Damage-free and rapid transfer of CVD-grown two-dimensional transition metal dichalcogenides by dissolving sacrificial water-soluble layers†

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As one of the most important family members of two-dimensional (2D) materials, the growth and damage-free transfer of transition metal dichalcogenides (TMDs) play crucial roles in their future applications. Here, we report a damage-free and highly efficient approach to transfer single and few-layer 2D TMDs to arbitrary substrates by dissolving a sacrificial water-soluble layer, which is formed underneath 2D TMD flakes simultaneously during the growth process. It is demonstrated, for monolayer MoS2, that no quality degradation is found after the transfer by performing transmission electron microscopy, Raman spectroscopy, photoluminescence and electrical transport studies. The field effect mobility of the post-transfer MoS2 flakes was found to be improved by 2–3 orders compared with that of the as-grown ones. This approach was also demonstrated to be applicable to other TMDs, other halide salts as precursors, or other growth substrates, indicating its universality for other 2D materials. Our work may pave the way for material synthesis of future integrated electronic and optoelectronic devices based on 2D TMD materials.

Introduction

2D TMDs have emerged as promising candidates for post-silicon electronics due to their atomically thin geometry and unique electronic properties.1–4 As a readily accessible and economical approach for industrial scale synthesis, the chemical vapor deposition (CVD) technique has achieved great success in the growth of graphene,5,6 2D TMDs and related heterostructures.7–10 These samples grown on certain substrates are not readily available for device fabrication owing to strong interactions between the samples and substrates. Therefore, a damage-free and efficient transfer of as-grown 2D TMD samples to target substrates is a predominantly key prerequisite for facilitating their future applications.

So far, two main types of methods developed to transfer 2D TMDs have been focused on the treatment after sample growth. One is the chemical etching of the growth substrates (for monolayer MoS2, that no quality degradation is found after the transfer by performing transmission electron microscopy, Raman spectroscopy, photoluminescence and electrical transport studies. The field effect mobility of the post-transfer MoS2 flakes was found to be improved by 2–3 orders compared with that of the as-grown ones. This approach was also demonstrated to be applicable to other TMDs, other halide salts as precursors, or other growth substrates, indicating its universality for other 2D materials. Our work may pave the way for material synthesis of future integrated electronic and optoelectronic devices based on 2D TMD materials.

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neath the MoS$_2$ flakes, which is formed spontaneously with MoS$_2$ via the sulfurization of a NaCl and MoO$_3$ mixture precursor. The approach is entirely different from the previously reported methods. No quality degradation was found after the transfer according to Raman and photoluminescence (PL) characterization. The whole lift-off and transfer processes could be accomplished within one minute. Field-effect transistors (FETs) made of the transferred MoS$_2$ flakes show that the mobility is improved by 2–3 orders when compared with that of the as-grown ones. This generic approach is also demonstrated to be applicable to other TMDs, such as MoSe$_2$.

**Experimental**

**Growth of MoS$_2$ flakes**

Monolayer MoS$_2$ flakes were synthesized in a two-temperature zone tube furnace. In a typical procedure, mixed NaCl and MoO$_3$ powders with a weight ratio of 9 : 1 in a quartz boat were placed in the high-temperature zone. Another quartz boat holding 100 mg pure sulfur was placed in the upwind low-temperature zone. The distance between the two quartz boats was fixed at 18 cm. The fresh SiO$_2$/Si substrate was faced down above the quartz boat containing the mixed NaCl/MoO$_3$ powders. Before the experiments, high purity (99.99%) Ar gas was passed through the tube at a flow rate of 400 standard-state cubic centimeter per minute (sccm) for 10 min to flush. The temperatures of the two boats were then gradually increased from room temperature (RT) to target temperatures (650 °C for mixed NaCl and MoO$_3$ powders, and 240 °C for sulfur powders) within 25 min and kept for 10 min with 200 sccm Ar flow, followed by a cooling down process (cooled down to RT within 2 hours).

**Transfer of MoS$_2$ flakes**

A thin layer of PMMA was first spin-coated onto an as-grown wafer. One edge of the MoS$_2$ growth area was partially scratched before the wafer was placed in a container with DI water being gradually added. The PMMA/MoS$_2$ layer was lifted off and floated on the water surface after the water-soluble layer was dissolved. The layer was then transferred to new SiO$_2$/Si or PET (polyethylene terephthalate) substrates (Video S1 and Video S2 in the ESI†). The post-transferred PMMA/MoS$_2$/new substrate was then dried in air, followed by the removal of PMMA in acetone.

**The device fabrication and electrical measurements**

The devices with two-terminal structures were fabricated on the as-grown and transferred SiO$_2$/Si substrates. The electrodes (5 nm Ag/50 nm Au) were patterned using a home-made shadow mask method and deposited by standard electron beam evaporation. All the devices were measured under a N$_2$ atmosphere at RT using an Agilent B1500A parameter analyzer.

**Optical, Raman, PL and TEM characterization**

Optical images were recorded in a Nikon DIGITAL SIGHT DS-Fi2 K18680 optical microscope. Raman and PL spectra were recorded using a Jobin–Yvon HR800 Raman system, equipped with a liquid-nitrogen-cooled charge-coupled device (CCD), a 100× objective lens (NA = 0.90) and several gratings. The excitation wavelength was 532 nm from a solid state laser. The resolutions of the Raman and PL system at 532 nm were 0.35 cm$^{-1}$ and 0.2 meV per CCD pixel depending on the grating used. TEM measurements were carried out at 200 kV.

**Results and discussion**

We chose NaCl and MoO$_3$ as precursors owing to their similar melting points (795 °C for MoO$_3$ and 801 °C for NaCl). As illustrated in Fig. 1a and b, they are heated to form vapor phases of MoO$_3$ and NaCl clusters. By considering that the dissociation energy of a Na–O bond (266 ± 4 kcal mol$^{-1}$) is larger than that of a Mo–O bond (145.1 ± 4 kcal mol$^{-1}$), the unsaturated oxygen atoms on the SiO$_2$ substrate surface prefer to form bonds with Na$^+$ rather than Mo$^{6+}$. Such a NaO$_2$ layer could be then vulcanized by sulfur vapor to form highly water-soluble NaS$_x$ on the SiO$_2$ surface. Simultaneously, MoS$_2$ clusters obtained via the sulfuration of MoO$_3$ clusters could nucleate and form MoS$_2$ flakes on the NaS$_x$ layer. In this case, the MoS$_2$ flakes might be easily lifted off and transferred after dissolving the water-soluble layer in water.

In our experiments, growth substrates (SiO$_2$ wafers) were placed face-up above the NaCl/MoO$_3$ precursors inside a tube furnace for MoS$_2$ synthesis (ESI Fig. S1†). Triangular monolayer MoS$_2$ flakes with typical sizes ranging from few ten to a few hundred micrometers (ESI Fig. S2a and S2c†) were successfully synthesized via the sulfuration of the NaCl/MoO$_3$ precursors. We indeed found that the MoS$_2$ flakes could be easily lifted off and transferred to target substrates by dissolving the water-soluble layer in water, as expected. As illustrated in Fig. 1c–f, a PMMA thin film was first spin-coated on the as-grown wafers. The PMMA film was then partially scratched along the edge of the MoS$_2$ area to allow water molecules to penetrate in. After that, the PMMA covered as-grown wafer was put into water to get the PMMA/MoS$_2$ film lifted off. The PMMA/MoS$_2$ film floating on the water surface was then transferred to the desired substrates. Lastly, the PMMA layer was removed by putting the PMMA/MoS$_2$/new substrate structure into acetone for several minutes. Fig. 1g–j exhibit the optical images of the same MoS$_2$ flake at different transfer steps. No wrinkles, cracks, or polymer residues on MoS$_2$ flakes or new substrates were found (Fig. 1j, ESI Fig. S2h, S2d†). In addition, the whole lift-off and transfer processes can be accomplished within one minute (ESI Videos S1 and S2†). We first performed detailed studies on the transferred monolayer MoS$_2$ by using transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS). Selected area electron diffraction (SAED) patterns acquired from various positions of a MoS$_2$ flake (Fig. 2a) are shown in Fig. 2b–d,
Fig. 1  Strategy design for the growth and transfer of MoS₂ flakes. (a, b) Schematic diagram of the growth of MoS₂ on a water-soluble layer. (c–f) Schematic diagrams of the release and transfer of MoS₂ in water. (g–j) Optical images of as-grown MoS₂, PMMA covered as-grown wafer, PMMA/MoS₂/new substrate and MoS₂/new substrate.

Fig. 2  TEM characterization and XPS spectra of the as-transferred MoS₂ flakes. (a) Low magnification TEM image of a monolayer MoS₂ flake supported on a holey carbon TEM grid. (b–d) SAED patterns taken at locations marked with 1 to 3 on the monolayer MoS₂ flake in (a). (e) HRTEM image of the monolayer MoS₂ flake acquired at the location marked with 4 in (a). (f–i) Mo 3p, S 2p, Na 1s and Cl 2p core-level XPS of transferred MoS₂ flakes.
which exhibit identical orientation and precise fit to the hexagonal symmetry of 2H-MoS$_2$. Such results demonstrate the single crystallinity of the obtained MoS$_2$ over a large area of tens of micrometers, indicating that our transfer processes are damage-free. As seen in Fig. 2e, the high-resolution TEM (HRTEM) image acquired at position 4 in Fig. 2a shows crystalline planes with a spacing of 0.274 nm, corresponding to the (10–10) planes of MoS$_2$. More importantly, no residual Na or Cl elements were detected on the transferred MoS$_2$ flakes based on our characterization results from XPS measurements (Fig. 2f–i, ESI Fig. S3†).

After the successful demonstration of the water-assisted transfer of MoS$_2$, identifying the composition of the water-soluble layer underneath the flakes is vital for understanding the growth mechanism. We scratched a MoS$_2$ flake partially and found a thin layer of substance underneath the MoS$_2$ flake as shown in Fig. 3a. A similar substance was also observed on certain parts of the growth substrate surface or beneath the edge of the MoS$_2$ flakes (ESI Fig. S4a†). Energy dispersive spectroscopy (EDS) analysis was carried out on this substance, with results shown in Fig. 3b and ESI Fig. S4b.† The data indicate that the major elemental compositions are Na, S and Cl, which likely originate from the NaS$_x$ and non-vulcanized NaCl. To further confirm this, we introduced plasma irradiation to etch the MoS$_2$ film and characterized the water-soluble substance underneath it.47 XPS measurement results clearly show that, after thinning MoS$_2$, the signals of Na and Cl elements got enhanced while that of Mo element got suppressed (ESI Fig. S5 and S6†), suggesting that Na and Cl are indeed two major elemental compositions of the water-soluble layer. More importantly, the thickness and the area of the sacrificial layer can be controlled by adjusting the experimental parameters, such as growth temperature (ESI Fig. S7 and S8†). The thickness of the sacrificial layer increased with the increasing growth temperatures from 500 °C to 800 °C (ESI Fig. S8†) and the typical thickness is ~2 nm for those synthesized at 650 °C (ESI Fig. S7c and d†). Also, we observed that the sacrificial layer is a quasi-continuous film (ESI Fig. S9†).

Since our transfer processes only involve the use of deionized water (DI water), PMMA and acetone (with no etching process involved), the approach could have advantages on keeping the pristine quality of the samples. In order to investigate it, Raman characterization was carried out on as-grown MoS$_2$ flakes (Fig. 4c) and the exact one after transfer (Fig. 4d) for comparison. As shown in Fig. 4a, the as-grown MoS$_2$ sheet exhibits two characteristic Raman bands at around 386.4 cm$^{-1}$ and 404.5 cm$^{-1}$, corresponding to the E$_{2g}^{1}$ (in-plane vibrations of Mo and S atoms) and A$_{1g}$ (out-of-plane vibrations of MoS$_2$).
S atoms) modes of MoS2 crystals, respectively. The frequency difference between the two modes is about 18.1 cm\(^{-1}\), indicating that the sample is indeed monolayer MoS2. After the transfer, while the position of the \(E_{2g}\) mode remains consistent, the \(A_{1g}\) mode shifts to a higher frequency located at around 405.5 cm\(^{-1}\). We also performed the Raman mapping measurement of the \(A_{1g}\) mode before and after the transfer to examine the spatial uniformity of the grown sample. As shown in Fig. 4e, the frequency of the \(A_{1g}\) mode ranged from 403.6 to 405.5 cm\(^{-1}\) (centered at 404.5 cm\(^{-1}\)) before the transfer, which implies that the as-grown MoS2 exhibits high crystallinity and good uniformity. In Fig. 4f, the frequency of the \(A_{1g}\) mode in a transferred MoS2 flake is shifted to the range of 405.0 to 406.1 cm\(^{-1}\) (centered at 405.5 cm\(^{-1}\)) and it still maintains a high homogeneity. This confirms that the transfer process is damage-free. Such a shift may arise from the reduced electronic-doping level after the removal of the water-soluble layer.

The slightly better spatial uniformity with a narrower distribution of the \(A_{1g}\) mode observed in the sample after the transfer demonstrates quality improvement after removing the water-soluble substances during the transfer processes.

PL measurements were also performed by using the same laser excitation at room temperature, with results shown in Fig. 4b. For the as-grown flake, the strong intensity peak at around 1.85 eV (A excitonic transitions) and the relatively weak intensity peak at around 1.99 eV (B excitonic transitions) come from the direct bandgap transitions at the Brillouin zone K point. The energy difference of 0.14 eV is ascribed to the splitting of the valence band induced by the spin–orbit coupling. The intensities of both A and B exciton peaks were found to be notably enhanced after the transfer, indicating improved sample quality and luminescence quantum efficiency. The energy of the A excitonic transition characterized by PL mapping (Fig. 4g and h) was observed to distribute in the ranges of 1.82–1.86 eV (centered around 1.84 eV) and 1.85–1.90 eV (centered around 1.87 eV) for the flake before and after the transfer, respectively. The PL peak at around A excitonic transition consists of two components in monolayer MoS2, namely A exciton (neutral exciton) and A\(^-\)trion (negatively charged exciton). The A\(^-\)trion appears in the MoS2 flake with the unintentional electron doping arising from surface defects and the substrate. The component weight of A exciton and A\(^-\)trion in the PL process can be tuned via electrostatic or substrate-induced doping, with more A\(^-\)trion component for heavier electron doping. Neutral excitons emit at a higher energy than charged excitons owing to the large exciton binding energy (~30 meV). Thus, the observed overall blue-shift of the A excitonic peak after the transfer can be explained by a relative increase in the luminescence emission from neutral excitons, which implies reduced electron doping on MoS2 after the removal of the water-soluble layer.

Since monolayer MoS2 is a representative 2D semiconducting material, the field effect mobility is an important parameter to assess sample quality. To evaluate the electrical performance of the MoS2 flakes, we fabricated FETs based on randomly selected 60 as-grown and 60 transferred MoS2 flakes on SiO\(_2\)/Si substrates. Fig. 5a presents the typical transfer curves of a transferred MoS2 flake, which shows n-type conduction behavior with the on/off ratio exceeding 10\(^7\) (ESI Fig. S10†). The field effect mobility can be extracted from the linear regime of the transfer curves using the equation \(\mu = \frac{\delta I_d/\delta V_{bg}}{W/C_g}\), where \(I_d\) and \(V_{bg}\) are the drain current and the back-gated voltage, respectively. The statistical distribution of the field effect mobility of the as-grown and after-transfer flakes is shown in Fig. 5b. More than half of the after-transfer mobility values fall in the range of 5 to 25 cm\(^2\) V\(^{-1}\) s\(^{-1}\), with the highest value of 24.3 cm\(^2\) V\(^{-1}\) s\(^{-1}\). When compared with that of the as-grown flakes, the mobility is improved by 2–3 orders, which is likely due to the improved metal contact and reduced substrate scattering after removing the water-soluble substances.

With the realization of the growth and transfer of MoS2, we also performed a series of systematic studies to demonstrate this approach in other 2D TMDs, by using different halide salts or different growth substrates. The results on the growth and transfer of MoSe2 are shown in Section S8 in the ESI. We found that many other halide salts can be used as precursors to grow and transfer MoS2 flakes, including NaBr, NaI, KCl and KI (Section S9 in the ESI†). These results also indicate that halide salts play a key role in the synthesis of 2D TMDs, which has also been reported in the recent literature.

We also synthesized and transferred MoS2 flakes on various substrates, such as sapphire and glass (Section S10 in ESI†). Furthermore, several literature studies have reported the successful growth of metal films, graphene and perovskite films on water-soluble NaCl and/or Sr\(_3\)Al\(_2\)O\(_6\) substrates. After dissolving these sacrificial substrates, high quality samples can be obtained. Thus, the synthesis of materials on water-soluble substrates can be used as a general way for the damage-free, rapid and inexpensive transfer of various materials in many fields.

Conclusions

In conclusion, we designed and realized a damage-free and highly efficient approach to transfer 2D TMDs to arbitrary sub-
substrates by dissolving a sacrificial water-soluble layer. Such a water-soluble layer can be formed underneath TMD flakes simultaneously during the growth process. It was demonstrated, for monolayer MoS₂, that no quality degradation was found after the transfer by performing careful TEM, Raman spectroscopy, PL and electrical transport studies. This approach was also demonstrated to be applicable to other TMDs, other halide salts as precursors, or other growth substrates, indicating its universality for other 2D materials. Our work may pave the way for the material synthesis of future integrated electronic and optoelectronic devices based on 2D TMD materials.

Conflicts of interest
The authors declare no conflict of interest.

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