Using graphene to suppress the selenization of Pt for controllable fabrication of monolayer PtSe₂

Zhong-Liu Liu^{1,§}, Zhi-Li Zhu^{1,§}, Xu Wu^{2,§}, Jin-An Shi¹, Wu Zhou¹, Li-Wei Liu², Ye-Liang Wang^{2,1,3} (\bowtie), and Hong-Jun Gao^{1,3} (\bowtie)

¹ Institute of Physics and University of Chinese Academy of Sciences, Chinese Academy of Sciences, Beijing 100190, China

² School of Information and Electronics, MIIT Key Laboratory for Low-Dimensional Quantum Structure and Devices, Beijing Institute of Technology, Beijing 100081, China

³ CAS Center for Excellence in Topological Quantum Computation, Beijing 100049, China

[§] *Zhong-Liu Liu, Zhi-Li Zhu, and Xu Wu contributed equally to this work.*

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ABSTRACT

Platinum diselenide (PtSe₂) is a promising transition metal dichalcogenide (TMDC) material with unique properties. It is necessary to find a controllable fabrication method to bridge PtSe₂ with other two-dimensional (2D) materials for practical applications, which has rarely been reported so far. Here, we report that the selenization of Pt(111) can be suppressed to form a Se intercalated layer, instead of a PtSe₂ monolayer, by inducing confined conditions with a precoating of graphene. Experiments with graphene-island samples demonstrate that the monolayer PtSe₂ can be controllably fabricated only on the bare Pt surface, while the Se intercalated layer is formed underneath graphene, as verified by atomic-resolution observations with scanning transmission electron microscopy (STEM) and scanning tunneling microscopy (STM). In addition, the orientation of the graphene island shows a negligible influence on the Se intercalated layer induced by the graphene coating. By extending the application of 2D confined reactions, this work provides a new method to control the fabrication and pattern 2D materials during the fabrication process.

KEYWORDS

PtSe₂, graphene, confined reaction, selenization, intercalation

1 Introduction

With their unique structural and electronic properties [1–4], two-dimensional (2D) transition metal dichalcogenides (TMDCs) have been considered promising candidates for low-dimensional electronic devices [5–9]. As a representative member of 2D group-10 TMDCs, the semiconducting monolayer (ML) platinum diselenide (PtSe₂) has been reported to have excellent properties, such as high charge-carrier mobility [10] and intervalley scattering [11]. Such fundamental properties of ML PtSe₂ offer major potential applications in electronics [12], spintronics [13], catalysts [14] and sensors [15]. While monolayer PtSe₂ has been successfully fabricated by direct selenization of a Pt(111) substrate [16], it is crucial to pattern [17–19] ML PtSe₂ or bridge it with other 2D materials [20–23] to extend the applications.

To pattern ML PtSe₂ into delicate nanostructures, it is necessary to find an effective bottom-up way to control the PtSe₂ morphology, because top-down etching may cause damages to PtSe₂ due to its structural fragility. Controlling the Pt selenization at different positions of the Pt substrate could serve as a feasible means for the morphology control. In addition, confined reactions at the interfaces of 2D materials [24–27] can be used to tune the growth product by employing intercalation [28–30] during the growth process. As reported previously, the confined effects of the interface can notably influence the chemical behavior of the molecules trapped inside, changing their chemical potentials and consequently leading to different reactions [31–36]. In addition to modulating the molecules, there have been several examples taking advantage of the interfaces in layered heterostructures to grow 2D materials in novel configurations [37], such as the growth of graphitic ML gallium nitride [38], rhenium diselenide [39] and silicone [40] at the interfaces of graphene heterostructures.

In this work, we report that the selenization of Pt can be suppressed by confined conditions at the interface between epitaxial graphene and the Pt(111) substrate, tuning the obtained 2D structures. While ML PtSe₂ is obtained on pristine Pt surface, scanning transmission electron microscopy (STEM) reveals that ML Se intercalation, rather than the formation of ML PtSe₂, occurs in the confined reaction with a graphene coating. The atomic stacking of such an intercalation sample is further characterized by scanning tunneling microscopy (STM) measurements. Moreover, using a Pt substrate covered by graphene islands, we demonstrate that heterostructures of PtSe2 and intercalated Se ML can be obtained, with PtSe₂ growing on the bare Pt and Se intercalation occurring under the graphene islands. With the combination of the low-energy electron diffraction (LEED) and STM imaging, we further show that the rotation angle of the graphene island has negligible influence on the

Address correspondence to Ye-Liang Wang, ylwang@iphy.ac.cn; Hong-Jun Gao, hjgao@iphy.ac.cn



confined reaction. These results demonstrate the possibility of applying a confined reaction to control Pt selenization, which can be used to pattern PtSe₂. Such a controllable method may be used to develop nanodevices based on 2D materials.

2 Experimental section

All samples were prepared in an ultrahigh-vacuum (UHV) system with a base pressure greater than 3×10^{-10} mbar and equipped with standard molecular beam epitaxy capabilities. The Pt(111) substrate was cleaned by several cycles of argon-ion sputtering, followed by annealing until sharp (1×1) diffraction spots appeared in the LEED pattern and clean surface terraces in the STM images were obtained. Then, the graphene samples were fabricated by annealing the Pt(111) substrate at 800 °C in a 1×10^{-6} mbar ethylene atmosphere for 2 min (full layer) or 10 s (islands). The high-purity Se (99.99%, Sigma-Aldrich) was evaporated from a Knudsen cell at about 125 °C. For intercalation and selenization, graphene/Pt(111) was maintained at 540 K during Se deposition. The Se deposition time was 30 min for complete intercalation and 5 min for partial intercalation.

STM and LEED measurements were performed in a UHV STM-LEED combined system with a base pressure of 3.0×10^{-10} mbar. The LEED pattens were obtained with a beam energy of 100 eV for the best display of the patterns from both graphene and PtSe₂. All the STM images of the samples were acquired in constant-current mode using an electrochemically etched tungsten tip. The bias voltages were applied to the sample with respect to the tip.

For STEM measurements, a prepared Se intercalated sample was sliced along the Pt[11 $\overline{2}$] zone axis by a focused ion beam (FIB) and was further thinned to approximately 40 nm thickness using low-energy ion milling. Cross-sectional high-angle annular dark-field (HAADF) imaging and electron energy loss spectroscopy (EELS) analysis were performed with an aberrationcorrected STEM operated at 100 kV. The probe current was set to approximately 11 pA, and the convergence semiangle was approximately 30 mrad. The EELS collection semiangle was set to ~ 92 mrad, and the HAADF images were collected from ~ 92 to 210 mrad.

3 Results and discussion

ML PtSe₂ can be fabricated via a direct selenization reaction

by depositing Se onto a clean Pt(111) substrate maintained at 540 K, as reported in our previous work [16]. Figure 1(a) shows the schematic for the selenization process of a Pt substrate partially covered with graphene islands. In addition to the direct selenization of the exposed Pt substrate, under confined conditions the selenization is suppressed at the graphene/Pt interface. Figure 1(b) depicts the zoom-in schematic of the edge area of the graphene island, where the graphene offers a confined condition to suppress the reaction. The product of such a confined reaction is an intercalated Se layer, instead of ML PtSe₂. In other words, the products of the selenization process of the Pt substrate are controlled by the confined condition introduced by graphene. Thus, this approach provides a promising method for controllable fabrication of PtSe2 into desired patterns on the exposed Pt surface, when combined with the graphene sculpting technique [41].

To verify the structure of the product in the suppressed reaction, we used atomic resolution STEM and STM to characterize a selenized sample fully precoated with graphene. As shown in the cross-sectional HAADF-STEM image in Fig. 2(a), there is an additional atomic layer at the interface between the epitaxial graphene and Pt(111). The interlayer distance between graphene and this additional atomic layer is 0.33 nm (Fig. 2(b)), which implies weak interlayer hybridization. With the EELS mapping of Se (L edge) and Pt (M edge) shown in Fig. 2(c), we can confirm that such an atomic layer contains only Se atoms. The positions of graphene, intercalated Se and the top-most layer of the Pt substrate are marked with white, orange and blue lines, respectively. Such results directly reveal that the Se atoms form ML Se intercalation in the confined condition under graphene, rather than ML PtSe₂.

As shown in the STEM image, the lateral periods of intercalated Se and Pt(111) are 0.37 and 0.28 nm, respectively, with a ratio of 4:3 (for more details see Fig. S1 in the Electronic Supplementary Material (ESM)). To characterize the stacking structure of the intercalated sample in detail, STM measurements were carried out. Figure 2(d) shows a representative STM image of the selenized sample with a clean and uniform surface. In the zoom-in image shown in Fig. 2(e), we can see the graphene lattice and a superlattice with a period of 1.12 nm, marked with a white rhombus. Since the atomic lattice of graphene obviously does not match this periodicity, such a superlattice can be considered a Se(3×3)/Pt(4×4) moiré pattern, which matches



Figure 1 Schematic of suppressing the selenization of Pt under the confined condition for controllable fabrication of $PtSe_2$. (a) Schematic of the controllable fabrication of $PtSe_2$ on Pt(111) by graphene islands, which suppress the selenization reaction via a confined condition and tune the product from $PtSe_2$ to ML Se intercalation. (b) Zoom-in schematic of the area marked with the black dashed lines in (a). This image shows that in areas with and without graphene, the suppressed reaction and direct reaction lead to different reaction products.



Figure 2 Structure of the graphene/Se/Pt heterostructure. (a) HAADF-STEM cross-sectional imaging of the selenized graphene/Pt(111) sample. (b) Image intensity line profile integrated along the yellow line in (a). The distance between each adjacent layer is measured. (c) Elemental EELS mapping of Se and Pt. The white, orange and blue lines indicate the graphene, intercalated Se, and the top-most Pt atomic layers, respectively. The lines in (a) and (c) are at identical positions. (d) STM topographic image of the same selenized sample. (e) Atomic-resolution STM image of the area marked by the blue square in (d). Both the Se(3×3)/Pt(4×4) moiré pattern and the atomic lattice of graphene on top can be observed.

well with the STEM results, without involvement of the graphene. Moreover, for the sample with a smaller amount of deposited Se (for more details, see Fig. S2 in the ESM), the product of the confined reaction is still Se intercalation exhibiting the same Se(3×3)/Pt(4×4) moiré pattern, with graphene/Pt(111) around the graphene(2 × 2)/Pt($\sqrt{3} \times \sqrt{3}$) moiré pattern. Therefore, we can see that the product of the confined reaction retains the same structure, despite the different amounts of Se.

Understood the structure of the product in the suppressed reaction, we investigated the controllable fabrication of $PtSe_2$ on a sample with partial coverage of graphene islands (see Figs. S3(a) and S3(b) in the ESM). The Se atoms were deposited on the Pt(111) substrate coated by graphene islands. Thus, the product of the reaction on the areas with and without graphene can be studied. Obviously, as shown in the STM image in Fig. 3(a), the area covered by graphene is higher than the area without graphene (for more details see Figs. S3(c) and S3(d) in the ESM). A direct and obvious feature is the difference in the moiré patterns. The zoom-in images shown in Figs. 3(b) and 3(c)

directly reveal the moiré patterns in areas with and without graphene. Though these two moiré patterns have the same period of 1.12 nm, the detailed features are significantly different between the honeycomb and triangular structures, which represent Se intercalation and PtSe₂, respectively, as shown by the atomic models in Figs. 3(d) and 3(e). Such a difference in the structure of the moiré patterns indicates that the deposited Se forms PtSe₂ on exposed Pt surface, while Se intercalation is obtained under the confined condition of the graphene island. These results further demonstrate that, comparing with the graphene fully-covered situation, the suppression effect of the confined condition remains the same under the graphene islands, whose shapes can control the patterns of the obtained Se-PtSe₂ lateral heterostructures.

It is well known that the epitaxial graphene islands on Pt(111) normally show different orientations [42, 43]. To study the confined reaction under graphene islands with different rotation with respect to the Pt substrate, we investigated the stacking feature of the graphene/Se/Pt(111) sample. As shown in Fig. 4(a),



Figure 3 Controllable fabrication of $PtSe_2$ with graphene islands on Pt(111). (a) STM topographic image of the sample with Pt(111) covered by graphene islands after selenization. (b) and (c) The zoom-in atomic-resolution STM images of the areas marked by the black and white squares in (a). The black and white rhombuses depict the $Se(3\times3)/Pt(4\times4)$ and $PtSe_2(3\times3)/Pt(4\times4)$ moiré patterns, respectively. (d) and (e) The atomic models of the $Se(3\times3)/Pt(4\times4)$ and $PtSe_2(3\times3)/Pt(4\times4)$ heterostructures in the top view. The Se and Pt atoms are shown by orange and blue balls, respectively.



Figure 4 Se intercalation beneath the graphene with different rotation angles. (a) LEED pattern of the graphene/Se/Pt(111) sample. The diffraction spots of graphene, Se intercalation layer and Pt(111) are marked with white, red and blue dashed lines, respectively. (b), (d) and (f) Atomic-resolution STM images of graphene with different rotation angles on the Se intercalation. (c), (e) and (g) The fast Fourier transform images of (b), (d) and (f), respectively. The spots of the Se(3×3)/Pt(4×4) moiré pattern and graphene lattice are marked with red and white circles, respectively.

the LEED pattern obtained from the selenized sample illustrates the overall stacking information. The diffraction spots of graphene, intercalated Se and Pt(111) indicate a single domain of the $Se(3\times3)/Pt(4\times4)$ superlattice with multiple domains of epitaxial graphene. To obtain the local stacking features of the sample, we performed STM measurements on the area with different graphene rotations. From the atomic-resolution STM images and the corresponding fast Fourier transform (FFT) patterns shown in Figs. 4(b)-4(g), we can see that the Se(3×3)/Pt(4×4) moiré pattern always shows the same honeycomb feature and maintains the same periodicity with only tiny difference induced by the rotated graphene lattice. The absence of the moiré pattern between Se and graphene can be attributed to the large period of the pattern and the weak hybridization between Se and graphene. According to the arcs in the LEED pattern, the rotational angles of graphene to the substrate are mainly distributed in the range from 10° to 30°, and the brightest spots on the arcs are from the domains with 23° rotation angle, matching with the STM image in Fig. 4(d), which is also the dominant case in STM measurements. It is clear that the product of the confined reaction is always the Se intercalation with the same structure underneath the graphene, even though the graphene lattice has different rotation angles.

4 Conclusions

We report on the suppression of the selenization of Pt under the confined condition at graphene/Pt(111) interface for the controllable fabrication of ML PtSe₂. With the confined condition by graphene coating, an intercalated Se layer, instead of PtSe₂, was observed by STEM measurements. STM measurements further show that such intercalation retains the same structure, despite different doses of Se and coverage of graphene. Moreover, the combination of LEED and STM measurements reveals that the stacking rotation between graphene and Pt(111) shows a negligible influence on the formation of ML Se at the interface. These results demonstrate a new approach to control the fabrication of PtSe₂, which not only shows potential in engineering the heterostructure of such 2D materials but also extends the application of confined reactions.

Acknowledgements

We acknowledge financial support from the National Key Research and Development Program of China (Nos. 2016YFA0202300 and 2018YFA0305800), the National Natural Science Foundation of China (Nos. 61725107 and 61971035), Beijing Natural Science Foundation (Nos. 4192054 and Z190006), and Strategic Priority Research Program of the Chinese Academy of Sciences (Nos. XDB30000000 and XDB28000000).

Electronic Supplementary Material: Supplementary material (details of STEM and STM measurements) is available in the online version of this article at https://doi.org/10.1007/s12274-020-2989-0.

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