# **Electronic Supplementary Information (ESI)**

# Novel polymorphic phase of two-dimensional VSe<sub>2</sub>: The 1T' structure and its lattice dynamics

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### 1. Bilayer VSe<sub>2</sub> grown on epitaxial bilayer graphene

Figures S1a and S1b show STM images of bilayer graphene substrate and bilayer VSe<sub>2</sub>, respectively. Corresponding 2D FFT images are given in Figs. S1c (graphene) and S1d (VSe<sub>2</sub>) where Bravais peaks of graphene and VSe<sub>2</sub> lattices are well aligned (white dashed lines).



**Figure S1.** Bilayer VSe<sub>2</sub> grown on bilayer graphene. High-resolution STM image of (a) graphene and (b) bilayer VSe<sub>2</sub>. (c-d) show the corresponding FFTs of (a-b), respectively. The white and yellow circles indicate Bravais lattice peaks of graphene and VSe<sub>2</sub>, respectively. The blue rectangle represents  $1 \times \sqrt{3}$  unit cell of 1T' phase. Scanning conditions: (a)  $V_b = -250$  mV,  $I_t = 30$  pA, (b)  $V_b = 30$  mV,  $I_t = 30$  pA

# 2. Symmetry of $1 \times \sqrt{3}$ unit cell in 1T' bilayer VSe<sub>2</sub>

 $1 \times \sqrt{3}$  unit cell of 1T' phase VSe<sub>2</sub> is clearly observed as shown Fig. S2. However, it is found that its symmetry (centered or asymmetric rectangular) can be changed in STM topography, possibly due to the change of tip states. In Fig. S2, most of area shows asymmetric rectangular unit cell (blue rectangle), but some local area presents rather centered rectangular unit cell (red rectangle).



Figure S2. Filled state STM image of 1T' bilayer VSe<sub>2</sub>.

## 3. Bias polarity dependence of the lattice dynamics

Figure S3a-f and S3g-k show the bias dependences of lattice dynamics for positive and negative polarities, respectively. Interestingly, the dynamic state can be formed at the lower bias voltages (below -0.2 V) for negative bias, and the atomic lattices become very indistinctive due to lattice vibrations as shown in Fig. S3i-k. For positive bias polarity, however, the transition is less affected by applied sample bias voltage; i.e. The  $\alpha$  and  $\beta$  rows, the signature of 1T' phase, are still visible up to 0.6 V (Fig. S3f) albeit the lattices look somewhat blurry.



**Figure S3.** The bias dependences of lattice dynamics for positive (a-f) and negative (g-k) polarities (scan size: 8 × 8 nm<sup>2</sup>).

## 4. Structures of monolayer and trilayer VSe<sub>2</sub>

### A. Monolayer VSe<sub>2</sub>

Figure S4a shows bilayer graphene substrate, and monolayer-bilayer VSe<sub>2</sub> areas. As shown in Fig. S4c, it is quite interesting that monolayer VSe<sub>2</sub> shows new charge density wave (CDW) with  $\sqrt{3} \times 2$  and  $\sqrt{3} \times \sqrt{7}$  periodicity, which is very different from 1T' structure of bilayer VSe<sub>2</sub> and 4  $\times 4 \times 3$  CDW of bulk VSe<sub>2</sub>. In our recent report, we suggested that the  $\sqrt{3} \times 2$  and  $\sqrt{3} \times \sqrt{7}$  CDW is driven by strong lattice distortions with metal-insulator transition.<sup>1</sup> The existence of  $\sqrt{3} \times 2$  and  $\sqrt{3} \times \sqrt{7}$  CDW in monolayer VSe<sub>2</sub> is also confirmed by other group.<sup>2</sup>



**Figure S4.** (a) STM topography shows monolayer and bilayer VSe<sub>2</sub> areas on top of bilayer graphene substrate. (b) Line profile taken along the blue arrow in (a) presents the thickness of each VSe<sub>2</sub> layer. (c) Monolayer VSe<sub>2</sub> image shows  $\sqrt{3} \times 2$  and  $\sqrt{3} \times \sqrt{7}$  superstructures marked by dotted black lines. (d) FFT image of (c) presents additional peaks corresponding to the superstructures. The pink circles indicate Bravais lattice peaks of VSe<sub>2</sub>.

### **B.** Trilayer VSe<sub>2</sub>

Figure S5a shows a topography containing bilayer and trilayer of VSe<sub>2</sub>. In Fig. S5c, trilayer VSe<sub>2</sub> also shows alternative bright ( $\alpha$ ) and dark ( $\beta$ ) lattice lines which are the signature of the 1T' phase. Its FFT in Fig. S5d clearly exhibits  $1 \times \sqrt{3}$  periodicity of the 1T' phase, consistent with that of bilayer VSe<sub>2</sub>, and we also observed very similar lattice dynamics in trilayer VSe<sub>2</sub> as well.



**Figure S5.** (a) STM topography shows bilayer and trilayer VSe<sub>2</sub> regions. (b) Line profile taken along the blue arrow in (a) shows single layer height of ~ 6.8 Å between bilayer and trilayer regions. (c) STM topography and (d) its FFT images of trilayer VSe<sub>2</sub> present 1T' structure. The blue rectangle represents  $1 \times \sqrt{3}$  unit cell of the 1T' phase.

# References

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