benchmark the potential of the gloveless anaerobic chamber to manipulate air-sensitive 2D materials, we monitor the evolution of the black phosphorus flake (transferred in figure 3) inside the anaerobic chamber through optical microscopy images with the system's zoom lens. Black phosphorus is well-

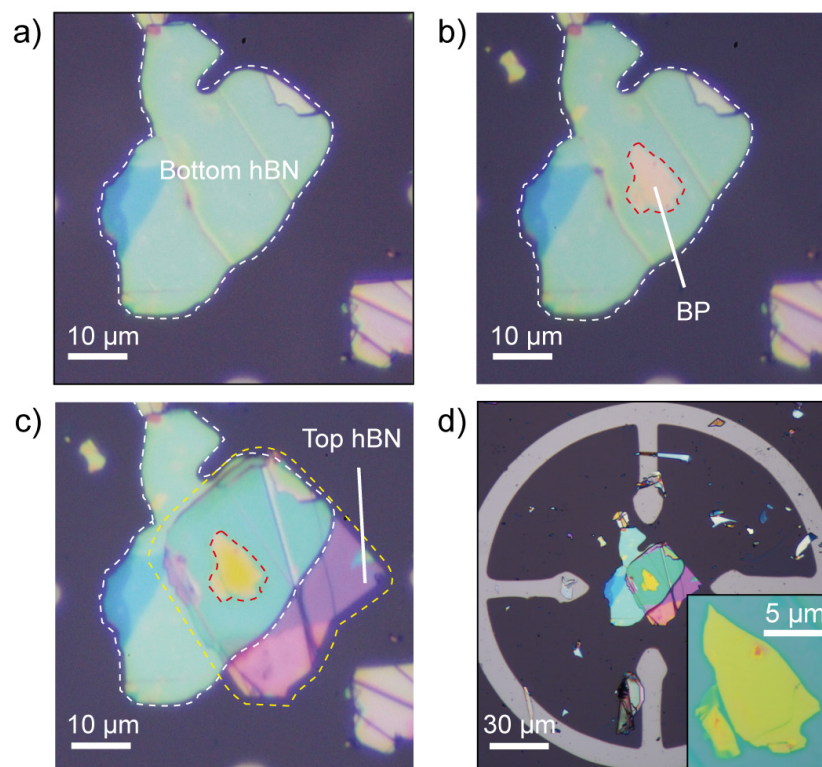


known for its instability under air exposure [22–24]. We do not notice any change in the optical microscopy images after 22 days inside the chamber. On the other hand, after taking the flake outside the chamber, it quickly shows signs of degradation from day 3 of air exposure (see inset in figure 5 with increased contrast) and it becomes severely damaged after 9 days of exposure. In figure 5, we show the optical contrast profiles acquired from the optical images of the black phosphorus sample along the black line indicated in the first panel. The profiles present a clear increase in roughness under air exposure due to the degradation, comparing with the profiles of the images of the flake inside the chamber. This illustrates the potential of this experimental setup for handling air-sensitive 2D materials.

Furthermore, we also checked the performance of the gloveless anaerobic chamber with even more unstable 2D materials. We studied a compound that belongs to the metal halide perovskites family that is known to quickly degrade upon atmospheric exposure [25–27]. The metal halide perovskites are a prominent

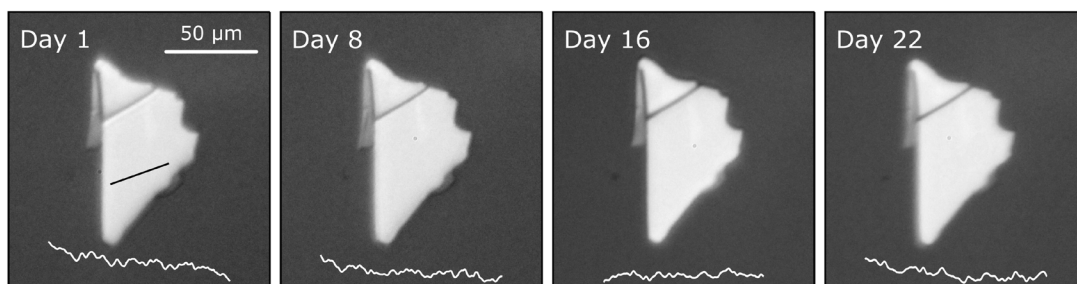
group of materials in the solar harvesting research [28–30], optoelectronics [31–33] and photovoltaics [34, 35] which degrade rapidly when exposed to air or light [25, 36, 37]. In our case, the compound used is phenethylammonium lead iodide (PEA<sub>2</sub>PbI<sub>4</sub>) 2D perovskites synthesized according to the techniques described in [27, 38, 39]. The bulk crystals are exfoliated and transferred to a SiO<sub>2</sub>/Si substrate inside the anaerobic chamber. Then, the sample is monitored for 5 h by acquiring microscope optical pictures, similar to the procedure used in the black phosphorus sample (figure 6). Again, no apparent change of the material is observed during the 5 h in inert atmosphere. However, the surface of the perovskite flakes quickly showed degradation signs after just 15 min outside the chamber. In this case, we show the optical contrast of the flake to illustrate the degradation upon air exposure (see the supporting information for the analysis of the time evolution of the optical contrast). Given the results, we conclude that the atmosphere in the anaerobic chamber allows the handling of very air-sensitive 2D materials.



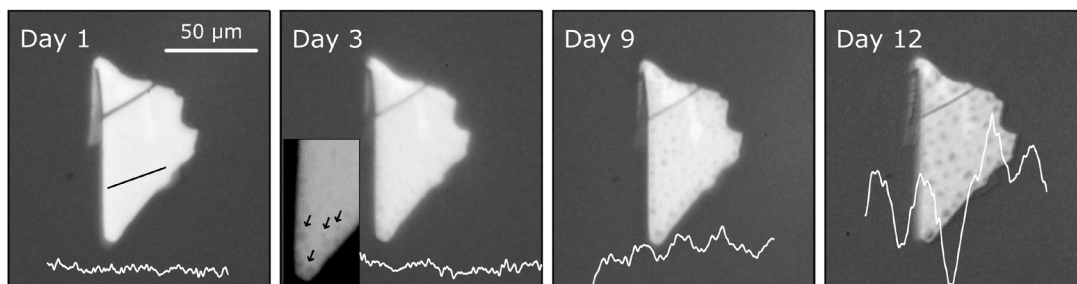


**Figure 4.** Fabrication of a van der Waals heterostructure under inert atmospheric conditions. (a) Optical image of hexagonal boron nitride (hBN) flake transferred onto a SiO<sub>2</sub>/Si substrate. (b) black phosphorus (BP) flake transferred onto the boron nitride flake. (c) a top hBN flake is transferred to complete the hBN/BP/hBN stack. (d) A low magnification image of the assembled heterostructure in the middle of a crosshair marker. The inset shows a higher magnification optical microscopy image of the hBN/BP/hBN heterostructure.

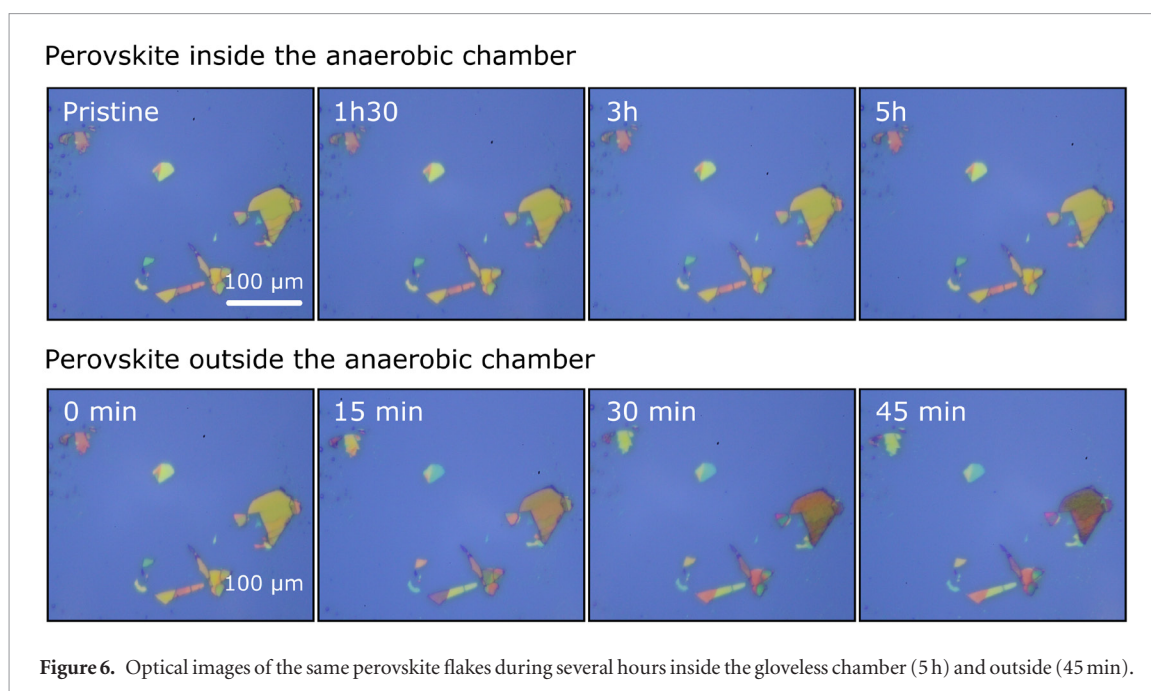
#### BP inside the anaerobic chamber



#### BP outside the anaerobic chamber



**Figure 5.** Optical images (showing the green channel which provides the highest contrast) of the same BP flake during several days inside the gloveless chamber (22 d) and outside it (12 d).



**Figure 6.** Optical images of the same perovskite flakes during several hours inside the gloveless chamber (5 h) and outside (45 min).

In summary, we have developed a system to precisely transfer 2D materials under inert atmosphere and we provide all necessary technical details to allow its implementation in other laboratories. Unlike other inert atmosphere transfer system used in the literature based on  $N_2$  or Ar over pressurized gloveboxes, our system relies on a gloveless anaerobic chamber with an active  $O_2$  catalytic capturing system. Our setup allows the operator to work with his/her bare hands within the chamber, which facilitate tasks as scissors cutting, tape peeling, tweezer handling, etc that are challenging to be done while wearing thick gloves required to access the interior of an over pressurized  $N_2$  or Ar glove-box. We illustrate the operation of our transfer setup by showing the deterministic transfer of a black phosphorus flake and by studying the stability of thin black phosphorus and perovskite flakes. We believe that the simple operation and the low cost (<20000 €) of this setup makes it highly attractive for other research groups that have not yet implemented a transfer system under inert atmosphere.

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