

MoS₂ Liquid Cell Electron Microscopy Through Clean and Fast Polymer-Free MoS₂ Transfer

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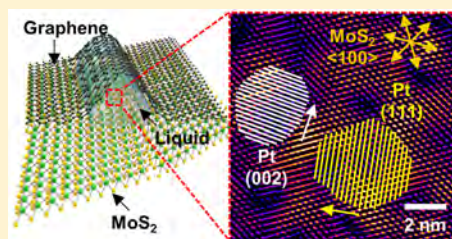
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Supporting Information

ABSTRACT: Two dimensional (2D) materials have found various applications because of their unique physical properties. For example, graphene has been used as the electron transparent membrane for liquid cell transmission electron microscopy (TEM) due to its high mechanical strength and flexibility, single-atom thickness, chemical inertness, etc. Here, we report using 2D MoS₂ as a functional substrate as well as the membrane window for liquid cell TEM, which is enabled by our facile and polymer-free MoS₂ transfer process. This provides the opportunity to investigate the growth of Pt nanocrystals on MoS₂ substrates, which elucidates the formation mechanisms of such heterostructured 2D materials. We find that Pt nanocrystals formed in MoS₂ liquid cells have a strong tendency to align their crystal lattice with that of MoS₂, suggesting a van der Waals epitaxial relationship. Importantly, we can study its impact on the kinetics of the nanocrystal formation. The development of MoS₂ liquid cells will allow further study of various liquid phenomena on MoS₂, and the polymer-free MoS₂ transfer process will be implemented in a wide range of applications.

KEYWORDS: Liquid cell electron microscopy, nanocrystal formation, MoS₂, heterostructures, polymer-free transfer



Liquid cell transmission electron microscopy (TEM), which allows imaging through liquids with high spatial and millisecond temporal resolution, has enabled the study of dynamic phenomena in liquids, ranging from nanoscale crystallization^{1–5} to transformation,^{6–10} self-assembly,^{11–14} electrochemical,^{15–17} and biological process.^{18,19} Recent application of two dimensional (2D) materials, such as graphene as the membrane window for liquid cells,^{20–27} has significantly enhanced the image contrast and spatial resolution by reducing electron beam scattering during imaging.²⁸ Indeed, graphene has been utilized as an excellent membrane material for conventional TEM^{29,30} due to its high thermal/electrical conductivity,³¹ chemical inertness,³² impermeability for small molecules,³³ high mechanical strength and flexibility.³⁴ Currently, the applications of 2D materials for liquid cell TEM have mostly focused on graphene^{19–27,35–38} or graphene oxide³⁹ and their roles are mostly limited to being the encapsulating material or mechanical support. Exploration of other 2D materials, that are not inert for various reactions, as the functional membranes as well as the support for liquid cell TEM

will allow the investigations of liquid reactions occurring on the 2D materials, which is significant for the study of formation mechanisms of heterostructured 2D materials.

Heterostructured 2D materials have emerged as an important class of materials offering unique properties due to synergistic effects between 2D materials and the nanomaterials counterpart with various dimensionalities (0D, 1D, and 2D).^{40–47} There have been tremendous efforts devoted to the synthesis and characterization of various forms of 2D heterostructures. Among them, heterostructures composed of MoS₂ and noble metal nanoparticles have attracted a lot of attention due to their enhanced catalytic performance.^{48–51} It is known that the properties of heterostructured 2D materials are highly sensitive to their atomic structures such as the relative crystal orientation of the constituent materials.^{52,53} Consequently, understanding and ultimately controlling noble metal nanoparticle formation

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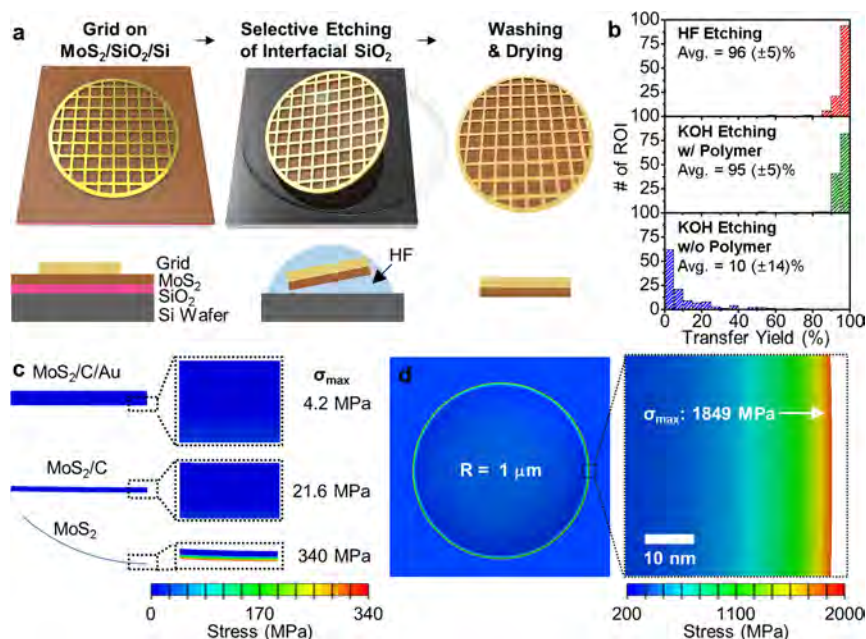


Figure 1. Polymer-free transfer process of MoS₂. (a) Schematic illustration of our polymer-free transfer method: (i) attachment of TEM grids on MoS₂/SiO₂/Si, (ii) selective etching of interfacial SiO₂, and (iii) washing/drying. (b) Histograms showing the distribution of the transfer yield within the region of interest (ROI) according to the transfer methods. 120 ROIs were used for each histogram, and each ROI contains ~100 Quantifoil holes. (c) FEM simulations of the stress distribution on MoS₂, MoS₂/carbon, and MoS₂/carbon/gold layered structures during bending by external forces. The thickness of MoS₂, carbon, and gold layers are 2, 10, and 20 nm, respectively for the simulation. The results are obtained under the same external pressure (5×10^{-5} Pa). The maximum stress is noted for each case. The images are drawn in scale. (d) FEM simulation of the stress distribution on a freestanding MoS₂ sheet by stretching due to the bubble attachment. The result is obtained for MoS₂ trapping a bubble with the radius of 1 μm . Additional simulation results are shown in Figures S8 and S9 in the SI.

on 2D substrates is of key importance in order to fully exploit them for further applications. Previous studies have been conducted mostly by ex situ structure characterization or in situ heating experiments under high vacuum.^{54–56} The development of MoS₂ liquid cell TEM will enable the direct real-time observation of nanoparticle formation on the 2D MoS₂ substrates and thus, it is highly desirable.

A clean, effective, and reproducible transfer process is one of the important prerequisites for practical applications of 2D materials that are usually grown on bulk inorganic substrates by chemical vapor deposition (CVD) methods.^{57–63} In order to transfer the 2D materials onto target substrates, spin-cast polymer layers have been employed to protect them from mechanical damage during the transfer process.^{64–69} However, it is difficult to completely remove the protection layer, and the polymer residues may deteriorate the optical, electrical, electrochemical, or mechanical properties of the 2D materials.^{70–74} For liquid cell TEM, the organic residues may introduce various side-reactions and significantly interrupt the imaging.^{35–38,75,76} Polymer-free transfer methods have been well developed for graphene^{77–79} since the CVD-substrate (Cu) can be easily etched under mild conditions without introducing significant mechanical damage or deformation to the graphene.^{19–27,35–38,79} However, transition metal chalcogenides, such as MoS₂, are usually grown on SiO₂/Si wafers. Harsh reaction conditions (e.g., high temperature alkaline solutions or high-energy ultrasonic processes) are required to remove the SiO₂/Si substrates, which can damage the 2D films.^{80–84} Thus, the development of an efficient polymer-free transfer for MoS₂ has been a challenging goal.

Here, we report the development of MoS₂ liquid cells through a fast and polymer-free transfer process for in situ TEM studies

of Pt nanocrystal growth on MoS₂. The selective etching of the interfacial SiO₂ layer between the MoS₂ and the Si wafer effectively reduces mechanical damage, resulting in high-yield transfer. The transferred MoS₂ is used in liquid cells as the functional substrate to investigate Pt nanocrystal formation on MoS₂ through in situ TEM. This reveals a van der Waals epitaxial relationship between Pt nanocrystals and MoS₂, which significantly affects the nanocrystal growth. Our work demonstrates a facile and clean transfer method for MoS₂ and facilitates the fundamental understanding of the 2D heterostructure formation.

The polymer-free MoS₂ transfer procedure for in situ liquid cell TEM is shown in Figure 1a (see Methods 1.1 and 1.2, Figures S1–S3 in the Supporting Information (SI) for experimental details). Quantifoil carbon grids with regular arrays of holes (diameter: ~1.2 or ~2.0 μm) are used as target substrates, which allows the application and further characterization of the regions of free-standing transferred-MoS₂ sheets. We directly attached the Quantifoil carbon TEM grids on a MoS₂/SiO₂/Si sample without polymer protection layers and used HF to selectively etch the interfacial SiO₂ layer. The MoS₂ sheet was then transferred onto the TEM grid. Scanning electron microscopy (SEM) images of the MoS₂-transferred TEM grids show high coverage of the Quantifoil holes with MoS₂ (Figures 1b, S4, and S5) regardless of window size (average transfer yields of ~96% and ~91% for the hole size of ~1.2 μm and ~2.0 μm , respectively).

For comparison, we also carried out MoS₂ transfer with the conventional method using KOH etching (see Methods 1.2 in the SI for experimental details). The gaseous byproducts (H₂) of KOH etching^{80–82} can easily damage the MoS₂ sheets. Therefore, the polymer layer is essential to protect the MoS₂

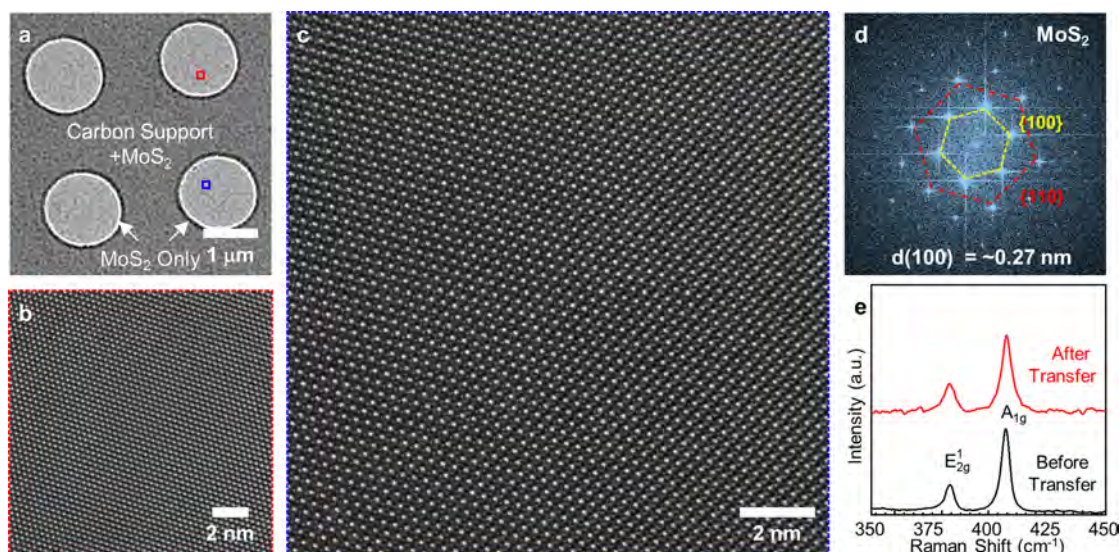


Figure 2. Characterization of polymer-free transferred MoS₂. (a) Low-resolution TEM image showing the support and holes of a MoS₂-transferred TEM grid. A MoS₂ membrane is transferred on the carbon support with $\sim 1.2 \mu\text{m}$ diameter holes. (b,c) High-resolution TEM images of transferred MoS₂. Crystal orientations of MoS₂ in the panel (b) and (c) are slightly different, because of the polycrystalline nature of multilayer MoS₂. The images are obtained from boxed area of the panel (a). (d) FFT image of panel (c). Data were acquired using a Tecnai at 200 kV. (e) Raman spectra of MoS₂ on SiO₂/Si (black, before the transfer process) and MoS₂ on a TEM grid (red, after the transfer process).

sheets from damage during the conventional transfer process. With polymer protection, a high transfer yield ($\sim 95\%$) is achieved (Figure 1b). However, the complete removal of polymer residues is challenging (Figure S6 in the SI), which would be problematic for further applications in liquid cell TEM, due to the poor visibility and undesirable side-reactions induced by the polymer residues during imaging. KOH etching without the polymer protection layer leads to a very low transfer yield ($\sim 10\%$), and the most of membranes are perforated (Figures 1b and S7).

Theoretical analysis based on finite element method (FEM) simulations validates the high transfer yield of our polymer-free MoS₂ transfer process (see Methods 1.3 in the SI for details). First, we test the role of the target substrate against bending stress. Figure 1c shows the representative stress distribution across MoS₂ sheets (three layers, $\sim 2 \text{ nm}$ thick) during the etching process with/without the prelaminated target substrate. The maximum applied stress on the MoS₂ sheets attached to the substrate (carbon/gold layer or carbon layer) is more than 1 order of magnitude lower than that of freestanding MoS₂ sheets under the same applied pressure (Figures 1c and S8). This implies that the target substrates can effectively act as a protecting layer. Second, FEM calculations estimate the mechanical impact of H₂ bubble generation on MoS₂ sheets floating in the etching solution (Figures 1d and S9). When bubbles are trapped under MoS₂ sheets, they can cause local stretching of the freestanding MoS₂ sheets. Especially at the edge of the bubbles, the local stress is significant regardless of the bubble size. This suggests that the vigorous bubble generation during the KOH etching process with the relatively long reaction time (tens of minutes) will likely break MoS₂ sheets. Our selective etching reaction takes a very short reaction time ($< \sim 1 \text{ s}$), which is 1000 times shorter than that of the conventional KOH etching (Figure S10 in the SI). This also helps to minimize the chance of mechanical damage to MoS₂ during the etching process.

Figure 2a shows a representative low-resolution TEM image of the MoS₂-transferred Quantifoil TEM grid (see Methods 1.5

in the SI). High-resolution TEM images of the two different freestanding MoS₂ region reveal the clean surface with the atomic structure of MoS₂ (Figure 2b,c). A fast Fourier transform (FFT) of the TEM image displays hexagonally arranged spots ($d = 0.27 \text{ nm}$), corresponding to the MoS₂ {100} lattice (Figure 2d).⁵⁶ A set of the spots corresponding to the MoS₂ {110} lattice planes ($\sim 0.17 \text{ nm}$) and higher order spots are also shown in the FFT pattern. Strikingly, with the clean MoS₂ surface, high-resolution TEM images of MoS₂ can be easily obtained without postimage processing or an advanced TEM such as one with aberration-correction or direct electron detection. A TEM image obtained at a broken region of the film indicates that the MoS₂ used in this study is 2–4 layers thick (Figure S11 in the SI). Furthermore, our clean transfer process can be applied to produce multiply stacked MoS₂ structures. TEM images of the stacked structures exhibit Moiré patterns according to the rotational alignment of MoS₂ sheets (Figure S12 in the SI).

We further characterize the MoS₂ sheets using Raman spectroscopy. Figure 2e shows the Raman spectra of MoS₂ before (i.e., MoS₂/SiO₂/Si) and after (i.e., MoS₂-transferred grids) the transfer process. Both spectra clearly exhibit the characteristic peaks of MoS₂ (E_{2g}^1 mode at $\sim 384 \text{ cm}^{-1}$ and A_{1g} mode at $\sim 407 \text{ cm}^{-1}$) without noticeable differences.^{85–87} A slight stiffening of the A_{1g} mode can be attributed to the substrate (SiO₂/Si) effect.^{86,87} Since Raman spectra of 2D materials are highly related to their structure,⁸⁸ these experimental results confirm that the structure of the MoS₂ is well maintained during the transfer process.

We fabricated MoS₂ TEM liquid cells to study Pt nanocrystal formation on MoS₂. The Pt nanocrystal growth solution can be successfully encapsulated between MoS₂- and graphene-transferred grids for TEM imaging (Figure 3a and Methods 1.4 in the SI). Low-resolution TEM images show that the liquid pockets containing Pt nanocrystals resemble a pseudorectangular shape (Figures 3b and S13). The formation of gas bubbles in the liquid pockets, which are produced by the solvent radiolysis by the electron beam,^{76,89} supports the successful encapsulation of liquid samples in MoS₂ liquid cells. The length (the longer axis)

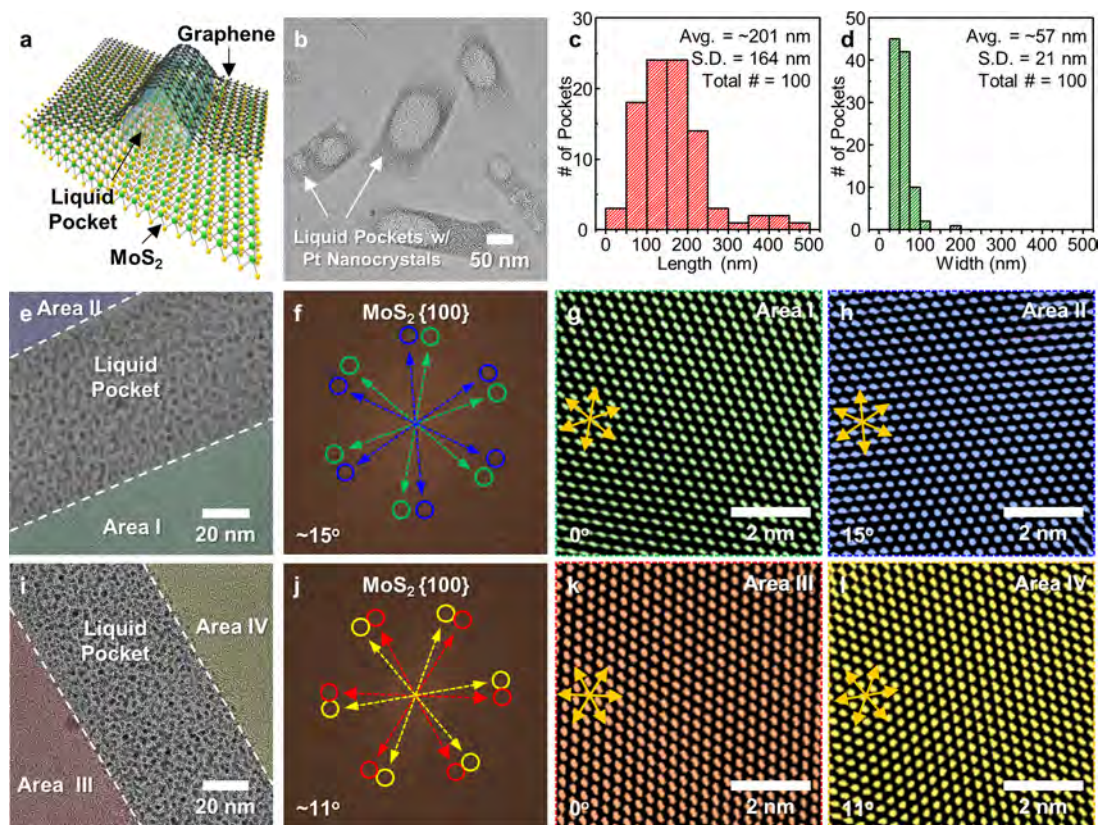


Figure 3. Liquid pocket formation in MoS₂ liquid cells. (a) Schematic illustration of the part of a MoS₂ liquid cell encapsulating liquid solution. (b) Low-resolution TEM image showing the overall morphology of the liquid pockets. (c,d) Histograms showing the distribution of (c) the length and (d) width of liquid pockets. (e) False-colored TEM image of a liquid pocket and (f) the corresponding FFT with the circled spots and arrows indicating different MoS₂ grains. The areas with different MoS₂ grains are highlighted by green (area I) and blue (area II). (g,h) Representative high-resolution masked inverse FFT images of area I and II. The orange arrows indicate the MoS₂ <100> directions. Area I and II are related to green and blue circled spots in the FFT image, respectively. (i) Another false-colored TEM image and (j) the corresponding FFT. The areas with the different MoS₂ grains are highlighted by red (area III) and yellow (area IV). (k,l) Representative high-resolution masked inverse FFT images of area III and IV. The orange arrows indicate the MoS₂ <100> directions. Area III and IV are related to red and yellow circled spots in the FFT image, respectively. Liquid cell TEM data were acquired using an aberration-corrected ThemIS at 300 kV.

and the width (the shorter axis) of the liquid pockets are in the range of several hundreds of nanometers and several tens of nanometers, respectively (Figure 3c,d). The aspect ratio (length/width) of the liquid pockets is large (3–8) as shown in the histogram in Figure S14 in the SI. The formation of the anisotropic liquid pockets with pseudorectangular shape is very different from previous studies using graphene liquid cells with a similar Pt growth solution, where the liquid pockets are highly irregular (Figure S15 in the SI). It is worth mentioning that MoS₂ liquid cells obtained by the conventional transfer process using polymer protection layers show significant carbon contamination under the electron beam exposure (Figure S16 in the SI), which limits any reliable liquid TEM study.

We further analyze TEM images of the liquid pockets (Figure 3e–l) to determine the distribution of MoS₂ grains around the liquid pockets (see Methods 1.5 in the SI). FFT patterns of each whole image exhibits several sets of hexagonally arranged spots corresponding to the MoS₂ lattice (Figure 3f,j). The multiple sets of spots with different rotations suggest the coexistence of the different MoS₂ grains, which is common in CVD-grown multilayer-2D materials. We perform FFT analysis to determine the position and orientations of each grain. The grain distribution is highlighted by the color mapping in the TEM images (Figure 3e,i) and the representative high-resolution masked inverse FFT images are displayed in Figure 3g,h and k,l.

TEM images without color-mapping and additional masked inverse FFT images acquired from subsets of each grain are presented in Figures S17 and S18 in the SI. We find that the liquid pockets tend to form between different grains of MoS₂. This is likely due to the different surface properties at the defect sites (grain boundary).³⁷ Other factors, such as membrane bulging³⁰ which is also expected to be significant at grain boundaries because of the low mechanical strength, may also affect the liquid distribution.

The successful fabrication of MoS₂ liquid cells provides the opportunity to investigate Pt nanocrystal formation on the MoS₂ with in situ liquid cell TEM. Because the growth of Pt nanocrystals has been well studied using traditional in situ liquid cell TEM,^{1,20,22} we can directly compare experimental results. This will facilitate our fundamental understanding on formation mechanisms of the heterostructures based on 2D MoS₂. The formation of Pt nanocrystals in MoS₂ liquid cells is observed by low-resolution in situ TEM imaging (Figure S19 and Movie S1 in the SI) and energy dispersive X-ray spectroscopy (Figure S20 in the SI). Most Pt nanocrystals are formed within a short period of time (less than 10 s) after initial exposure to the electron beam. As the reaction proceeds, the growth of nanocrystals results in an increased image contrast. The Pt nanocrystals show a narrow size distribution with an average diameter of ~2.5 nm (standard deviation of ~0.3 nm, Figure S21 in the SI).

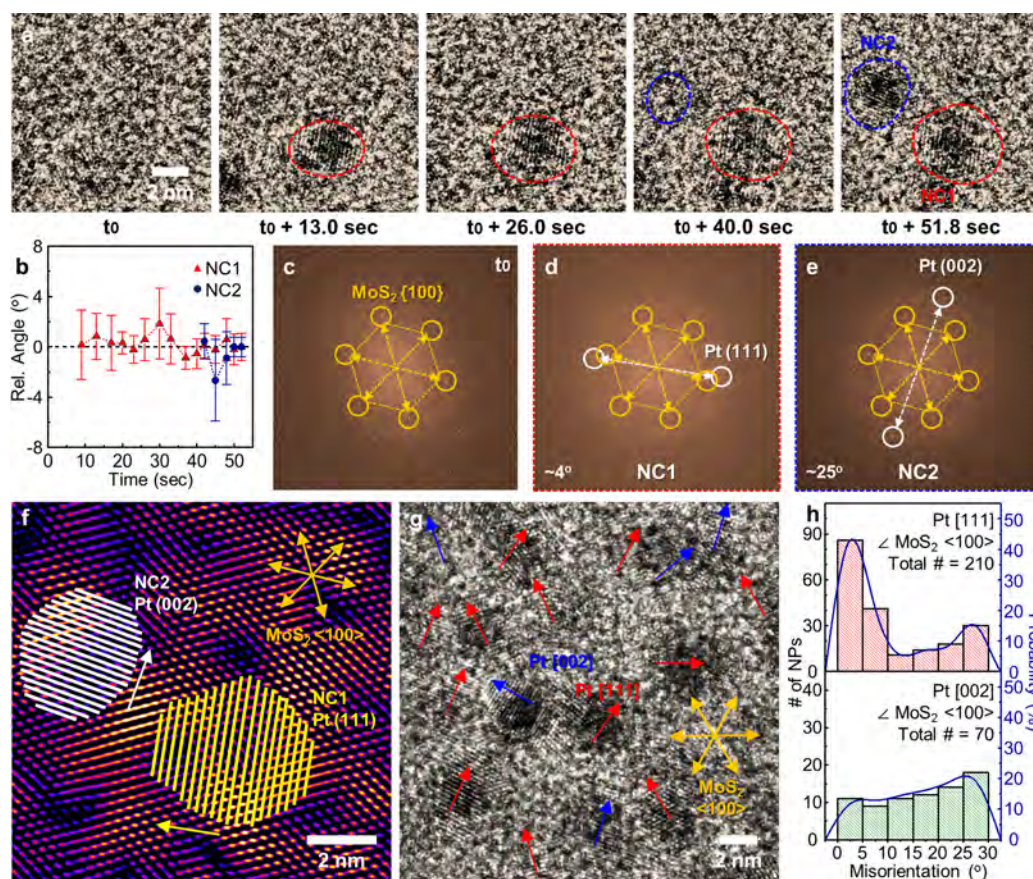


Figure 4. Formation of Pt nanocrystals on MoS₂. (a) Time-series of high-resolution in situ TEM images showing the formation of individual Pt nanocrystals. The corresponding movie is displayed in [Movie S2](#). (b) plot showing the relative orientation of Pt nanocrystals as a function of the time. The orientation at the last time frame is set as 0° for the both nanocrystals. (c–e) FFT of the first image (t_0) and NC1 and NC2 in the last frame ($t_0 + 51.8$ s). (f) Image showing the relative crystalline orientation of Pt nanocrystals and MoS₂. The image is obtained by overlapping the lattice fringes of Pt nanocrystals on inverse FFT image (a fire color lookup table) of MoS₂ in the final frame ($t_0 + 51.8$ s). (g) TEM image showing as-grown Pt nanocrystals where the orientation of Pt [111] and Pt [002] are marked with blue and red arrows, respectively. MoS₂ <100> directions are indicated by the orange arrows. (h) Histograms showing the misalignment angles between Pt nanocrystals (Pt [111] and Pt [002] directions) and MoS₂ (one of the MoS₂ <100> directions). Data were acquired from 210 nanocrystals for Pt [111] and 70 nanocrystals for Pt [002]. Liquid cell TEM data were acquired using an aberration-corrected ThemIS at 300 kV.

High-resolution in situ TEM images ([Figure 4a](#) and [Movie S2](#)) reveal the growth trajectories of individual Pt nanocrystals in MoS₂ liquid cells, showing two representative populations of nanocrystals. One nanocrystal (marked as NC1) appears within ~10 s and the other nanocrystal (marked as NC2) is formed much later after ~50 s. This is different from previous observations indicating that most nanocrystals are formed concurrently with a burst nucleation.^{91,92} Additional high-resolution in situ TEM data show consistent results ([Figures S22, S23](#) and [Movie S3](#) in the SI) in that there are two populations of Pt nanocrystals corresponding to the two different formation times. In addition, the translational and rotational motions of Pt nanocrystals are suppressed during growth ([Figure 4b](#)), which is in contrast with previous observations that small Pt nanocrystals (~2–3 nm) actively move and rotate in graphene liquid cells ([Figure S24](#) and [Movie S4](#) in the SI) under similar experimental conditions (i.e., with the similar solvent and electron beam intensity).^{20,22} This comparison implies that the MoS₂ sheets strongly interact with Pt nanocrystals, which will be discussed further below.

The FFT image of the first frame (t_0) of [Figure 4a](#) exhibits hexagonally arranged spots corresponding to MoS₂ {100} lattice spacing ([Figure 4c](#)). As Pt nanocrystals appear in the in situ

TEM images ([Figure 4a](#)), we can observe the emergence of additional spots in the FFT patterns (marked with white circles in [Figure 4d,e](#)). The observed lattice fringes for NC1 and NC2 correspond to Pt (111) and Pt (002) planes, respectively, and the measured lattice parameters (Pt (111): 2.30 Å and Pt (200): 1.95 Å) are similar to those of the bulk crystals (Pt (111): 2.27 Å and Pt (200): 1.96 Å).⁹³ Strikingly, the spots for Pt (111) of NC1 are aligned with those of MoS₂ (100) with a slight misorientation (<5°) ([Figure 4d,f](#)). Additional high-resolution in situ TEM data show the consistent orientation relationship between the Pt [111] direction and one of the MoS₂ <100> directions ([Figures S22](#) and [S23b](#) in the SI); there appears to be no obvious relationship for Pt [002] (compare [Figures 4e,f](#), [S22](#), and [S23c](#)). We further analyze more Pt nanocrystals grown on MoS₂, and most of them show the Pt (111) and (002) lattice. The relative crystal orientations between Pt nanocrystals (Pt [111] and Pt [002] directions) and MoS₂ (one of the MoS₂ <100> directions) are measured ([Figures 4g](#), [S25](#), and [S26](#)). The results from this measurement show that a large fraction of the Pt nanocrystals are aligned with MoS₂ with the relationship of Pt [111]//MoS₂ [100], while the alignment between Pt [002] and MoS₂ crystal directions seems not clear ([Figure 4h](#)). The alignment between the Pt [111] direction and one of the MoS₂

$\langle 100 \rangle$ directions can be explained by van der Waals epitaxy, which may stabilize the MoS₂-Pt heterostructures. Our results are consistent with previous studies on solution-phase synthesis of Pt nanocrystals on MoS₂, where coexistence of both epitaxially aligned and randomly oriented Pt nanocrystals was observed.⁵⁴ Interestingly, the two different growth trajectories of Pt nanocrystals observed (NC1 and NC2) are correlated with the epitaxial relationship between Pt nanocrystals and the MoS₂ substrate. Pt nanocrystals that are epitaxial with MoS₂ (NC1 in Figure 4a and NC3 in Figure S22 in the SI) are formed earlier than those with random orientation (NC2 in Figure 4a and NC4 in Figure S22 in the SI). This observation suggests that the reduced energy barrier for heterogeneous nucleation of Pt nanocrystals on MoS₂ with the van der Waals epitaxy may accelerate the nanocrystal formation.^{40–46,54,56,94,95} It is worthwhile to mention that Pt nanocrystals in graphene liquid cells are known to freely rotate^{20,22} and thus do not show orientational relationship. This highlights the importance of the development of MoS₂ liquid cells to study interactions of nanocrystals with 2D materials.

In summary, we have developed an efficient polymer-free MoS₂ transfer method and have showcased the MoS₂ liquid cell electron microscopy with the study of Pt nanocrystal formation on MoS₂. Polymer-free MoS₂ transfer is achieved by the selective etching of the interfacial SiO₂ layer. FEM analysis supports that our polymer-free transfer method can greatly reduce mechanical damage on the MoS₂, resulting in a high transfer yield. The resulting clean MoS₂ surface is useful for fundamental studies and diverse applications. Our liquid cell TEM study of Pt nanocrystal formation on MoS₂ shows that the $[111]$ direction of Pt nanocrystals has the strong tendency to align with one of the $\langle 100 \rangle$ directions of MoS₂. This suggests that there exists a van der Waals epitaxial relationship between Pt nanocrystals and the supporting MoS₂ sheet, which heavily influences the nanocrystal formation kinetics. Our study offers a new prototype to reveal dynamic processes in liquid on 2D materials and provides an effective method for polymer-free transfer of MoS₂, which is potentially applicable to a wide range of investigations.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.nanolett.8b04821.

Experimental methods, schematic illustrations, SEM images, FEM simulation results, and additional TEM analysis data (PDF)

In situ TEM movie showing Pt nanocrystal formation in a MoS₂ liquid cell (AVI)

In situ TEM movie 1 showing Pt nanocrystal formation in a MoS₂ liquid cell (AVI)

In situ TEM movie 2 showing Pt nanocrystal formation in a MoS₂ liquid cell (AVI)

In situ TEM movie showing translational movement of Pt nanocrystals in a graphene liquid cell (AVI)

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

- (1) Zheng, H.; Smith, R. K.; Jun, Y.-w.; Kisielowski, C.; Dahmen, U.; Alivisatos, A. P. *Science* **2009**, *324*, 1309–1312.
- (2) Nielsen, M. H.; Aloni, S.; De Yoreo, J. J. *Science* **2014**, *345*, 1158–1162.
- (3) Woehl, T. J.; Evans, J. E.; Arslan, I.; Ristenpart, W. D.; Browning, N. D. *ACS Nano* **2012**, *6*, 8599–8610.
- (4) De Yoreo, J. J.; Sommerdijk, N. A. J. M. *Nat. Rev. Mater.* **2016**, *1*, 16035.
- (5) Sutter, P.; Li, Y.; Argyropoulos, C.; Sutter, E. *J. Am. Chem. Soc.* **2017**, *139*, 6771–6776.
- (6) Hauwiller, M. R.; Zhang, X.; Liang, W.-I.; Chiu, C.-H.; Zhang, Q.; Zheng, W.; Ophus, C.; Chan, E. M.; Czarnik, C.; Pan, M.; Ross, F. M.; Wu, W.-W.; Chu, Y.-H.; Asta, M.; Voorhees, P. W.; Alivisatos, A. P.; Zheng, H. *Nano Lett.* **2018**, *18*, 6427–6433.
- (7) Liao, H.-G.; Zhrebetsky, D.; Xin, H.; Czarnik, C.; Ercius, P.; Elmlund, H.; Pan, M.; Wang, L.-W.; Zheng, H. *Science* **2014**, *345*, 916–919.
- (8) Sutter, E.; Jungjohann, K.; Bliznakov, S.; Courty, A.; Maisonhaute, E.; Tenney, S.; Sutter, P. *Nat. Commun.* **2014**, *5*, 4946.
- (9) Gao, W.; Hou, Y.; Hood, Z. D.; Wang, X.; More, K.; Wu, R.; Xia, Y.; Pan, X.; Chij, M. *Nano Lett.* **2018**, *18*, 7004–7013.
- (10) Kim, B. H.; Yang, J.; Lee, D.; Choi, B. K.; Hyeon, T.; Park, J. *Adv. Mater.* **2018**, *30*, 1703316.
- (11) Powers, A. S.; Liao, H.-G.; Raja, S. N.; Bronstein, N. D.; Alivisatos, A. P.; Zheng, H. *Nano Lett.* **2017**, *17*, 15–20.
- (12) Lee, W. C.; Kim, B. H.; Choi, S.; Takeuchi, S.; Park, J. *J. Phys. Chem. Lett.* **2017**, *8*, 647–654.
- (13) Tan, S. F.; Chee, S. W.; Lin, G.; Mirsaidov, U. *Acc. Chem. Res.* **2017**, *50*, 1303–1312.
- (14) Luo, B.; Smith, J. W.; Ou, Z.; Chen, Q. *Acc. Chem. Res.* **2017**, *50*, 1125–1133.
- (15) Williamson, M. J.; Tromp, R. M.; Vereecken, P. M.; Hull, R.; Ross, F. M. *Nat. Mater.* **2003**, *2*, 532–536.
- (16) Gu, M.; Parent, L. R.; Mehdi, B. L.; Unocic, R. R.; McDowell, M. T.; Sacci, R. L.; Xu, W.; Connell, J. G.; Xu, P.; Abellan, P.; Chen, X.; Zhang, Y.; Perea, D. E.; Evans, J. E.; Lauthon, L. J.; Zhang, J.-G.; Liu, J.; Browning, N. D.; Cui, Y.; Arslan, I.; Wang, C.-M. *Nano Lett.* **2013**, *13*, 6106–6112.

- (17) Zeng, Z.; Zheng, W.; Zheng, H. *Acc. Chem. Res.* **2017**, *50*, 1808–1807.
- (18) Park, J.; Park, H.; Ercius, P.; Pegoraro, A. F.; Xu, C.; Kim, J. W.; Han, S. H.; Weitz, D. A. *Nano Lett.* **2015**, *15*, 4737–4744.
- (19) Liv, N.; van Oosten Slingeland, D. S.; Baudoin, J. P.; Kruit, P.; Piston, D. W.; Hoogenboom, J. P. *ACS Nano* **2016**, *10*, 265–273.
- (20) Yuk, J. M.; Park, J.; Ercius, P.; Kim, K.; Hellebusch, D. J.; Crommie, M. F.; Lee, J. Y.; Zettl, A.; Alivisatos, A. P. *Science* **2012**, *336*, 61–64.
- (21) Chen, Q.; Smith, J. M.; Park, J.; Kim, K.; Ho, D.; Rasool, H. I.; Zettl, A.; Alivisatos, A. P. *Nano Lett.* **2013**, *13*, 4556–4561.
- (22) Park, J.; Elmlund, H.; Ercius, P.; Yuk, J. M.; Limmer, D. T.; Chen, Q.; Kim, K.; Han, S. H.; Weitz, D. A.; Zettl, A.; Alivisatos, A. P. *Science* **2015**, *349*, 290–295.
- (23) Ye, X.; Jones, M. R.; Frechette, L. B.; Chen, Q.; Powers, A. S.; Ercius, P.; Dunn, G.; Rotskoff, G. M.; Nguyen, S. C.; Adiga, V. P.; Zettl, A.; Rabani, E.; Geissler, P. L.; Alivisatos, A. P. *Science* **2016**, *354*, 874–877.
- (24) Dahmke, I. N.; Verch, A.; Hermannsdorfer, J.; Peckys, D. B.; Weatherup, R. S.; Hofmann, S.; de Jonge, N. *ACS Nano* **2017**, *11*, 11108–11117.
- (25) Nagamanasa, K. H.; Wang, H.; Granick, S. *Adv. Mater.* **2017**, *29*, 1703555.
- (26) Kelly, D.; Zhou, M.; Clark, N.; Hamer, M. J.; Lewis, E. A.; Rakowski, A. M.; Haigh, S. J.; Gorbachev, R. V. *Nano Lett.* **2018**, *18*, 1168–1174.
- (27) Textor, M.; de Jonge, N. *Nano Lett.* **2018**, *18*, 3313–3321.
- (28) de Jonge, N. *Ultramicroscopy* **2018**, *187*, 113–125.
- (29) Meyer, J. C.; Girit, C. O.; Crommie, M. F.; Zettl, A. *Nature* **2008**, *454*, 319–322.
- (30) Nair, R. R.; Blake, P.; Blake, J. R.; Zan, R.; Anisimova, S.; Bangert, U.; Golovanov, A. P.; Morozov, S. V.; Geim, A. K.; Novoselov, K. S.; Latychevskaia, T. *Appl. Phys. Lett.* **2010**, *97*, 153102.
- (31) Bolotin, K. I.; Sikes, K. J.; Jiang, Z.; Klima, M.; Fudenberg, G.; Hone, J.; Kim, P.; Stormer, H. L. *Solid State Commun.* **2008**, *146*, 351–355.
- (32) Aliofkhaezrai, M.; Ali, N.; Milne, W. I.; Ozkan, C. S.; Mitura, S.; Gervasoni, J. L. *Graphene science handbook: electrical and optical properties*; CRC Press: Boca Raton, FL, 2016.
- (33) Xu, K.; Cao, P.; Heath, J. R. *Science* **2010**, *329*, 1188–1191.
- (34) Lee, C.; Wei, X.; Kysar, J. W.; Hone, J. *Science* **2008**, *321*, 385–388.
- (35) Cho, H.; Jones, M. R.; Nguyen, S. C.; Hauwiller, M. R.; Zettl, A.; Alivisatos, A. P. *Nano Lett.* **2017**, *17*, 414–420.
- (36) Wang, H.; Nagamanasa, K. H.; Kim, Y.-J.; Kwon, O.-H.; Granick, S. *ACS Nano* **2018**, *12*, 8572–8578.
- (37) Yang, J.; Alam, S. B.; Yu, L.; Chan, E.; Zheng, H. *Micron* **2019**, *116*, 22–29.
- (38) Keskin, S.; de Jonge, N. *Nano Lett.* **2018**, *18*, 7435–7440.
- (39) Krueger, M.; Berg, S.; Stone, D.; Strelcov, E.; Dikin, D. A.; Kim, J.; Cote, L. J.; Huang, J.; Kolmakov, A. *ACS Nano* **2011**, *5*, 10047–10057.
- (40) Huang, X.; Qi, X.; Boey, F.; Zhang, H. *Chem. Soc. Rev.* **2012**, *41*, 666–686.
- (41) Butler, S. Z.; Hollen, S. M.; Cao, L.; Cui, Y.; Gupta, J. A.; Gutiérrez, H. R.; Heinz, T. F.; Hong, S. S.; Huang, J.; Ismach, A. F.; Johnston-Halperin, E.; Kuno, M.; Plashnitsa, V. V.; Robinson, R. D.; Ruoff, R. S.; Salahuddin, S.; Shan, J.; Shi, L.; Spencer, M. G.; Terrones, M.; Windl, W.; Goldberger, J. E. *ACS Nano* **2013**, *7*, 2898–2926.
- (42) Geim, A. K.; Grigorieva, I. V. *Nature* **2013**, *499*, 419–425.
- (43) Yu, J. H.; Lee, H. R.; Hong, S. S.; Kong, D.; Lee, H.-W.; Wang, H.; Xiong, F.; Wang, S.; Cui, Y. *Nano Lett.* **2015**, *15*, 1031–1035.
- (44) Ban, H. W.; Park, S.; Jeong, H.; Gu, D. H.; Jo, S.; Park, S. H.; Park, J.; Son, J. S. *J. Phys. Chem. Lett.* **2016**, *7*, 3627–3635.
- (45) Liu, Y.; Weiss, N. O.; Duan, X.; Cheng, H.-C.; Huang, Y.; Duan, X. *Nat. Rev. Mater.* **2016**, *1*, 16042.
- (46) Yang, J.; Kim, K.; Lee, Y.; Kim, K.; Lee, W. C.; Park, J. *FlatChem.* **2017**, *5*, 50–68.
- (47) Woods, J. M.; Jung, Y.; Xie, Y.; Liu, W.; Liu, Y.; Wang, H.; Cha, J. *J. ACS Nano* **2016**, *10*, 2004–2009.
- (48) Deng, J.; Li, H.; Xiao, J.; Tu, Y.; Deng, D.; Yang, H.; Tian, H.; Li, J.; Ren, P.; Bao, X. *Energy Environ. Sci.* **2015**, *8*, 1594–1601.
- (49) Deng, D.; Novoselov, K. S.; Fu, Q.; Zheng, N.; Tian, Z.; Bao, X. *Nat. Nanotechnol.* **2016**, *11*, 218–230.
- (50) Li, H.; Wang, L.; Dai, Y.; Pu, Z.; Lao, Z.; Chen, Y.; Wang, M.; Zheng, X.; Zhu, J.; Zhang, W.; Si, R.; Ma, C.; Zeng, J. *Nat. Nanotechnol.* **2018**, *13*, 411–417.
- (51) Li, Y.; Majewski, M. B.; Islam, S. M.; Hao, S.; Murthy, A. A.; DiStefano, J. G.; Hanson, E. D.; Xu, Y.; Wolverton, C.; Kanatzidis, M. G.; Wasielewski, M. R.; Chen, X.; Dravid, V. P. *Nano Lett.* **2018**, *18*, 7104–7110.
- (52) Zhang, Y.; Tang, T.-T.; Girit, C.; Hao, Z.; Martin, M. C.; Zettl, A.; Crommie, M. F.; Shen, Y. R.; Wang, F. *Nature* **2009**, *459*, 820–823.
- (53) Yankowitz, M.; Xue, J.; Cormode, D.; Sanchez-Yamagishi, J. D.; Watanabe, K.; Taniguchi, T.; Jarillo-Herrero, P.; Jacquod, P.; LeRoy, B. *J. Nat. Phys.* **2012**, *8*, 382–386.
- (54) Huang, X.; Zeng, Z.; Bao, S.; Wang, M.; Qi, X.; Fan, Z.; Zhang, H. *Nat. Commun.* **2013**, *4*, 1444.
- (55) Li, H.; Wang, S.; Sawada, H.; Han, G. G. D.; Samuels, T.; Allen, C. S.; Kirkland, A. I.; Grossman, J. C.; Warner, J. H. *ACS Nano* **2017**, *11*, 3392–3403.
- (56) Wang, S.; Sawada, H.; Chen, Q.; Han, G. G. D.; Allen, C.; Kirkland, A. I.; Warner, J. H. *ACS Nano* **2017**, *11*, 9057–9067.
- (57) Kim, K. S.; Zhao, Y.; Jang, H.; Lee, S. Y.; Kim, J. M.; Kim, K. S.; Ahn, J.-H.; Kim, P.; Choi, J.-Y.; Hong, B. H. *Nature* **2009**, *457*, 706–710.
- (58) Li, H.; Wu, J.; Huang, X.; Yin, Z.; Liu, J.; Zhang, H. *ACS Nano* **2014**, *8*, 6563–6570.
- (59) Akinwande, D.; Petrone, N.; Hone, J. *Nat. Commun.* **2014**, *5*, 5678.
- (60) Chang, H.-Y.; Yang, S.; Lee, J.; Tao, L.; Hwang, W.-S.; Jena, D.; Lu, N.; Akinwande, D. *ACS Nano* **2013**, *7*, 5446–5452.
- (61) Choi, C.; Choi, M. K.; Liu, S.; Kim, M. S.; Park, O. K.; Kim, J.; Kim, C.; Qin, X.; Lee, G. J.; Cho, K. W.; Kim, M.; Joh, E.; Lee, J.; Son, D.; Kwon, S.-H.; Jeon, N. L.; Song, Y. M.; Lu, N.; Kim, D.-H. *Nat. Commun.* **2017**, *8*, 1664.
- (62) Hong, X.; Kim, J.; Shi, S.-F.; Zhang, Y.; Jin, C.; Sun, Y.; Tongay, S.; Wu, J.; Zhang, Y.; Wang, F. *Nat. Nanotechnol.* **2014**, *9*, 682–686.
- (63) Schmidt, H.; Wang, S.; Chu, L.; Toh, M.; Kumar, R.; Zhao, W.; Neto, A. H. C.; Martin, J.; Adam, S.; Özyilmaz, B.; Eda, G. *Nano Lett.* **2014**, *14*, 1909–1913.
- (64) Zhan, Y.; Liu, Z.; Najmaei, S.; Ajayan, P. M.; Lou, J. *Small* **2012**, *8*, 966–971.
- (65) Zhang, Z.; Du, J.; Zhang, D.; Sun, H.; Yin, L.; Ma, L.; Chen, J.; Ma, D.; Cheng, H.-M.; Ren, W. *Nat. Commun.* **2017**, *8*, 14560.
- (66) Suk, J. W.; Kitt, A.; Magnuson, C. W.; Hao, Y.; Ahmed, S.; An, J.; Swan, A. K.; Goldberg, B. B.; Ruoff, R. S. *ACS Nano* **2011**, *5*, 6916–6924.
- (67) Lock, E. H.; Baraket, M.; Laskoski, M.; Mulvaney, S. P.; Lee, W. K.; Sheehan, P. E.; Hines, D. R.; Robinson, J. T.; Tosado, J.; Fuhrer, M. S.; Hernandez, S. C.; Walton, S. G. *Nano Lett.* **2012**, *12*, 102–107.
- (68) Song, J.; Kam, F.-Y.; Png, R.-Q.; Seah, W.-L.; Zhuo, J.-M.; Lim, G.-K.; Ho, P. K. H.; Chua, L.-L. *Nat. Nanotechnol.* **2013**, *8*, 356–362.
- (69) Gao, L.; Ni, G.-X.; Liu, Y.; Liu, B.; Neto, A. H. C.; Loh, K. P. *Nature* **2014**, *505*, 190–194.
- (70) Lin, Z.; Zhao, Y.; Zhou, C.; Zhong, R.; Wang, X.; Tsang, Y. H.; Chai, Y. *Sci. Rep.* **2016**, *5*, 18596.
- (71) Choi, M. K.; Park, I.; Kim, D. C.; Joh, E.; Park, O. K.; Kim, J.; Kim, M.; Choi, C.; Yang, J.; Cho, K. W.; Hwang, J.-H.; Nam, J.-M.; Hyeon, T.; Kim, J. H.; Kim, D.-H. *Adv. Funct. Mater.* **2015**, *25*, 7109–7118.
- (72) Bae, S.; Kim, H.; Lee, Y.; Xu, X.; Park, J.-S.; Zheng, Y.; Balakrishnan, J.; Lei, T.; Kim, H. R.; Song, Y. I.; Kim, Y.-J.; Kim, K. S.; Ozyilmaz, B.; Ahn, J.-H.; Hong, B. H.; Iijima, S. *Nat. Nanotechnol.* **2010**, *5*, 574–578.

(73) Wang, X.; Tao, L.; Hao, Y.; Liu, Z.; Chou, H.; Kholmanov, I.; Chen, S.; Tan, C.; Jayant, N.; Yu, Q.; Akinwande, D.; Ruoff, R. S. *Small* **2014**, *10*, 694–698.

(74) Jung, W.; Kim, D.; Lee, M.; Kim, S.; Kim, J.-H.; Han, C.-S. *Adv. Mater.* **2014**, *26*, 6394–6400.

(75) Abellan, P.; Woehl, T. J.; Parent, L. R.; Browning, N. D.; Evans, J. E.; Arslan, I. *Chem. Commun.* **2014**, *50*, 4873–4880.

(76) Woehl, T. J.; Abellan, P. *J. Microsc.* **2017**, *265*, 135–147.

(77) Regan, W.; Alem, N.; Alemán, B.; Geng, B.; Girit, C.; Maserati, L.; Wang, F.; Crommie, M.; Zettl, A. *Appl. Phys. Lett.* **2010**, *96*, 113102.

(78) Lin, W.-H.; Chen, T.-H.; Chang, J.-K.; Taur, J.-I.; Lo, Y.-Y.; Lee, W.-L.; Chang, C.-S.; Su, W.-B.; Wu, C.-I. *ACS Nano* **2014**, *8*, 1784–1791.

(79) Zhang, J.; Lin, L.; Sun, L.; Huang, Y.; Koh, A. L.; Dang, W.; Yin, J.; Wang, M.; Tan, C.; Li, T.; Tan, Z.; Liu, Z.; Peng, H. *Adv. Mater.* **2017**, *29*, 1700639.

(80) Tsai, M.-L.; Su, S.-H.; Chang, J.-K.; Tsai, D.-S.; Chen, C.-H.; Wu, C.-I.; Li, L.-J.; Chen, L.-J.; He, J.-H. *ACS Nano* **2014**, *8*, 8317–8322.

(81) Gurarlan, A.; Yu, Y.; Su, L.; Yu, Y.; Suarez, F.; Yao, S.; Zhu, Y.; Ozturk, M.; Zhang, Y.; Cao, L. *ACS Nano* **2014**, *8*, 11522–11528.

(82) Yu, H.; Liao, M.; Zhao, W.; Liu, G.; Zhou, X. J.; Wei, Z.; Xu, X.; Liu, K.; Hu, Z.; Deng, K.; Zhou, S.; Shi, J.-A.; Gu, L.; Shen, C.; Zhang, T.; Du, L.; Xie, L.; Zhu, J.; Chen, W.; Yang, R.; Shi, D.; Zhang, G. *ACS Nano* **2017**, *11*, 12001–12007.

(83) Ma, D.; Shi, J.; Ji, Q.; Chen, K.; Yin, J.; Lin, Y.; Zhang, Y.; Liu, M.; Feng, Q.; Song, X.; Guo, X.; Zhang, J.; Zhang, Y.; Liu, Z. *Nano Res.* **2015**, *8*, 3662–3672.

(84) Lee, Y.-H.; Yu, L.; Wang, H.; Fang, W.; Ling, X.; Shi, Y.; Lin, C.-T.; Huang, J.-K.; Chang, M.-T.; Chang, C.-S.; Dresselhaus, M.; Palacios, T.; Li, L.-J.; Kong, J. *Nano Lett.* **2013**, *13*, 1852–1857.

(85) Jimenez Sandoval, S.; Yang, D.; Frindt, R. F.; Irwin, J. C. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1991**, *44*, 3955–3962.

(86) Li, H.; Zhang, Q.; Yap, C. C. R.; Tay, B. K.; Edwin, T. H. T.; Olivier, A.; Baillargeat, D. *Adv. Funct. Mater.* **2012**, *22*, 1385–1390.

(87) Zhang, X.; Qiao, X.-F.; Shi, W.; Wu, J.-B.; Jiang, D.-S.; Tan, P.-H. *Chem. Soc. Rev.* **2015**, *44*, 2757–2785.

(88) Ferrari, A. C.; Meyer, J. C.; Scardaci, V.; Casiraghi, C.; Lazzeri, M.; Mauri, F.; Piscanec, S.; Jiang, D.; Novoselov, K. S.; Roth, S.; Geim, A. K. *Phys. Rev. Lett.* **2006**, *97*, 187401.

(89) Grogan, J. M.; Schneider, N. M.; Ross, F. M.; Bau, H. H. *Nano Lett.* **2014**, *14*, 359–364.

(90) de Jonge, N.; Peckys, D. B.; Kremers, G. J.; Piston, D. W. *Proc. Natl. Acad. Sci. U. S. A.* **2009**, *106*, 2159–2164.

(91) Sugimoto, T. *Adv. Colloid Interface Sci.* **1987**, *28*, 65–108.

(92) Kwon, S. G.; Hyeon, T. *Small* **2011**, *7*, 2685–2702.

(93) Wyckoff, R. W. G. *Crystal structures*, 2nd ed.; Interscience: New York, 1963.

(94) Lee, W. C.; Kim, K.; Park, J.; Koo, J.; Jeong, H. Y.; Lee, H.; Weitz, D. A.; Zettl, A.; Takeuchi, S. *Nat. Nanotechnol.* **2015**, *10*, 423–428.

(95) Jang, J.; Lee, Y.; Yoon, J.-Y.; Yoon, H. H.; Koo, J.; Choe, J.; Jeon, S.; Sung, J.; Park, J.; Lee, W. C.; Lee, H.; Jeong, H. Y.; Park, K.; Kim, K. *Nano Lett.* **2018**, *18*, 6214–6221.