

Reliable Exfoliation of Large-Area High-Quality Flakes of Graphene and Other Two-Dimensional Materials

Yuan Huang,[†] Eli Sutter,[‡] Norman N. Shi,[§] Jiabao Zheng,[∥] Tianzhong Yang,[⊥] Dirk Englund,[∥] Hong-Jun Gao,[⊥] and Peter Sutter^{*,#}

[†]Center for Functional Nanomaterials, Brookhaven National Laboratory, Upton, New York 11973, United States, [‡]Department of Mechanical & Materials Engineering, University of Nebraska—Lincoln, Lincoln, Nebraska 68588, United States, [§]Department of Applied Physics and Applied Mathematics, Columbia University, New York, New York 10027, United States, ^{II} Electrical Engineering and Computer Science, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, United States, ^{II} Institute of Physics, Chinese Academy of Sciences, P.O. Box 603, Beijing 100190, China, and [#]Department of Electrical & Computer Engineering, University of Nebraska—Lincoln, Lincoln, Nebraska 68588, United States

ABSTRACT Mechanical exfoliation has been a key enabler of the exploration of the properties of two-dimensional materials, such as graphene, by providing routine access to high-quality material. The original exfoliation method, which remained largely unchanged during the past decade, provides relatively small flakes with moderate yield. Here, we report a modified approach for exfoliating thin monolayer and few-layer flakes from layered crystals. Our method introduces two process steps that enhance and homogenize the adhesion force between the outermost sheet in contact with a



substrate: Prior to exfoliation, ambient adsorbates are effectively removed from the substrate by oxygen plasma cleaning, and an additional heat treatment maximizes the uniform contact area at the interface between the source crystal and the substrate. For graphene exfoliation, these simple process steps increased the yield and the area of the transferred flakes by more than 50 times compared to the established exfoliation methods. Raman and AFM characterization shows that the graphene flakes are of similar high quality as those obtained in previous reports. Graphene field-effect devices were fabricated and measured with back-gating and solution top-gating, yielding mobilities of ~4000 and 12 000 cm²/(V s), respectively, and thus demonstrating excellent electrical properties. Experiments with other layered crystals, *e.g.*, a bismuth strontium calcium copper oxide (BSCCO) superconductor, show enhancements in exfoliation yield and flake area similar to those for graphene, suggesting that our modified exfoliation method provides an effective way for producing large area, high-quality flakes of a wide range of 2D materials.

KEYWORDS: 2D materials · graphene · exfoliation · van der Waals force · processing

ince the first successful exfoliation of monolayer graphene in 2004,¹ graphene and other 2D materials, such as h-BN, MoS₂, SnS₂, and others,²⁻⁴ have gained large attention due to their distinctive properties. Graphene as the first discovered 2D material has provided access to new physics at single atomic thickness, such as unique electrical,^{5,6} mechanical,⁷ optical,⁸ and sensing properties.^{9,10} BN is widely used as an ideal electrically insulating substrate for vertical heterostructures with other 2D materials.^{11–13} Layered metal dichalcogenides (MX₂) exhibit interesting properties when their thickness is reduced to single- or few layers,^{3,14} and MX₂ field-effect transistors

(FETs) demonstrated device properties such as current on/off ratio up to 10⁸ (ref 3) and high charge carrier mobility.^{15,16}

Exfoliation of monolayer or few-layer flakes from layered bulk crystals has played a central role in the development of 2D materials,¹⁷ and it continues to be the primary method to rapidly gain access to highquality flakes for exploring novel materials systems. For example, nearly all of the novel properties of graphene were first discovered and measured on exfoliated flakes: the unusual quantum Hall effects in monolayer and bilayer graphene,^{6,18} Berry's phase,⁶ the thickness-dependent Raman spectrum,¹⁹ *etc.* Scalable growth techniques such as

* Address correspondence to psutter@unl.edu.

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chemical vapor deposition (CVD) have been used to grow large-area graphene films on different substrates, such as copper (Cu),²⁰ ruthenium (Ru)^{21,22} SiC²³ and others. But the development of optimized growth and isolation approaches has proven to be a time-consuming process, since phenomena such as the formation of defects^{23,24} and grain boundaries²⁵ during growth need to be understood and controlled before a materials quality similar to that obtained by exfoliation can be achieved. Hence, it can be expected that exfoliation will continue to play a prominent role in the development of 2D materials.

More than 10 years after the first isolation of graphene, the highest quality samples are still produced by the nearly unchanged original top-down mechanical exfoliation method with relatively low yield and small size of the resulting single- or few-layer flakes, though efforts have been made to improve the exfoliation yield. Jayasena et al. devised a lathe-like experimental setup to cleave HOPG samples for generating graphene flakes,²⁶ but the thinnest resulting flakes typically have a thickness of tens of nanometers. Coleman and co-workers first reported the high-yield production of graphene by sonication assisted liquidphase exfoliation of graphite,²⁷ but the relatively small size of monolayer flakes, along with low quality and low yield, limits its use in both research and applications. Shukla et al. reported a different exfoliation approach based on anodic bonding of graphite to insulating (Pyrex, borosilicate glass) supports.²⁸ Moldt and co-workers later reported a detailed survey of the process parameter space in the anodic bonding process, identified conditions for large-yield production of graphene flakes on glass, and transferred the flakes on SiO₂/Si substrates to demonstrate high carrier mobility (up to 6000 $\text{cm}^2/(\text{V s})$) in electrical measurements on back-gated devices.²⁹ While capable of substantially increasing the yield and flake size over conventional exfoliation methods, anodic bonding suffers from a number of practical difficulties: the need of applying high voltage (0.6-1.2 kV) between the support and a graphite crystal at high temperatures (~180–250 °C) and, most importantly, the limitation to certain classes of materials, e.g., electrically conducting layered crystals (ruling out important systems, such as h-BN) and substrates with relatively mobile ions, such as borosilicate glass. The latter not only makes the identification of thin graphene sections difficult due to low optical contrast, but also complicates device fabrication (e.g., for back-gated transport measurements) by requiring additional transfer steps to other substrates. There were other reports of very large graphene flakes in the literature. For example, Geim showed a large (~0.9 \times 0.5 mm) exfoliated graphene flake, 30 but no explanation was provided about the way such flakes are obtained and the reproducibility of the method used. To our knowledge, there are no reports on

mechanistic studies of the original mechanical exfoliation method developed by Novoselov;¹ hence, a simple and effective way of exfoliating large-area graphene with high quality is still lacking.

Besides the quality of the layered bulk crystal, the competition of van der Waals forces between the sheets in a layered crystal and between the outermost sheet and a substrate is critical for exfoliation of thin flakes with high yield and large area. To identify a possible optimization of the exfoliation process, we studied ways of enhancing the interaction between graphene and a substrate during exfoliation by creating large, uniform contact areas that maximize the overall van der Waals interaction that transfers a thin flake from its mother crystal. Our results allow us to formulate an effective method for exfoliating graphene with high quality, high yield, and exceptionally large area. The generality of this exfoliation process is demonstrated by isolating large flakes of BSCCO. We expect that our process can be applied to the exfoliation of a wide variety of 2D materials.

RESULTS AND DISCUSSION

Figure 1 illustrates the process steps in our modified exfoliation method, shown here for the example of graphene exfoliation. Similar to the established processes, we used SiO₂/Si as the substrate and ordinary adhesive tape as the transfer medium. Contact with the tape transfers thick graphite flakes from a highly oriented pyrolitic graphite (HOPG) crystal (Figure 1a). Prior to exfoliating thin graphene from these flakes, the SiO₂/Si substrate is ultrasonically cleaned in acetone, 2-propanol, and deionized (DI) water, and then subjected to oxygen plasma to remove ambient adsorbates from its surface (Figure 1b). Following the plasmacleaning step, the graphite-loaded tape is brought in contact with the substrate. Instead of immediately removing it to complete the exfoliation, the substrate with the attached tape is annealed for 2-5 min at \sim 100 °C in air on a conventional laboratory hot plate (Figure 1c). After the sample is cooled to room temperature, the adhesive tape is removed (Figure 1d), which completes the exfoliation. Inspection by optical microscopy shows the successful transfer of few-layer graphene to the SiO₂/Si substrate. The linear dimensions of areas with uniform thickness are routinely in the range from \sim 20 μ m to well above 100 μ m, and the thin (few-layer) sections of the flakes are up to several 100 μ m in size (Figure 1f).

Figure 2 shows optical micrographs comparing graphene flakes prepared by the standard exfoliation method and our modified approach. The graphene flakes were exfoliated onto Si substrates terminated by 300 nm SiO₂ to benefit from the enhanced optical contrast of graphene.³¹ Additional optical images of exfoliated graphene are shown in the Supporting Information (Figure S1). We also exfoliated graphene

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Figure 1. Illustration of the modified exfoliation process for layered crystals (shown here for graphene). (a) Optical image of the SiO₂/Si substrate and adhesive tape with graphite flakes, which adhere after contact with a HOPG crystal. (b) Oxygen plasma cleaning of the SiO₂/Si substrate. (c) Contact between the graphite decorated tape and the substrate surface, followed by heating of the substrate (with tape) on a hot plate in air at ~100 °C for 2 min. (d) Removal of the substrate from the hot plate and peeling off of the tape. (e) Optical image of the substrate after graphene exfoliation. (f) Optical micrograph of one of the graphene flakes on the substrate in (e). The flake has a thickness varying in steps between 1-4 layers.



Figure 2. Optical images of graphene flakes prepared by the standard exfoliation method and our modified method. (a and b) Optical microscopy images of typical monolayer to trilayer graphene prepared by the standard method, including a solvent wash and O_2 plasma cleaning of the substrate followed by graphene transfer. (c and d) Optical microscopy images of two graphene flakes prepared by the new, modified method, with O_2 plasma clean of the SiO₂/Si surface, followed by contact with graphite-loaded tape, annealing to 100 °C, cooling to room temperature and peel-off.

onto 100 nm SiO₂/Si substrates and obtained similar results (Figure S2). The size of the monolayer exfoliated by the standard method is around $20 \times 20 \,\mu$ m², typical for large monolayer flakes prepared by this approach. Previous reports^{5,6} show graphene flakes with size less than $\sim 20 \times 20 \,\mu$ m². Figure 2b is an optical image of a bilayer and trilayer flake with size of $\sim 40 \times 40 \,\mu$ m², larger than previously reported bilayer and trilayer graphene devices.³² Figure 2c,d shows typical graphene flakes prepared by our modified exfoliation method. The flake size in Figure 2c is $\sim 500 \times 350 \,\mu$ m², more than 400 times larger than the flake shown in Figure 2a.

The bilayer flake in Figure 2d is \sim 700 \times 200 μ m². From the comparison, we conclude that our modified method makes it easier to obtain large-area flakes than the standard method.

It is important to point out that monolayer and few layer graphene flakes are cleaved from multilayer graphite, and not from the tape itself. Hence, the actual exfoliation step is governed by a competition of attractive forces between the layers in the thick flakes of layered crystal held by the tape and between the outermost layer and the substrate. This suggests that it is not necessary-and likely even detrimental-to attach the thinnest possible materials to the tape and then bring them in contact with the SiO₂ surface, because it is hard to transfer monolayer graphene directly from tape to substrate. In addition, our experience shows that exfoliating graphite too many times will split the flake into small pieces, which makes it impossible to transfer large area graphene flakes. In practice, we only exfoliate the graphite pieces adhered to the tape 3 to 4 times after removing them from bulk graphite, and the flakes on the tape are still guite thick before we make contact with the SiO₂ surface.

To further compare the standard exfoliation with our modified method, we prepared 4 samples each by both approaches, using similar sized (2 cm \times 2 cm) substrates and graphite flakes obtained from the same bulk graphite crystal. We put a blank tape onto a section of tape with 4 graphite zones (analogous to the 3 zones shown in Figure 1a), and separated the two tapes before putting the graphite flakes in contact with the 8 SiO₂/Si substrates. This ensured that the sizes of both substrate and graphite flakes were the same. Following our modified exfoliation method, we annealed 4 of the substrates together with graphite/tape on a hot plate at 100 °C for 2 min; the other 4 substrates were left at room temperature and the tape peeled off

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agnanc www.acsnano.org after manually pressing the tape–substrate sandwich for 1 min. After the sample was gently pressed and cooled to room temperature, the tape was likewise peeled off the 4 annealed samples. We then inspected all samples by optical microscopy. Figure 3 shows a comparison of the combined surface areas of the resulting graphene flakes on each sample. The total graphene area on the $2 \times 2 \text{ cm}^2 \text{ SiO}_2/\text{Si}$ substrates 1-4(*i.e.*, those prepared by standard exfoliation) is on the order of a few thousand square micrometers. For example, the third sample shows a total graphene area of $1500 \,\mu\text{m}^2$, whereas the best sample has 8 graphene flakes with a total graphene area of $3500 \,\mu\text{m}^2$. For the samples prepared by the modified exfoliation method with annealing prior to tape separation, the total



Figure 3. Total area of exfoliated graphene on 8 different samples. Samples 1–4 were prepared by the standard exfoliation process; samples 5–8 were prepared by the method introduced here. The size of all substrates was $2 \times 2 \text{ cm}^2$.

graphene areas for all samples are above 60 000 μ m², with the best sample showing 85 200 μ m² graphene. We conclude that the yield (i.e., the total area of graphene obtained in a single exfoliation experiment) of our modified method is 20-60 times higher than that of the standard method. We performed additional experiments aimed at identifying the role of time and temperature of the annealing step introduced here. The results of these experiments are summarized in the Supporting Information, Table S1. Within the probed parameter range, the exfoliation yield was generally high. Indeed, the total graphene area did not strongly depend on anneal time and temperature as we changed the annealing time from 2 to 30 min, and temperature from 80 to 140 °C. The highest yield, obtained for annealing at 100 °C for 2 min, was \sim 60% higher than the lowest yield observed (140 °C, 2 min), with all samples yielding substantially larger overall quantities of exfoliated graphene than the standard method, in line with the results shown above. From a practical perspective, increasing the annealing time and temperature has another negative effect, namely a substantially larger amount of glue residue distributed from the adhesive tape to the substrate surface (see Figure S4). Hence, we find that annealing at 100 °C for 2 min represents a good overall compromise of large graphene flakes, high exfoliation yield, and minimal amounts of residual glue.

AFM imaging provides an independent measurement of the absolute thickness and morphology of 2D materials. Figure 4a shows a graphene flake with one folded ribbon, and an AFM measurement of this flake is shown in Figure 4b. The height of the section in Figure 4b above SiO_2 is 0.48 nm (Figure 4c),



Figure 4. Characterization of graphene flakes. (a) Optical micrograph of a graphene flake prepared on 100 nm SiO₂/Si substrate. (b) AFM image of part of the flake in (a). (c) Height profile of the graphene edge in (b). The measured thickness of the monolayer flake above the Si substrate is \sim 0.48 nm. (d) Raman spectroscopy of graphene flakes with thickness between 1–4 layers. The G peak is at 1587 cm⁻¹ for all the flakes. The 2D peak is at 2675 cm⁻¹ for monolayer graphene, and at 2690 cm⁻¹ for 2–4 layer graphene.



which is a little lower than previous measurements for single-layer graphene.³³ Although the actual thickness of monolayer graphene is \sim 0.33 nm, the measured value is always around 1 nm, which is due to the trapping of adsorbed molecules, as we will discuss later. The surface of the flake is smooth and uniform; no obvious defects were found.

Raman spectroscopy has proven to be a versatile tool for studying 2D materials, and especially in detecting defects and identifying the number of layers.^{19,34} We used Raman spectroscopy to assess if the additional annealing step to 100 °C in air causes any defects in the graphene exfoliated by the modified method, e.g., by chemical reactions with H₂O, O₂, etc. (see Figure 4d). Our Raman spectra generally show very low intensity of the D-band (at \sim 1350 cm⁻¹) within each of the transferred graphene layers, which implies that the flakes have low defect density. The highest observed D-band intensity (for exfoliated monolayer graphene) is below 0.4% of the intensity of the 2D peak. We also used Raman spectroscopy to quantify the thickness of few-layer graphene (Figure 1d). For monolayer graphene, the G band is at 1587 cm⁻¹, and the 2D peak at 2675 cm⁻¹. The G band for 2—4 layer graphene is also at 1587 cm⁻¹, but the 2D peak, positioned at ${\sim}2690~\text{cm}^{-1}$ is split into two distinct peaks at 2688 and 2703 cm⁻¹. Our Raman results are consistent with previous reports on graphene flakes with different number of layers. From the fact that the spectra of graphene exfoliated by the two methods are indistinguishable, we conclude that the additional annealing step in the modified method does not cause any detectable increase in defect density.

The interactions between the layers in graphite and between the graphite surface and the SiO₂ substrate during exfoliation are van der Waals forces. Exfoliation of graphene onto SiO₂ represents a competition between the interlayer and interfacial forces: Only when the force between the outermost graphene sheet and the substrate exceeds that between the layers can a sheet be separated from graphite and transferred onto the SiO₂ surface.

Figure 5 gives a schematic diagram of the key steps of our modified graphene exfoliation process, and illustrates how the two additional process steps, oxygen plasma cleaning and mild annealing, can increase the interaction at the graphite/support interface and thus enhance the exfoliation process. Before putting graphite in contact with the SiO₂ surface, oxygen plasma was used to eliminate organic adsorbates from the surface (Figure 5a). We also tested the use of an argon plasma, as well as exfoliation onto substrates that had not been plasma cleaned, but in both cases, we were unable to reliably exfoliate large-area graphene. After the oxygen plasma treatment, graphite was put in contact with the surface and the entire sample annealed at 100 °C (Figure 5b). This step promotes



Figure 5. Key steps of the modified exfoliation process for 2D materials. (a) Oxygen plasma cleaning removes adsorbates from the SiO_2/Si substrate. (b) Annealing of the substrate in contact with graphite on adhesive tape. The increase in temperature builds pressure at the graphite—support interface, which is released by the escape of gas. (c) Cooling to room temperature and a now tightened boundary result in a reduction of the pressure at the interface. The resulting pressure difference causes a small and uniform graphite—support spacing, which in turn enhances the van der Waals interaction at the interface.

the removal of gas molecules between graphite and the SiO₂ surface via the edge, driven by an increase in pressure at the interface. Subsequently, the sample was cooled to room temperature and the exfoliation completed by removing the tape and graphite. Our results suggest that the flake edges act in this process effectively as a one-way valve: they allow pressure built up during annealing to be released by the transfer of gas away from the interface; however, once a tighter, more uniform contact is established between the outermost graphite layer and the support, the now increased van der Waals force prevents gas from re-entering during cooling. As a result, trapped species are eliminated from the interface and a tighter, more uniform contact is established. This scenario is supported by the reduced thickness of monolayer graphene on SiO₂/Si measured by AFM (Figure 4b), and also by occasional observations of bubbles at the interface between single- or few-layer graphene and the substrate. In these cases, the molecules under graphite could not be removed completely, but they instead accumulated in larger bubbles wrapped tightly by the surrounding graphene (Figure S3). Ultimately, the additional annealing step acts in three ways to increase the force between graphite and SiO₂ surface: via the established pressure difference, increased contact area, and decreased overall contact distance. This combination of factors should facilitate the transfer of large-area graphene flakes from bulk graphite.

We believe that similar principles underlie adhesion processes in nature based on van der Waals interactions. The gecko, for example, uses van der Waals forces to be able to climb freely even along smooth vertical surfaces. The microstructure of the gecko's foot consists of nearly 500 000 keratinous hairs or setae on each foot, with each seta containing hundreds of spatula-shaped structures (Figure S6).³⁵ The setae are $\sim 2-10 \ \mu$ m wide and 100 $\ \mu$ m long, while the individual spatulae are only $\sim 200 \ nm$ in diameter (Figure S6b,c). Proposed mechanisms of adhesion of these hierarchically structured feet to support surfaces include van der Waals interaction between the setae

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Figure 6. Electrical transport in a FET device made from graphene obtained by our modified exfoliation method. (a) Schematic diagram of the geometry of graphene devices with SiO_2/Si back gate and DI water top gate. (b) Transfer characteristics of a back-gated graphene device, measured with gate voltage sweeps from -30 to 30 V. The Dirac point lies at -4.8 V. (c) Set of transfer characteristics of the same device with concurrent back-gating and DI water top-gating. For zero back-gate bias, the Dirac point lies at a top-gate voltage of -0.29 V, and moves toward more positive values when decreasing the back-gate voltage. (d) Shift in Dirac point as a function of back gate voltage, deduced from the transfer curves in (c).

and the support,³⁶ capillarity,³⁷ as well as electrostatic interactions at the contact.³⁸ Since the individual nanoscale spatulae, which define the interface to the support, are not flat but are concave (cup-shaped, Figure S6d), they cannot fully contact a flat surface without a preload force. A normal force applied for a brief period of time, however, could remove the gas molecules between the spatula and the support surface and create a more extended planar interface, thus maximizing the van der Waals force between each spatula and the surface. We suggest that in a similar way the sequence of mild annealing and subsequent cooling releases gas and homogenizes the contact area for enhanced van der Waals interaction between a layered crystal and a support surface in our modified exfoliation method.

To determine the electronic transport properties of graphene prepared by the modified exfoliation method, we fabricated field-effect transistors (FETs) from graphene flakes (Figure 6). Figure 6a shows the overall configuration of our devices, which offer the possibility of gating either separately or concurrently *via* the 100 nm SiO₂ dielectric and *via* the electrical doublelayer of a DI water drop used as a top gate. After fabricating back gated graphene FET devices by optical lithography and depositing Ti/Au (5 nm/50 nm) as contact electrodes, we spin-coated PMMA as an additional insulating layer and opened windows for access of the liquid to the FET channel, as illustrated in Figure 6a. Figure 6b–d summarizes measurements on a representative device. With back-gate voltage V_{BG} varied from -30 to 30 V, the source-drain current, I_{SD} (measured at 2 mV source-drain bias, V_{SD}), first decreases from 1.9 μ A to 900 nA and then increases again to 1.6 μ A, *i.e.*, it shows the typical ambipolar transport in graphene. The Dirac point for this device lies at about -5 V back-gate voltage. The field-effect mobility, μ , has been calculated using

$$\mu = \frac{\mathrm{d}I_{\mathrm{SD}}}{\mathrm{d}V_{\mathrm{G}}} \cdot \frac{L}{WC(\mathrm{SiO}_2)V_{\mathrm{SD}}}$$

where *L* and *W* are the length and width of the device (here, L/W = 8), and C(SiO₂) = 34 nF/cm² is the capacitance of the 100 nm SiO₂ layer. On the basis of the data shown in Figure 6b, we deduce a room temperature mobility of 4000 cm²/(V s).

Experiments on monolayer MoS₂ and SnS₂ transistors have shown that top gating by a high-K dielectric, such as HfO₂, Al₂O₃, or DI water can effectively screen scattering centers in the SiO₂ support while maintaining very high on—off current ratios.^{3,4,39} Solution gating has been widely used recently, primarily because it is a simple way to achieve very high carrier densities by field-effect doping of different materials, such as MoS₂,⁴⁰ graphene,⁴¹ and several superconductors.⁴² Here, we used top-gating *via* a drop of DI water ($\varepsilon \sim$ 80 ε_0). The characteristics of DI water top gate measurement are similar to the results measured with back gate,

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Figure 7. Optical images of $Bi_2Sr_2CaCu_2O_x$ (BSCCO) flakes prepared by standard exfoliation and by the modified method introduced here. (a and b) Images of typical monolayer to trilayer BSCCO prepared by routine method: Acetone wash, O_2 plasma cleaning, and transfer. (c and d) Optical images of two BSCCO flakes prepared by the modified method: O_2 plasma cleaning of the SiO₂/Si surface, contact between BSCCO and substrate, heating of the substrate with BSCCO attached, and peel-off/exfoliation.

but over a much smaller gate voltage range (-0.7 to 0.5 V). The I-V curves of the solution-gated FET device still show linear and symmetric behavior, indicating ohmic contacts and the absence of leakage currents (Figure S5). The Dirac point of the device at zero back gate voltage is at $V_{TG} = -0.29$ V, much closer to zero bias than in the back-gated measurement. To be able to determine the carrier mobility in the solution gated FET devices, we performed additional transport experiments aimed at measuring the specific double-layer capacitance of DI water in contact with the graphene device channel. The capacitance of the solution gate is determined using a lever-arm principle, by measuring the change in the transfer characteristics of the solution-gated device (I_{SD} vs V_{TG}) due to different applied back gate bias voltages, V_{BG}. Back-gating induces welldefined shifts in the transfer characteristic, which can be quantified by a linear fit to determine the shift in the neutrality point, $^{43}\Delta V_{\text{Dirac}}$, for different values of $V_{\rm BG}$. From the linear dependence shown in Figure 6d, the solution gate capacitance C_{TG} can be determined via $C_{TG}/C_{BG} = \Delta V_{BG}/\Delta V_{Dirac}$. Using the known specific capacitance of the 100 nm SiO₂ dielectric of the back gate, $C_{BG} = 34 \text{ nF/cm}^2$, we determine a specific capacitance of the DI water solution top gate in contact with a graphene FET channel of 325 nF/cm², from which we calculate field-effect mobilities of our solution gated FETs of \sim 12000 cm²/(V s). We conclude that our graphene flakes prepared by the modified exfoliation method show excellent electrical performance.

To demonstrate the generality of our approach for efficiently exfoliating large flakes of a wide range of 2D

materials from layered crystals, we performed experiments with a layered $Bi_2Sr_2CaCu_2O_x$ (BSCCO) superconductor. 2D crystals consisting of ultrathin BSCCO flakes were first reported by Novoselov *et al.* in 2005, but the flake size obtained was of the order of a few micrometers.¹⁷ Figure 7 shows representative results of BSCCO flakes obtained by our modified exfoliation method in comparison with the standard exfoliation approach.

Similar to our experiments with graphene, we find substantial gains in both the area of thin flakes and the exfoliation yield when exfoliating thin flakes from a layered BSCCO crystal using our modified method, in which the sandwich of substrate and adhesive tape-supported thick BSCCO flakes is annealed prior to the actual exfoliation step. Figure 7 documents this by comparing optical microscopy images of flakes obtained with the standard exfoliation method (few tens of micrometers in size, Figure 7a,b) and by the modified approach (flakes of up to several 100 μ m, Figure 7c,d).

CONCLUSIONS

In summary, a modified exfoliation method was developed for preparing large-area flakes of graphene and other 2D materials. With the addition of a brief annealing step of the substrate in contact with the layered crystal (*e.g.*, graphite) held by adhesive tape, the exfoliation yield quantified *via* the total graphene area obtained in a single exfoliation step on substrates of the same size was 20–60 times larger than for the standard exfoliation method. Graphene flakes produced by this approach

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were characterized by AFM imaging and Raman spectroscopy, which demonstrated that the monolayer and few layer graphene have high quality. In particular, no additional defects were introduced by the annealing in air prior to completing the exfoliation process. We propose a mechanism underlying the improved exfoliation that involves a tightening and homogenization of the contact between the outermost layer of the source crystal and the substrate, enabled by a release of pressure from the interface during annealing. We suggest that this process is analogous to the adhesion process that allows geckos to be suspended on smooth vertical walls and ceilings. The electrical properties measured on graphene FET devices using both back-gating and solution topgating further demonstrate that the graphene flakes prepared by our method are of high quality. Experiments on exfoliation of Bi₂Sr₂CaCu₂O_x, which show similar improvements as for graphene, suggest that the exfoliation approach demonstrated here is applicable to a wide range of 2D materials. Hence, our study may accelerate the exploration of new 2D materials by providing an efficient pathway to large, high-quality flakes derived from layered crystals *via* exfoliation.

ARTICLE

METHODS

After transferring graphene onto a SiO₂/Si wafer, thin (monolayer, bilayer, few layer) graphene flakes were initially identified by optical microscopy (Nikon L200N), and the size of each flake was measured for determining the total graphene area. Atomic force microscopy (Veeco Multimode V) and confocal Raman spectroscopy/microscopy (WITec Alpha 300) were used to measure the properties and thickness of exfoliated graphene. A laser wavelength of 532 nm and spot size of ~0.5 μ m was used to obtain the Raman spectra.

The electrical transport properties of monolayer graphene were determined using microfabricated field-effect transistors (FETs). After exfoliating graphene flakes onto 100 nm SiO₂/Si, we fabricated test devices using standard optical lithography (MA6) and deposited Ti/Au (5 nm/50 nm) as contact electrodes using electron-beam evaporation. To test the contacts, currentvoltage characteristics were first measured after metal contact deposition. The final devices were annealed in high vacuum (10⁻⁸ Torr) at 300 °C for 2 h in order to remove resist residues and enhance the metallic contacts. After measuring graphene FETs back-gated via the SiO₂/Si substrate, we also used deionized (DI) water for top-gating. In these devices, the metal contacts were isolated by spin-coating PMMA onto the entire chip, and opening windows defined by electron beam lithography over the FET channel. DI water was dropped onto the center of the device, ensuring that the metal electrodes were not contacted by water during the measurement.

Conflict of Interest: The authors declare no competing financial interest.

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Additional experimental data. (PDF)

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