# Supplementary Material

# Microscopic Detection of Self-intercalated Mechanism and In-situ Electronic Properties in Chromium Selenide

**Jinding Zhang[1], Yulong Xiao[1], Kaihui Li[1], Ying Chen[1], Songlong Liu[3], Wenjie Luo[1], Xueying Liu[1], Shiying Liu[1]，Yiliu Wang[3], Si-Yu Li[1,4,*], Anlian Pan[1,2,*]**

[1]Key Laboratory for Micro-Nano Physics and Technology of Hunan Province, Hunan Institute of Optoelectronic Integration and College of Materials Science and Engineering, Hunan University, Changsha 410082, People's Republic of China
[2]School of Physics and Electronics, Hunan Normal University, Changsha 410081, People's Republic of China
[3]School of Physics and Electronics, Hunan University, Changsha 410082, People's Republic of China
[4]Greater Bay Area Institute for Innovation, Hunan University, Guangzhou 511300, People's Republic of China
*Correspondence and requests for materials should be addressed to S.Y.L (e-mail: lisiyu@hnu.edu.cn) and A.L.P. (e-mail: anlian.pan@hnu.edu.cn).

## EXPERIMENTAL METHOD

**CVD synthesis route of $Cr_{1+n}Se_2$ nanoflakes on mica.** We use Se (100 mg, Aladdin, 99.9%) and anhydrous $CrCl_3$ powder (10 mg, Aladdin, 99.9%) as the sources of the reaction and put them into the upstream and downstream of the tube, respectively. Then the freshly cleaved mica is placed inclined downstream of the $CrCl_3$, which is about 1cm away from $CrCl_3$. Before the heating process, high-purity argon (Ar, 2000 sccm) gas is loaded to purge the reaction tube for 5 min. The temperature of the tube furnace is increased from room temperature to 700–730°C within 20 min with a mixture of Ar (45 sccm) and hydrogen ($H_2$, 3 sccm), and the furnace temperature is maintained for 5 min for sample growth.

**The transfer processes of CVD-synthesized 2D $Cr_{1+n}Se_2$ nanoflakes.** First of all, the Self-prepared propylene carbonate (PPC) solutions were spin coated onto $Cr_{1+n}Se_2$/mica. We paste a layer of heat-resistant double-sided tape on top of the dried PPC, and then paste a glass slide on top of the double-sided tape. After such a simple transfer device is ready, we can enter the formal transfer process. The process can be divided into two parts: 1) We soaked the prepared transfer device in deionized water and then used tweezers to gently separate the mica from the PPC along the edge of the mica. At this point, $Cr_{1+n}Se_2$ on mica has been transferred to PPC. 2) The PPC with the sample is attached to the target substrate and heated to 70 ° C, and then the sample is transferred to the target substrate because of the thermal release property of PPC. Finally, the PPC connected with the heat-resistant tape and the glass slide is taken apart together.

**The STM/STS measurements.** The scanning tunneling microscopy (STM) system was an ultrahigh vacuum single-probe scanning probe microscope USM-1400 from UNISOKU in Japan. All STM and scanning tunneling spectroscopy (STS) measurements were performed at liquid-nitrogen temperature (78 K) and the STM images were taken in a constant-current scanning mode. The STM tips were obtained by chemical etching from a wire of Pt(80%) Ir(20%) alloys. Lateral dimensions observed in the STM images were calibrated using a standard graphene lattice as well as a Si (111)-(7×7) lattice and the STS spectra were calibrated using a graphene. The STS spectrum, i.e., the dI/dV-V curve, was carried out with a standard lock-in technique by applying alternating current modulation of the bias voltage of 10 mV (771 Hz) to the tunneling bias.

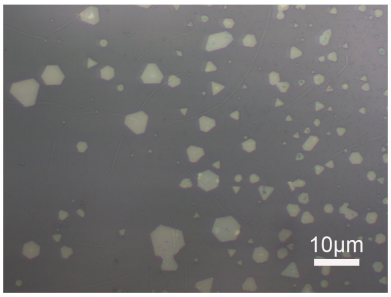


**Figure S1.** OM images of the $Cr_{1+n}Se_2$ nanoflakes on mica grown by horizontal placement of substrate.

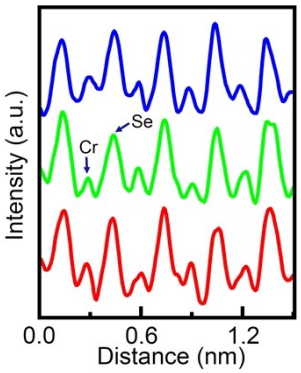


**Figure S2.** The three profile lines along vertical direction taken at the Se-Cr-Se-Cr-Se structure area.

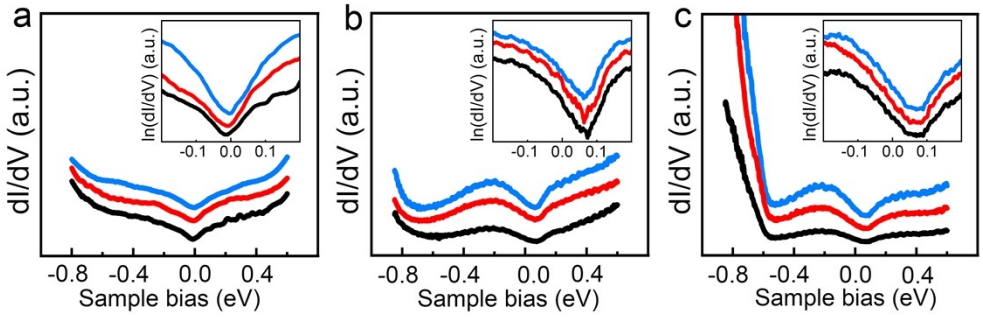


**Figure S3.** More STS spectra obtained in the $Cr_2Se_2$, $Cr_{1.5}Se_2$ and $Cr_{1.25}Se_2$ regions, respectively. The inset shows the same spectra near the Fermi level in logarithmic

form.

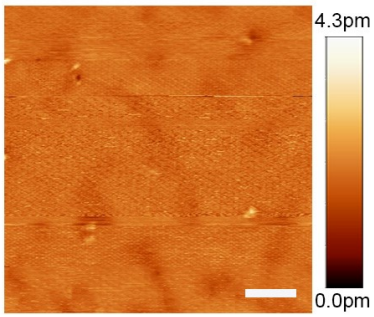


**Figure S4.** The STM image of the original flat region in the $Cr_{1+n}Se_2$ nanoflake before the tip pulse (I=100 pA, $V_{sample}$=1.6V). Scale bar: 5 nm.

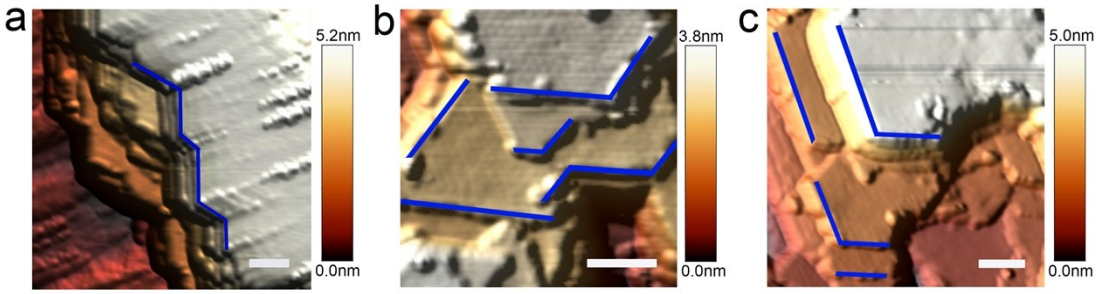


**Figure S5.** The STM images of cut boundaries after the tip pulse (I=100 pA, $V_{sample}$=1.5V). Scale bar: 5 nm. The directions of the boundary edges are highlighted by the blue lines.