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

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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
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 x 10^-3 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.64-66 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.57-59 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.64-67 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.68-71 For liquid cell TEM, the organic residues may introduce various side-reactions and significantly interrupt the imaging.72 Polymer-free transfer methods have been well developed for graphene73-75 since the CVD-substrate (Cu) can be easily etched under mild conditions without introducing significant mechanical damage or deformation to the graphene.76-79 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 etching80-82 can easily damage the MoS2 sheets. Therefore, the polymer layer is essential to protect the MoS2.
sheets from damage during the conventional transfer process. With polymer protection, a high transfer yield (∼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 (∼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, ∼2 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 (< 1 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 nm), corresponding to the MoS2 {100} lattice (Figure 2d). A set of the spots corresponding to the MoS2 {110} lattice planes (∼0.17 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 (E1g mode at ∼384 cm−1 and A1g mode at ∼407 cm−1) without noticeable differences.85–87 A slight stiffening of the A1g 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,86,89 supports the successful encapsulation of liquid samples in MoS2 liquid cells. The length (the longer axis)
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 ($3 \leq 8$) 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 MoS$_2$ 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–I) to determine the distribution of MoS$_2$ 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 MoS$_2$ lattice (Figure 3fj). The multiple sets of spots with different rotations suggest the coexistence of the different MoS$_2$ 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 MoS$_2$. This is likely due to the different surface properties at the defect sites (grain boundary). Other factors, such as membrane bulging, 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 MoS$_2$ liquid cells provides the opportunity to investigate Pt nanocrystal formation on the MoS$_2$ with in situ liquid cell TEM. Because the growth of Pt nanocrystals has been well studied using traditional in situ liquid cell TEM, we can directly compare experimental results. This will facilitate our fundamental understanding on formation mechanisms of the heterostructures based on 2D MoS$_2$. The formation of Pt nanocrystals in MoS$_2$ 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 $\sim 2.5$ nm (standard deviation of $\sim 0.3$ nm, Figure S21 in the SI).
High-resolution in situ TEM images (Figure 4a and Movie S2) reveal the growth trajectories of individual Pt nanocrystals in MoS$_2$ 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 MoS$_2$ 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 MoS$_2$ {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 MoS$_2$ (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 MoS$_2$ ⟨100⟩ directions (Figures S22 and S23). 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 MoS$_2$, 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 MoS$_2$ (one of the MoS$_2$ ⟨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 MoS$_2$ with the relationship of Pt [111]//MoS$_2$ [100], while the alignment between Pt [002] and MoS$_2$ crystal directions seems not clear (Figure 4h). The alignment between the Pt [111] direction and one of the MoS$_2$
development of MoS₂ liquid cells to study interactions of Pt nanocrystals on MoS₂, where coexistence of both epitaxially aligned and randomly oriented Pt nanocrystals was observed. 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.

In summary, we have developed an efficient polymer-free MoS₂ transfer method and have showcased the MoS₂ liquid cell electron microscopy with the MoS₂ 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 nanocrystals in graphene liquid cells are known to freely rotate 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 situ TEM movie showing Pt nanocrystal formation in a graphene liquid cell (AVI)

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

ASSOCIATED CONTENT

Supporting Information

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100 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. 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.

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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 3 showing translational movement of Pt nanocrystals in a graphene liquid cell (AVI)

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