Supporting Information for

## Agent-Assisted VSSe Ternary Alloy Single Crystals Towards Efficient Stable Electrocatalyst for Hydrogen Evolution Reaction

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Figure S1. CVT system for single-crystal growth of VS<sub>2</sub>, VSe<sub>2</sub>, VSSe-I and VSSe-V.

Initially, the temperature of source zone (Zone 1: Vanadium, sulfur and/or selenide and transport agent) was kept at 920 °C and that of growth zone (Zone 2) at 980 °C to allow the constituents to react completely without formation of unwanted additional phases/compounds. After this period, ampoules were subjected to a two-zone temperature profile of 980 °C (source zone) to 920 °C (growth zone) for a period of 168 hours. In the end, the temperatures were lowered down, and the plate-like crystals were subsequently obtained from the ampoule for further characterizations and measurements.

The transport agent ( $I_2$  or VCl<sub>3</sub>) is employed to react with vanadium to form exclusively vapour phase reaction products, which is easy to transport. After that, the other easy sublimized solid (S and Se) will react with the vapour phase reaction products to form our target product. <sup>[1-2]</sup>

Figure S2. Optical images of VSSe-I.



**Figure S3**. a) XRD patterns of VSSe-I crystals compared with VS<sub>2</sub> (JCPDS #00-036-1139) and VSe<sub>2</sub> (JCPDS #01-089-1641). For the sake of demonstrating the peaks clearly, only (00*l*) peaks of VS<sub>2</sub> and VSe<sub>2</sub> standard card are presented. b-e) XRD patterns of (001), (002), (003) and (004) peak of VSSe-I crystals compared with VS<sub>2</sub> and VSe<sub>2</sub>.



Figure S4. The semi-quantitative analysis of as-grown VSSe-V crystal.



Figure S5. The SEM and EDAX mapping results of VSSe-I.



Figure S6. The semi-quantitative analysis of as-grown VSSe-I crystal.

59 <sup>(5)</sup>	•	Spectrum 5
0 2 4 Full Scale 6108 cts Cursor: 0.	6 8 000	9 9 10 12 14 keV
Element	Mass %	Atom %
S	22.07	35.51
V	31.06	32.16
Se	46.87	32.33

Figure S7. Raman spectra of VSSe-V and VSSe-I.



Figure S8. The spotted Tyndall effect of the exfoliated VSSe-V (a) and VSSe-I (b).



Figure S9. The SEM images of exfoliated VSSe-V (a) and VSSe-I (b) samples.



Figure S10. The EDAX mappings of exfoliated VSSe-V (a) and VSSe-I (b)samples.

Element	Weight%	Atomic%	Element	Weight%	Atomic%
S K	22.25	36.37	S K	21.55	35.81
VK	31.66	32.44	VK	31.94	32.88
Se L	46.09	31.19	Se L	46.51	31.31



Figure S11. Four terminal measurement of electrical conductivity.

Thickness is measured by an optical surface profiler (Zeiss Smart Proof 5).

The bulk resistivity can be calculated by using following equation: <sup>[3]</sup>

$$\rho = \frac{\pi}{\ln 2} \left(\frac{V}{I}\right) t$$
 [V: voltage; I: current; t: thickness]

Then, the conductivity is converted from the resistivity.

*V* is obtained by measuring the voltage between electrode 2 and 3. *I* is obtained by measuring the voltage between electrode 1 and 4.

**Figure S12.** Cyclic voltammograms in the region of 0.2–0.4 V vs. RHE for the (a) VSSe-V and (b) VSSe-I.



Using a simple cyclic volatammetry (CV) method, we can determine the double layer capacitance ( $C_{dl}$ ) which is expected to be linearly proportional to effective active surface area. The double layer capacitance is estimated by plotting the  $\Delta J$  ( $J_a$ - $J_c$ ) at 0.3 V vs. RHE against the scan rate, where the slope is twice  $C_{dl}$ .

The possible reaction of transport agent in the growth process.

For  $I_2$  used as transport agent:

$$V + 2I_2 = VI_4$$

$$VI_4 + S + Se = VSSe + 2I_2$$

For VCl<sub>3</sub> used as transport agent:

$$\begin{aligned} 2VCl_3 &= 2VCl_2 + Cl_2 \\ V + 2Cl_2 &= VCl_4 \\ VCl_4 + 3S + 3Se &= VSSe + 2SSeCl \\ 2VCl_2 + 2SSeCl &= 2VCl_4 + 2S + 2Se \\ 2VCl_4 &= 2VCl_3 + Cl_2 \end{aligned}$$

## References

[1] Chemical Vapor Transport Reactions–Methods, Materials, Modeling. Advanced Topics on Crystal Growth. 2013, Publisher: Intech Open.

[2] Crystal Growth Via the Gas Phase by Chemical Vapor Transport Reactions. Handbook of Solid State Chemistry, 2017, 351–374.

[3] F. M. Smits, "Measurement of sheet resistivities with the four-point probe", Bell System Technical Journal, vol. 34, pp. 711-718, 1958.