

Supplementary Information

High-Performance Field Emission Based on Nanostructured Tin Selenide for Nanoscale Vacuum Transistors

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1 **Chemical synthesis of tin selenide**

2 Tin selenide nano-flower (SnSe NF) was synthesized by added SnCl₄•5H₂O (0.4mmol,
3 140 mg), SeO₂ (0.4 mmol, 44 mg), and oleylamine (OAM, 20 mL) into a three-neck flask at
4 room temperature. The flask was then sealed and the mixture is stirred continuously for five
5 minutes. Afterwards, the mixture was sonicated for 30 minutes at room temperature. The mixture
6 was degassed with pure N₂ then aged at 150°C for 10 minutes while being stirred continuously
7 under N₂ atmosphere. Finally, the mixture was slowly heated to 350°C at rate ~10°C/min and
8 aged at 350°C for 15 to 20 minutes. After this process, SnSe NF was extracted and cleaned with
9 excess ethanol. SnSe NF is then dried and stored for following characterizations.

10 Single-crystal (SC) SnSe was synthesized by chemical vapor transport method. High
11 quality of Sn and Se powder (99.999% purity, from Alfa Aesar) were mixed together and placed
12 into the quartz tube. The quartz tube is evacuated and flame sealed under high vacuum (10⁻⁵
13 torr). We place quartz tube on the multi-zone furnace. Temperature was set the 950 °C and 900
14 °C as a reaction temperature for hot zone and cold zone, respectively. Temperature of furnace
15 was slowly heated from room temperature to reaction temperature for 12 hours and hold on 96
16 hours at reaction temperature, and slowly cool down to the room temperature.

17
18 **Electrical measurement**

19 The electrical measurement was performed in air at room temperature and ambient
20 pressure. The SnSe cathode is grounded and the anode voltage was increased at 0.01 V per step
21 using a Precision Source/Measure Unit (SMU) (Keysight 2902A). The emission current was
22 measured and averaged with every five measurements.

23

24 Data analysis

25 The Fowler-Nordheim (FN) equation is given as

$$26 \quad I = A \frac{aV^2\beta^2}{h^2\varphi} \exp\left(-\frac{b\varphi^{1.5}h}{V\beta}\right) \quad (\text{S1})$$

27 where I is emission current, A is emission area, V is operating voltage, h is vacuum channel
28 length between anode and cathode emitter, φ is emitter's work function, β is field enhancement
29 factor, a and b are constant with $a = 1.54 \times 10^{-6} \text{ AeV}/V^2$ and $b = 6.83 \times 10^9 \text{ eV}^{-1.5}Vm^{-1}$.

30 The field enhancement factor β is extracted from eq. S1 by rewrite eq. S1 as:

$$31 \quad \frac{d\left(\ln\left(\frac{I}{V^2}\right)\right)}{d\frac{1}{V}} = \frac{d \ln\left(\int \int \frac{\beta^2}{h(x,y)^2} \exp\left(-\frac{b\varphi^{1.5}h(x,y)}{V\beta}\right) dx dy\right)}{d\frac{1}{V}} \quad (\text{S2})$$

32 The 3D tip geometry and channel length of NF emitters are determined using AFM and
33 SEM images (for example, Figure 1e and 2c in main text). The tip profile is fitted using a
34 parabolic equation. We extract the linear slope from FN plot (for example, see Figure 3b in main
35 text) and calculate field enhancement factor of NF using eq. (S2).

36 For the single crystal (SC) emitters, eq. S2 is simplified as:

$$37 \quad \frac{d\left(\ln\left(\frac{I}{V^2}\right)\right)}{d\frac{1}{V}} = -\frac{b\varphi^{1.5}h}{\beta} \quad (\text{S3})$$

38 The left-hand-side of eq. (S3) represents the linear slope extracted from FN plot (Figure
39 3b in main text) which is used to calculate the field enhancement factor.