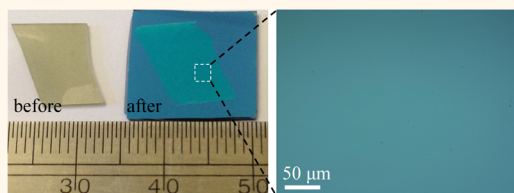


Surface-Energy-Assisted Perfect Transfer of Centimeter-Scale Monolayer and Few-Layer MoS₂ Films onto Arbitrary Substrates

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ABSTRACT The transfer of synthesized 2D MoS₂ films is important for fundamental and applied research. However, it is problematic to translate the well-established transfer processes for graphene to MoS₂ due to different growth mechanisms and surface properties. Here we demonstrate a surface-energy-assisted process that can perfectly transfer centimeter-scale monolayer and few-layer MoS₂ films from original growth substrates onto arbitrary substrates with no observable wrinkles, cracks, and polymer residues. The unique strategies used in this process include leveraging the penetration of water between hydrophobic MoS₂ films and hydrophilic growth substrates to lift off the films and dry transferring the film after the lift off. This is in stark contrast with the previous transfer process for synthesized MoS₂ films, which explores the etching of the growth substrate by hot base solutions to lift off the films. Our transfer process can effectively eliminate the mechanical force caused by bubble generations, the attacks from chemical etchants, and the capillary force induced when transferring the film outside solutions as in the previous transfer process, which consists of the major causes for the previous unsatisfactory transfer. Our transfer process also benefits from using polystyrene (PS), instead of poly(methyl methacrylate) (PMMA) that was widely used previously, as the carrier polymer. PS can form more intimate interaction with MoS₂ films than PMMA and is important for maintaining the integrity of the film during the transfer process. This surface-energy-assisted approach can be generally applied to the transfer of other 2D materials, such as WS₂.



KEYWORDS: molybdenum disulfide · 2D materials · tungsten disulfide · surface energy · large scale

Two-dimensional (2D) transition metal dichalcogenide (TMDC) materials have recently emerged as a topical research area.^{1–12} These materials present an attractive semiconductor option at the atomic scale that promises to scale all semiconductor devices including integrated circuits, lasers, light-emitting diodes, and photodetectors down to a truly atomic level. However, to fully explore the potential of 2D TMDC materials requires the ability to perfectly transfer synthesized 2D TMDC materials from the growth substrates onto other substrates without compromising the quality and properties. This is because the substrates used for the growth of 2D TMDC materials are often different from those required for fundamental or applied research. It has been

demonstrated that centimeter-scale and high-quality 2D TMDC materials such as MoS₂ can be synthesized using chemical vapor deposition (CVD) processes that involve high temperature (usually >800 °C), corrosive vapor (sulfur vapor), and substrates with atomically smooth surfaces.^{13,14} However, the substrates required for the research of 2D TMDC materials may not be able to survive the harsh environment of the growth process or to support the growth of high-quality 2D TMDC materials. One example is polymer substrates for the development of flexible devices.^{15–17} Additionally, the capability of perfect transfer is necessary for the fabrication of 2D heterostructures that consist of dissimilar layers stacked in the vertical direction. The 2D heterostructures have

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Received for review August 24, 2014 and accepted October 27, 2014.

Published online October 27, 2014
10.1021/nn5057673

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been known to hold great promise to enable novel functionality that cannot be obtained with typical single-component 2D materials.^{18–24}

However, the transfer of synthesized 2D materials is challenging due to the extreme mechanical delicacy of the atomically thin structure. While the transfer of graphene has been extensively studied,^{1,25–30} simply translating the transfer processes for graphene to 2D TMDC materials such as MoS₂ is problematic because of the differences in the growth mechanism and surface properties.^{13,14,31–33} The transfer process generally involves two steps, the lift off of 2D materials from the original growth substrates and the release of the lift 2D materials onto target substrates. It usually starts by coating a layer of polymer on top of the as-grown 2D materials to act as carrier polymers that help with the handling of the atomically thin materials. A perfect transfer would mean a complete lift off of the materials from the growth substrates and a complete release of the lift materials onto target substrates. Much of the difference between the transfer of graphene and that of 2D MoS₂ lies in the lift-off process. For graphene films, the lift off can be achieved by dissolving the growth substrate (*i.e.*, copper or nickel) into, for instance, FeCl₃ solutions.^{26–30} In contrast, the lift off of MoS₂ films is more difficult because the growth substrate of MoS₂ films, which is typically ceramic materials like sapphire,^{13,14,34} cannot be dissolved as easily. Current transfer processes for synthesized MoS₂ films predominantly use poly(methyl methacrylate) (PMMA) as the carrier polymer and leverage the etching of the growth substrate by a hot base (NaOH or KOH) solution bath to lift off the films.^{13,34} However, the bubble generation in the hot solution may severely damage the film, and the capillary force induced when transferring the film out of the solution bath may cause wrinkles, wrapping, and cracks in the film. Recent studies also reported using polydimethylsiloxane (PDMS) (as the carrier polymer) and cold water to lift off synthesized MoS₂ films.³⁵ This requires the presence of a water-soluble layer underlying the as-grown films, which is not typical in the synthesis. Additionally, the removal of the PDMS from the MoS₂ film after the transfer relies on mechanical forces and may end up releasing only a part of the film onto the target substrates.³⁵

Here we present a surface-energy-assisted process that can perfectly transfer centimeter-scale monolayer or few-layer MoS₂ films onto arbitrary substrates with no observable wrinkles, cracks, and polymer residues. This process is carefully designed to minimize the mechanical forces or chemical attacks experienced by the atomically thin MoS₂ film during the transfer. One key strategy is exploiting the penetration of water molecules between the synthesized MoS₂ film and the growth substrate to lift off the film at room temperature, which is different from what was used in the previous transfer methods that rely on the etching of growth

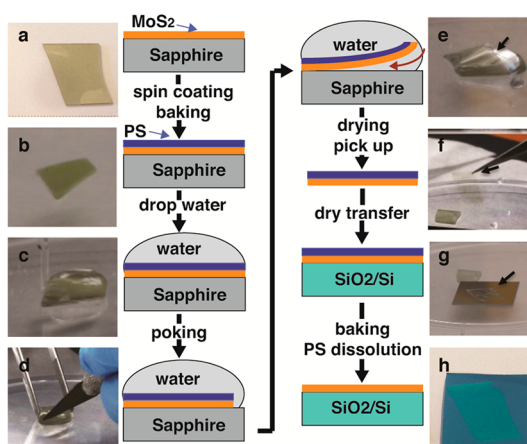


Figure 1. Illustration of the surface-energy-assisted transfer process. (a–h) Typical images of the transfer process. The arrows in (e–g) point toward the MoS₂ film for visual convenience.

substrates by hot base solutions for the lift off. We find that the synthesized MoS₂ film is hydrophobic, while the growth substrate (sapphire) is hydrophilic (see the contact angle measurement given in Supporting Information Figure S1). The different surface energies can drive water molecules to penetrate underneath the film, and this is why our process is termed surface-energy-assisted transfer. The mild lift off by water penetration at room temperatures eliminates the mechanical force caused by bubble generations and the attacks from chemical etchants as in the previous transfer process.^{13,34} Other unique strategies used in this process include the use of polystyrene as the carrier polymer, instead of PMMA that was used previously,^{13,34} and dry transfer of the film after the lift off.

RESULTS AND DISCUSSION

The transfer process is schematically illustrated in Figure 1 (see a video in the Supporting Information). We first spin-coat a layer of polystyrene (PS) onto as-grown MoS₂ films on sapphire substrates followed by a baking process at 80–90 °C for 15 min (Figure 1a,b). A water droplet is then dropped onto the PS layer (Figure 1c). While the water may have a natural tendency to penetrate between the MoS₂ film and the substrate due to different surface energies, the penetration actually cannot start by itself. This is because the intimate adhesion of the synthesized film with the substrate may effectively hinder the start of the penetration. We find that a gentle poking at the edge of the polymer/MoS₂ assembly with a sharp object, which might create cracks at the edge, is necessary to initiate the water penetration (Figure 1d). The polymer/MoS₂ assembly can be lifted off instantly after the poking (Figure 1e) and floats on top of the water droplet. The detached polymer–MoS₂ assembly can be dried by simply sucking the water droplet away with a paper towel. We can then readily pick the assembly using

tweezers (Figure 1f) and dry transfer it onto arbitrary target substrates (Figure 1g). After that, we bake the transferred assembly at 80 °C for 1 h to remove water residues and then at 150 °C for 30 min to spread the polymer for the elimination of possible wrinkles. The last step of the transfer process is dissolving the polymer with toluene (Figure 1h).

Our transfer process for the centimeter-scale synthesized MoS₂ films bear substantial difference from what was reported previously that employs the penetration of water between hydrophobic and hydrophilic surfaces to transfer small (micrometer-scale) exfoliated 2D materials.^{36–38} The difference mainly lies in the lift off of the materials from the original substrate and is caused by the different sizes of the materials in the study as well as the different strengths of the interaction between the materials and the substrate. The previous works dealt with small (micrometer-scale) exfoliated 2D materials that had been predeposited onto substrates.^{36–38} The exfoliated 2D materials were first coated by a carrier polymer, and the polymer-exfoliated 2D material assembly could then be lifted off from the original substrate by simply immersing the entire sample into water.^{36–38} However, such a simple immersion into water cannot lift off our synthesized MoS₂ films from the growth substrate. Unlike the exfoliated 2D materials, which is much smaller than the polymer overlayer and its lift off actually relies on the penetration of water between the carrier polymer and the substrate, the synthesized film in our experiments covers the entire growth substrate and is the same size as the overlayer of the carrier polymer. As a result of the big size, to lift off the synthesized film requires the penetration of water molecules between the film and the substrate. This is more difficult because the synthesized film intimately adheres to the growth substrate, which may hinder the water penetration. External forces, such as poking, are necessary to initiate the water penetration underneath the synthesized film for the lift off, as we have demonstrated in the preceding text. The intimate adhesion of the synthesized film with the growth substrate also imposes additional requirements on the choice of the carrier polymer. To facilitate the lift off of 2D materials, ideally the adhesion between the carrier polymer and the 2D materials should be stronger than that between the substrate and the 2D materials. Unlike exfoliated 2D materials, which have relatively weaker adhesion with the substrate that can be easily overcome by the interaction with arbitrary polymers,^{36–38} to successfully lift off the synthesized film requires the carrier polymer to form strong adhesion with the film in order to overcome the intimate adhesion of the film with the growth substrate. We find that PS is a better choice than PMMA as the carrier polymer to lift off the synthesized films as only part of the synthesized film may be lifted off and transferred when using PMMA as the carrier polymer (Figure S2). This is because PS can form stronger

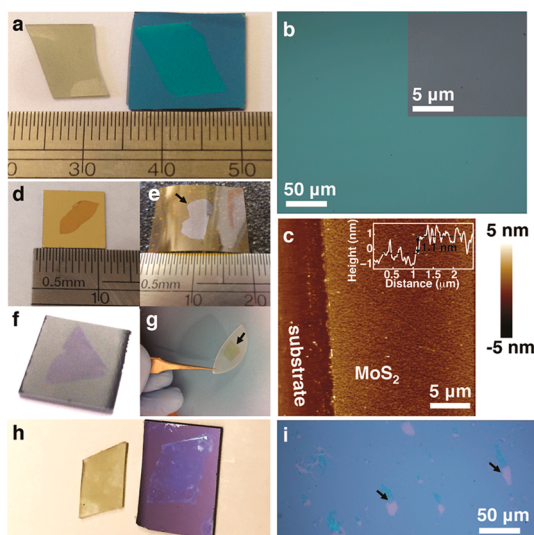


Figure 2. Transfer of MoS₂ films onto arbitrary substrates. (a) Monolayer MoS₂ film transferred onto a SiO₂/Si substrate and the sapphire substrate that the film was originally grown on. (b) Optical images of the transferred monolayer MoS₂. Inset: Optical image of the transferred monolayer with larger magnification. (c) Typical AFM image of the transferred monolayer MoS₂ film. Inset: Typical height profile showing the thickness of the film, and MoS₂ atomically thin films transferred onto various substrates including (d) gold, (e) kapton, (f) glassy carbon, and (g) quartz. The arrows serve to guide the eyes to the transferred film. (h) Monolayer MoS₂ film transferred onto a SiO₂/Si substrate by using the previous transfer process and the sapphire substrate that the film was originally grown on. (i) Optical images of the monolayer MoS₂ transferred by using the previous transfer process. The arrows indicate cracks/holes in the transferred film.

adhesion with the film than PMMA due to a larger hydrophobicity (Figure S3). As further evidence for the requirement of strong adhesion of the synthesized film with the polymer, we also find in experiments that it is difficult to lift off the film with a relatively rough surface, in which the rough surface could prevent strong interaction between the polymer and the film.

Our process can perfectly transfer centimeter-scale MoS₂ films onto arbitrary substrates. Without losing generality, we use the transfer of MoS₂ films onto SiO₂/Si substrates to illustrate this notion. Figure 2a shows a monolayer film transferred onto a SiO₂/Si substrate and the sapphire substrate that the film was originally grown on. The transferred MoS₂ film shows an identical size and shape as the growth substrate, indicating a perfect lift off and release. Under an optical microscope, the transferred film appears to be very uniform, continuous, and clean with no observable wrinkles, cracks, and polymer residues (Figure 2b). This remarkable uniformity is similar to what was observed on the as-grown MoS₂ films.¹⁴ It is worthwhile to point out that the presence of wrinkles, cracks, or polymer residues, if any, can be easily identified under optical microscopes due to distinct contrast (Figure S4). The uniformity and cleanness of the transferred film can be further confirmed by AFM measurements. The surface roughness of the transferred

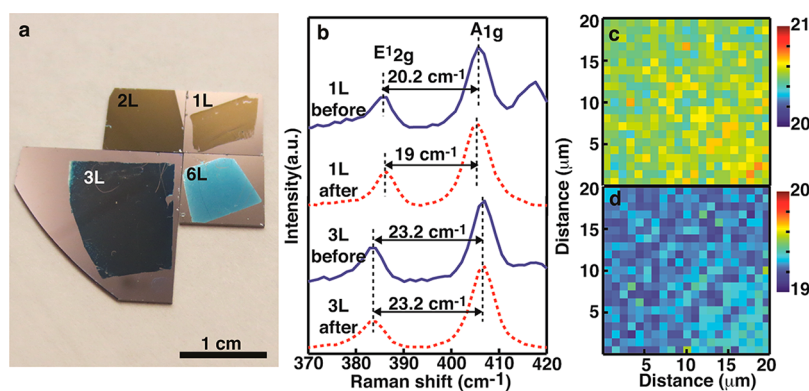


Figure 3. Unchanged layer number, crystalline quality, and uniformity of the transferred MoS₂ films. (a) MoS₂ films with different layer numbers transferred onto SiO₂/Si substrates. (b) Raman spectra of the as-grown MoS₂ films on sapphire substrates (before) and the transferred films on SiO₂/Si substrates. Only the results for monolayer (1L) and trilayer (3L) MoS₂ are given here. More can be seen in Figure S4. Mapped frequency differences between the characteristic Raman peaks A_{1g} and E_{2g}¹ for (c) as-grown monolayer MoS₂ on sapphire substrates and (d) monolayer MoS₂ transferred onto SiO₂/Si substrates.

monolayer film is measured to be around 0.4 nm (Figure 2c), comparable to what was previously observed with the as-grown MoS₂ films on sapphire substrates.¹⁴ AFM measurements also indicate that the transferred film has a thickness of 1.1 nm. This is slightly larger than what was observed with as-grown monolayers,¹⁴ likely due to a larger spatial separation between the film and the substrate after the transfer. The transfer process is very robust, and we have successfully used it to transfer MoS₂ films onto many different substrates, including gold (Figure 2d), kapton (Figure 2e), glassy carbon (Figure 2f), and quartz (Figure 2g).

To further illustrate the advantage of our process, we also transferred synthesized MoS₂ films from the growth substrate (sapphire) to SiO₂/Si substrates using the process widely used previously, in which the film was lifted off by etching the growth substrate with hot NaOH solution and PMMA used as the carrier polymer. The typical result is given in Figure 2h,i. Unlike the perfect transfer enabled by our process (Figure 2a,b), only part of the film can be lifted off and transferred from the original growth substrate to the target substrate by using the previous process,^{13,34} as a substantial amount of voids may be found at the transferred film (Figure 2h) and MoS₂ materials at the original growth substrate after the transfer. This is likely due to the relatively weaker interaction of PMMA with the MoS₂ film compared to PS. The weaker interaction of PMMA with the hydrophobic MoS₂ film is supported by our contact angle measurements that show PMMA is less hydrophobic than PS (see the result in Figure S2). Additionally, we can find numerous micrometer-scale cracks/holes in the transferred films (Figure 2i). These cracks/holes are caused by bubbling in the hot solution and/or by the capillary force induced when transferring the film out of the solution. In contrast, our transfer process exploits the water penetration at room temperature to provide a mild lift off of the film. It eliminates the mechanical force generated by the bubbling and the possible attacks

from chemical etchants as in the previous transfer process. Our transfer process also exploits the removal of the water droplet right after the lift off to make the subsequent transfer of the polymer–MoS₂ assembly essentially a dry process. This may minimize the capillary force experienced by the film. Capillary forces are well-known as a major cause of warping or wrinkles in the transferred atomically thin films and may trap a significant amount of water residue between the target substrate and the films, which may lead to the formation of cracks in the following baking step.

Our transfer process may maintain the layer number, crystalline quality, and uniformity of the MoS₂ films. Figure 3a shows the MoS₂ films with different layer numbers transferred onto SiO₂/Si substrates, whose strikingly different colors originate from optical interferences and depend on the thickness of the SiO₂ layer. All of these transferred films are in the same shapes and dimensions as the corresponding growth substrates (Figure S5). We have confirmed that no MoS₂ materials are left behind on the growth substrate after the transfer using an optical microscope imaging and Raman measurements. This indicates a complete lift off of the film from the growth substrate regardless of the layer number. Raman measurements also confirm that the layer number of the transferred film is the same as that of the as-grown one, indicating a complete release of the film onto the target substrate. Figure 3b shows the Raman spectra collected from as-grown MoS₂ films on sapphire substrates and the films transferred onto SiO₂/Si substrates (more results can be seen in Figure S6). The frequency difference Δk between the two characteristic peaks A_{1g} and E_{2g}¹, which has been widely used as an indicator for the layer number of MoS₂,³⁹ is essentially unchanged after the transfer. For instance, the Δk of trilayer MoS₂ films remains at 23.2 cm⁻¹ before and after the transfer. Note that the Δk of the monolayer MoS₂ does show a slight change from 20.2 to \sim 19 cm⁻¹ after the transfer, but this

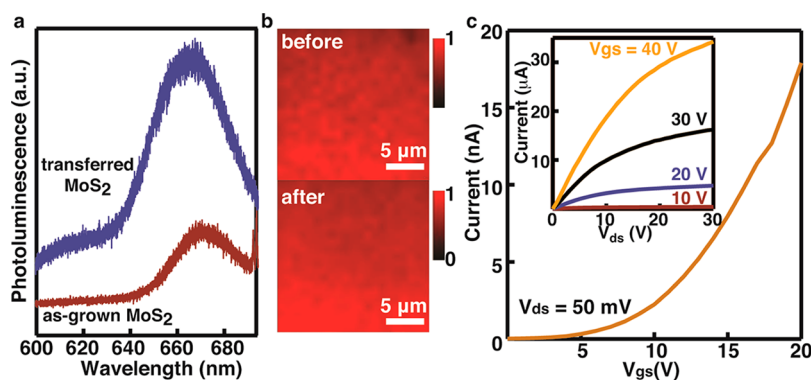


Figure 4. Optical and electrical qualities of transferred MoS₂ films. (a) Photoluminescence spectra and (b) mapped PL intensity (integrated over 650–670 nm) from an as-grown monolayer MoS₂ film on sapphire substrates (before) and the same film transferred onto SiO₂/Si substrates. (c) Transfer characteristic for a FET built upon monolayer MoS₂ transferred onto SiO₂/Si substrates with a source drain bias V_{ds} of 50 mV. Inset: I_{ds} – V_{ds} curve for the FET with gating voltages V_{gs} of 10, 20, 30, and 40 V.

change is caused by changes in the interaction of the film with substrates rather than by a change in the layer number.⁴⁰ Our AFM measurement has already confirmed that the as-grown monolayer film remains as a monolayer after the transfer (Figure 2c). It has been well-known that the interaction with substrates may affect the Raman frequencies of MoS₂,⁴⁰ and the as-grown film may likely interact with substrates more strongly than the transferred film. Similar decrease of the Δk can also be seen in the monolayer film transferred from the original sapphire growth substrate to another bare sapphire substrate (Figure S7). Except for the Raman frequencies, the full width at half-maximum (fwhm) of the E_{2g}^1 peak, which may be used as an indicator for crystalline quality,³⁹ remains unchanged as well during the transfer process. For instance, the E_{2g}^1 fwhm is 5.2 cm⁻¹ for both as-grown and transferred MoS₂ monolayers and 5.4 cm⁻¹ for the trilayers.³⁹ This indicates that the transfer process does not compromise the crystalline quality of the films. Additionally, our optical microscope imaging indicates that the transfer films exhibit comparable uniformity as the as-grown counterpart (Figure 2b). This is further confirmed by Raman mapping measurements. For instance, the Raman mapping results of monolayer MoS₂ films show the Δk always in a narrow range before (20.2–20.8 cm⁻¹) and after (19.0–19.6 cm⁻¹) the transfer (Figure 3c,d).

The transferred films show good optical and electrical properties. The PL from the film transferred onto SiO₂/Si substrates can be found to be even stronger than that of the as-grown one on sapphire substrates (Figure 4a). This PL enhancement is caused by the optical interference effect in the SiO₂/Si substrates as reported

previously.^{40,41} We also observed similar enhancement in the Raman spectrum of the transferred monolayer on SiO₂/Si substrates (Figure S8). Nevertheless, the strong PL clearly indicates that the optical quality of the film is not compromised by the transfer process. The PL mapping results indicate comparable optical uniformity in the as-grown and transferred films (Figure 4b), consistent with the comparable structural uniformity illustrated in Figures 2 and 3. We also fabricated field-effect transistors (FETs) with transferred monolayer MoS₂ films to measure the mobility. The devices show clear current saturation due to the pinch-off of the channel, and the mobility is measured to be 0.03 cm²/V·s, reasonably consistent with the mobility measured at exfoliated monolayer MoS₂ with similar gating configuration and ambient environments.⁴²

CONCLUSION

In conclusion, we have demonstrated a unique surface-energy-assisted transfer process that can perfectly transfer synthesized centimeter-scale MoS₂ films onto arbitrary substrates without compromising the crystalline/surface quality and properties. Although this work mainly focuses on the transfer of the MoS₂ films grown by using MoCl₅ as the precursor, the process can be applied to the transfer of MoS₂ materials synthesized using other methods, for instance, the CVD process with MoO₃ being the precursor (Figure S9). We believe that the key strategy of leveraging the difference in surface energies between the synthesized materials and the growth substrate can be generally applied to the transfer of other 2D materials. For instance, we have demonstrated a successful transfer of synthesized WS₂ films by using this transfer process (Figure S10).

METHODS

Synthesis of Centimeter-Scale MoS₂ Films. The centimeter monolayer and few-layer MoS₂ films were grown using a CVD process in a tube furnace that we have previously reported.¹⁴ In a typical

growth, 4–20 mg of molybdenum chloride (MoCl₅) powder (99.99%, Sigma-Aldrich) and 1 g of sulfur powder (Sigma-Aldrich) were placed upstream of the furnace. Receiving substrates (typically sapphire) were placed downstream of the tube.

Typical conditions for high-quality MoS₂ thin film growth include a temperature of 850 °C, a flow rate of 50 sccm, and a pressure around 2 Torr. During the synthesis, the vapor of the precursor materials reacted to produce gaseous molybdenum sulfide species, which could subsequently precipitate onto receiving substrates. The layer number was controlled by controlling the amount of precursors (MoCl₅) used in the synthesis (see the Supporting Information of ref 14).

Transfer of Centimeter-Scale MoS₂ Films. In a typical transfer process, 9 g of PS with a molecular weight of 280 000 g/mol was dissolved in 100 mL of toluene and then the PS solution was spin-coated (3500 rpm for 60 s) on as-grown MoS₂ films on sapphire substrates. This was followed by a baking at 80–90 °C for 15 min to facilitate intimate adhesion of the PS layer with the MoS₂ film. A water droplet was then dropped on top of the sample. To facilitate the penetration of water molecules, we poked the PS layer with a sharp object from the edge. Once the PS layer was scratched from the edge, water molecules could penetrate all the way through the MoS₂ film, resulting in the delamination of the PS–MoS₂ assembly. The water droplet was then removed from the detached PS–MoS₂ assembly with a paper towel. We could pick up the assembly with tweezers and transfer it onto the target substrate. To ensure the uniformity of the transferred MoS₂ film, we baked the transferred PS–MoS₂ assembly as follows: a mild baking at 80 °C for 1 h to remove the water residues and a final baking for 30 min at 150 °C to spread the polymer for the elimination of possible wrinkles. Finally, PS was removed by rinsing with toluene several times. The transfer using poly(methyl methacrylate) (950 K, Microchem) followed a previously report.¹³ Briefly, a layer of PMMA was spin-coated onto the as-grown MoS₂ films on sapphire substrates first, and then the sample was immersed into hot (90 °C) NaOH solution for hours. After being lifted off from the original substrates, the polymer–MoS₂ assembly was fished out onto target substrates. This was followed by a baking process at 90 °C for 1 h, and the PMMA was dissolved by acetone afterward.

Characterizations of MoS₂ Films. The structure and composition of the as-grown and transferred MoS₂ were characterized by a variety of tools. The thickness and surface topology were measured using atomic force microscope (AFM, Veeco Dimension-3000). Raman measurements were typically performed with a Raman spectroscope (Renishaw-1000) with an excitation wavelength of 514.5 nm, except for the Raman mapping that was carried out using Horiba Labram HR800 Raman microscopy with an excitation wavelength of 532 nm. Photoluminescence (PL) measurements were also carried out with a Horiba Labram HR800 Raman microscope. The field-effect transistor device was fabricated by using standard photolithography, development, and metallization processes. Ti/Au (30/250 nm) was evaporated onto top of MoS₂ films transferred to degenerately doped Si substrates with 80 nm thick silicon oxide. Typical devices were features with a channel length of 5 μm and a width of 400 μm. The electrical measurements were performed in ambient conditions using a probe station (Karl Suss PSM6).

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

Acknowledgment. This work was supported by a Young Investigator Award from the Army Research Office (W911NF-13-1-0201) and, partially, by a CAREER award from the National Science Foundation (DMR-1352028). Y.Z. acknowledges the support of the Bissell Distinguished Professorship. The authors acknowledge the use of the Analytical Instrumentation Facility (AIF) at North Carolina State University, which is supported by the State of North Carolina and the National Science Foundation.

Supporting Information Available: More results including a video for the transfer process. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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