## **Supplementary Information**

## Synergetic oxide-chalcogenide heterostructure in metallic two-dimensional VSe<sub>2</sub> for the hydrogen-evolution reaction

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Sample	Atom	ratio
VSe₂ <sup>vc</sup>	V	1
	Se	1.99
VSe <sub>2</sub> -LO <sup>vc</sup>	V	1
	Se	1.04
	0	0.96
VSe₂-HO <sup>vc</sup>	V	1
	Se	0.33
	0	2.05

Table S1. Stoichiometry of VSe2vc, VSe2-LOvc, and VSe2-HOvc samples

The stoichiometry was determined by calculating the area ratios of the V 2p, Se 3d, and O 1s peaks from the XPS spectra. Because the sensitivity factor depends on the atomic species and their respective orbitals, we considered the partial ionization cross section and inelastic mean free path values at the employed photon energy<sup>1-4</sup>.

VSe <sub>2</sub> samples	Methods	Overpotential (mV at 10 mA/cm <sup>2</sup> )	Tafel slope (mV dec⁻¹)	Ref
VSe <sub>2</sub> -LO <sup>ec</sup> film	MBE	542	110	Our work
VSe <sub>2</sub> flake	MBE	543~608*	160~203	5
VSe <sub>2</sub> flake	Exfoliation	796	134	6
VSe <sub>2</sub> flake	Exfoliation	900~1000	112	7
VSe <sub>2</sub> nanosheet	Hydrothermal	414	142	8
VSe <sub>2</sub> nanosheet	Colloidal	387	108	9
VSe <sub>2</sub> nanosheet	Colloidal	547	101	10

 $^{\ast}$  The overpotential values are obtained at 1 mA/cm^{2}

**Table S2.** Comparison of HER performances in our  $VSe_2$ -LO<sup>ec</sup> film and other previouslyreported  $VSe_2$  samples<sup>5-10</sup>



**Figure S1. a**, RHEED image of graphene/SiC substrate **b**, Line profiles extracted from the dashed rectangular regions of the RHEED images in Figure **S1a** and Figure **1b-d**.



**Figure S2. a-c.** XPS spectra of Se 3*d* in the  $VSe_2^{vc}$  (a),  $VSe_2$ -LO<sup>vc</sup> (b), and  $VSe_2$ -HO<sup>vc</sup> (c) samples. **d.** Area ratio of the deconvoluted components for the  $VSe_2^{vc}$ ,  $VSe_2$ -LO<sup>vc</sup>, and  $VSe_2$ -HO<sup>vc</sup> samples.

The Se 3*d* peak was deconvoluted into Se<sup>2-</sup>, Se<sup>1-</sup> and Se<sup>0</sup>, with binding energies centered at 53.68 eV, 54.48 eV, and 55.78 eV, respectively. Se<sup>2-</sup> is associated coordinated V-Se bonds within octahedral 1T-VSe<sub>2</sub><sup>11,12</sup>. Se<sup>1-</sup> arises from Se in a more positive oxidation states than Se<sup>2-</sup>, derived from Se interstitials, Se near V-O bonding, or partially bound Se near V vacancies<sup>11,12</sup>. Se<sup>0</sup> corresponds to pure Se and it can be attributed to remnant of the Se capping layer<sup>11</sup>. As the degree of oxidation increases, the area ratio of the Se<sup>2-</sup> component decreases, while those of Se<sup>1-</sup> and Se<sup>0</sup> increase in Figure **S2d**. Additionally, we clearly confirm that no selenium oxide (SeO<sub>x</sub>) component, indicated by the black arrows at 59.90 eV, is observed in any of the samples.



Figure S3. a, Atomic structure of  $1\text{T-VSe}_2$  and rutile VO<sub>2</sub> (R-VO<sub>2</sub>). b, Fast Fourier transformation (FFT) patterns of distinct VSe<sub>2</sub> and R-VO<sub>2</sub> phases in the pristine VSe<sub>2</sub><sup>vc</sup> and VSe<sub>2</sub>-HO<sup>vc</sup> samples described by gray, orange, and blue dashed boxes in Figure 1g,i.



**Figure S4**. **a,b**, Deconvolution of the O 1*s* peaks of the VSe<sub>2</sub>-LO<sup>vc</sup> (**a**) and VSe<sub>2</sub>-HO<sup>vc</sup> (**b**) films under various conditions: UHV after H<sub>2</sub>O exposure and UHV annealing at 200°C. **c,d**, Area ratio of the deconvoluted oxygen components in the VSe<sub>2</sub>-LO<sup>vc</sup> (**c**) and VSe<sub>2</sub>-HO<sup>vc</sup> (**d**) films.



**Figure S5**. **a,b**, Comparison of the core level XPS spectra of V 2p (**a**) and Se 3d (**b**) measured under UHV and H<sub>2</sub>O (0.5 mbar) environments.

![](_page_10_Figure_0.jpeg)

**Figure S6**. Relative Gibbs free energies  $\Delta G$  of the calculated VSe<sub>2-x</sub>O<sub>x</sub> models presented as a function of the relative oxygen chemical potential  $\Delta \mu_0$  under (left) Se-poor and (right) Se-rich conditions. All VSe<sub>2-x</sub>+*n*O models are depicted by blue solid lines with varying intensity, while the L-VO<sub>2</sub> and VSe<sub>2-x</sub>+VO<sub>2</sub>(100) models are shown in blue and red dashed lines, respectively. The oxygen chemical potential  $\Delta \mu_0$  is converted into a temperature scale at partial pressures of

 $O_2 gas ({}^{p}O_2)$  of 0.004 mbar, 0.5 mbar, and 0.2 bar, and it is shown on the upper x-axis.

![](_page_11_Figure_0.jpeg)

**Figure S7**. Surface free energies  $(\gamma^{(100),\sigma}_{surf})$  of (1×1) R-VO<sub>2</sub>(100) with varying surface coverage of oxygen atoms presented as a function of the relative oxygen chemical potential  $\Delta\mu_0$ . V-rich, stoichiometric, and O-rich surfaces are depicted by red, yellow, and blue lines, respectively. Their atomic structures are illustrated in the right panel. The reconstructed structure of the Vrich surface, in which the topmost V-O layer transforms into a L-VO<sub>2</sub>-sheet-like structure, is indicated by the red dashed line. The thermodynamic stability of R-VO<sub>2</sub> is delineated by two vertical gray dashed lines, representing the formation energies of R-VO<sub>2</sub> and V<sub>2</sub>O<sub>5</sub> from left to right, and R-VO<sub>2</sub> remains stable in the range of  $\Delta\mu_0$  between these lines.

We calculated the surface free energies of the R-VO<sub>2</sub>(100) surfaces as a function of  $\Delta\mu_0$  to investigate the phase transformation of oxidized VSe<sub>2</sub> into the R-VO<sub>2</sub> phase (Supplementary Figure S5). The (100) surface was specifically chosen because 1T-like surface reconstructions have been identified in rutile RuO<sub>2</sub>(100) <sup>13</sup>, and VO<sub>2</sub> is expected to exhibit a similar behavior. Three different oxygen coverages ( $\Theta_0 = 0.0$ , 0.5, and 1.0 ML, representing V-rich, stoichiometric, and O-rich conditions, respectively) were considered within the (1 × 1) surface unit cell. The solid lines in the phase diagram correspond to the locally optimized bulktruncated surfaces for each coverage level. Throughout the  $\Delta\mu_0$  range between the formation energies of R-VO<sub>2</sub> and V<sub>2</sub>O<sub>5</sub>, the stoichiometric surface remained the most stable. As expected, a 1T-like surface reconstruction of the V-rich termination was identified, where the topmost vanadium atom shifted into a subsurface cavity, forming a surface motif resembling the topmost L-VO<sub>2</sub> layer (indicated by the dashed red line in Supplementary Figure **S5**). Intriguingly, this reconstructed surface is more stable than the locally optimized V-rich termination by 0.8 eV/Å<sup>2</sup>, and it even exhibits slightly lower surface energy than the stoichiometric surface near the V-rich limit (denoted by the vertical gray dashed line at the VO<sub>2</sub> formation energy). However, as  $\Delta\mu_0$  increases toward more oxidative conditions, the structure rapidly transforms into the stoichiometric structure. This suggests that under oxidative conditions, the outermost VO<sub>2</sub> layer in the VSe<sub>2-x</sub>+8O model may reconstruct into a rutile-like local structure, as also demonstrated by our experiments.

![](_page_13_Figure_0.jpeg)

Figure S8. a-e, Potential energy profile of the DFT-converged NEB calculations for the water dissociation in the VSe<sub>2-x</sub>O<sub>x</sub> models. The activation energy  $E_a$  and the enthalpy change  $\Delta E$  are indicated in each figure. Further details can be found in the main text. **f**, Adsorption energy of water  $\Delta E^{ad}_{H2O}$  for each model.

![](_page_14_Figure_0.jpeg)

**Figure S9. a** Comparison of VSe<sub>2</sub> samples prepared for two different purposes: surface analysis under vacuum condition (vc) and electrochemical experiments (ec). **b** XPS spectra of V 2*p* and O 1*s* obtained for various samples. **c,d** O 1*s* (**c**) and V 2*p* (**d**) spectra with deconvoluted components for the air-exposed VSe<sub>2</sub> film.

![](_page_15_Figure_0.jpeg)

**Figure S10. a-c**. Electrocatalytic HER stability of the  $VSe_2^{ec}$ ,  $VSe_2$ -LO<sup>ec</sup>, and  $VSe_2$ -HO<sup>ec</sup> samples in a 0.5M H<sub>2</sub>SO<sub>4</sub> solution. LSV curves were recorded from the initial cycle up to 20 cycles. During the 20 cycles, the overpotential gradually rises by 14 mV, 26 mV, and 25 mV for respective samples.

![](_page_16_Figure_0.jpeg)

**Figure S11**. **a-c**, Convergence with the kinetic cutoff energy for the wave function (**a**), number of k points (**b**), and thickness of the vacuum layer for  $VSe_2$  (**c**). Total energy difference with respect to the tightest setting result. **d**, Convergence of the H<sub>2</sub>O binding energy with respect to the size of the VSe<sub>2</sub> surface supercell. **e–g**, Same as (a–c) but for R-VO<sub>2</sub>. **h**, Convergence of the R-VO<sub>2</sub> surface free energy with respect to the number of relaxed atomic layers.

![](_page_17_Figure_0.jpeg)

**Figure S12**. **a,b**, Band structures of bulk VSe<sub>2</sub> (**a**), bulk L-VO<sub>2</sub> (**b**), and bulk R-VO<sub>2</sub> (**c**). The upper panels display the spin-polarized results, while the lower panels are derived from nonmagnetic calculations. In the 0 K DFT calculations, the ferromagnetic states of bulk VSe<sub>2</sub>, bulk L-VO<sub>2</sub>, and bulk R-VO<sub>2</sub>, are slightly more stable than their nonmagnetic counterparts by -0.08, -0.21, and -0.19 eV per formula unit, respectively.

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