Electronic Supplementary Material (ESI) for Nanoscale.

Layer-dependent electrical and optoelectronic responses of $ReSe_2$ nanosheet transistors

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EXPERIMENTIAL SECTION

Mechanical Exfoliation of $ReSe_2$. Single- and few-layer (four-layer) $ReSe_2$ nanosheets were isolated from bulk $ReSe_2$ single crystals (Lamellae Co.) and then deposited onto the freshly cleaned Si substrates covered by a 300 nm thick SiO_2 layer using the scotch tape-based mechanical exfoliation method.

Thermal Annealing. The samples were heated to 400 °C in a 25 °C/min rate and the temperature was held at 400 °C for one hour in vacuum. After annealing, the furnace was cooled down to room temperature and the samples were taken out of the furnace.

FET devices were fabricated as follows. Metal electrodes were fabricated using electron-beam lithography (Vistec EBPG 5000plus ES) followed by electron beam evaporation (EB700-I) of 5-nm-thick Cr and 50-nm-thick gold. Electrical characterization for the transistors was measured using a semiconductor parameter analyzer and shielded probe station. Photo-response experiments were all performed with a CHI660D electrochemical workstation in a conventional three-electrode electrochemical cell.

Raman Spectroscopy. Analysis of the monolayer $ReSe_2$ nanosheet by Raman spectroscopy was carried out on a WITec CRM200 confocal Raman microscopy system with the excitation line of 532 nm and an air-cooling charge-coupled device (CCD) as the detector (WITec Instruments Corp, Germany).

SEM image and EDX analysis. SEM image was measured by NanoSEM430 from FEI Company. EDX was utilized for the estimation of the composition of $ReSe_2$ as shown in Fig. S4. The EDX was equipped on the SEM instrument.

Molecule adsorption calculations. First-principles spin-polarized calculations are carried out within density-functional theory (DFT) as implemented in the Vienna *ab initio* simulation package (VASP) [1,2]. The 4×4 supercell of $ReSe_2$ monolayer with single gas molecule adsorbed to it, is chosen as the studied model. The exchange-correction interaction is treated by the van der Waals density functional (vdW-DF) [3] to describe the adsorbed system. The kinetic cutoff energy is set to be 450 eV and the Monkhorst-Pack grid [4] of 5×5×1 is employed for the Brillouin zone integration. The vacuum layer is larger than 15 Å so that the interaction between two adjacent $ReSe_2$ monolayers can be eliminated. The geometric structure is fully relaxed by using conjugate gradient method until the Hellmann-Feynman force on each atom is smaller than 0.02 eV/Å. The charge transfer between $ReSe_2$ and gas molecule is obtained based on the Bader analysis [5]. The adsorption energy is defined as $E_a = E_{\mathrm{ReSe_2+molecule}} - (E_{\mathrm{ReSe_2}} + E_{\mathrm{molecule}})$, where $E_{\mathrm{ReSe_2+molecule}}$, $E_{\mathrm{ReSe_2}}$ and E_{molecule} are the total energies of molecule adsorbed $ReSe_2$, bare $ReSe_2$ and isolated molecule, respectively. The charge density difference is calculated by the formula $\triangle\rho = \rho_{\mathrm{ReSe_2+molecule}} - (\rho_{\mathrm{ReSe_2}} + \rho_{\mathrm{molecule}})$, where $\rho_{\mathrm{ReSe_2+molecule}}$, $\rho_{\mathrm{ReSe_2}}$ and ρ_{molecule} are the charge densities of molecule adsorbed $ReSe_2$, bare $ReSe_2$ and isolated molecule, respectively.

Electronic structure and density of states (DOS) calculations. The calculations are performed using the projector augmented wave (PAW) method [6] with the generalized gradient approximation of Perdew-Burke-Ernzerhof (GGA-PBE) [7] exchange-correction functional including van der Waals corrections [3], as implemented in the VASP code [1]. Energy cutoff for plane-wave expansion is set to 500 eV. A large vacuum layer more than 15 Å is adopted to avoid the interaction between adjacent images. Brillouin zone sampling is performed with Monkhorst-Pack (MP) [4] special k points meshes including Γ point. K-points grids of 5×5×5 and 5×5×1 are chosen for the optimization calculations of bulk and two dimensional (2D) systems, respectively. And much denser meshes (15×15×15 and 15×15×1 for bulk and 2D systems) are used for the DOS calculations. All the structures are fully relaxed using the conjugated gradient method until the Hellmann-Feynman force on each atom is less than 0.01 eV/Å.

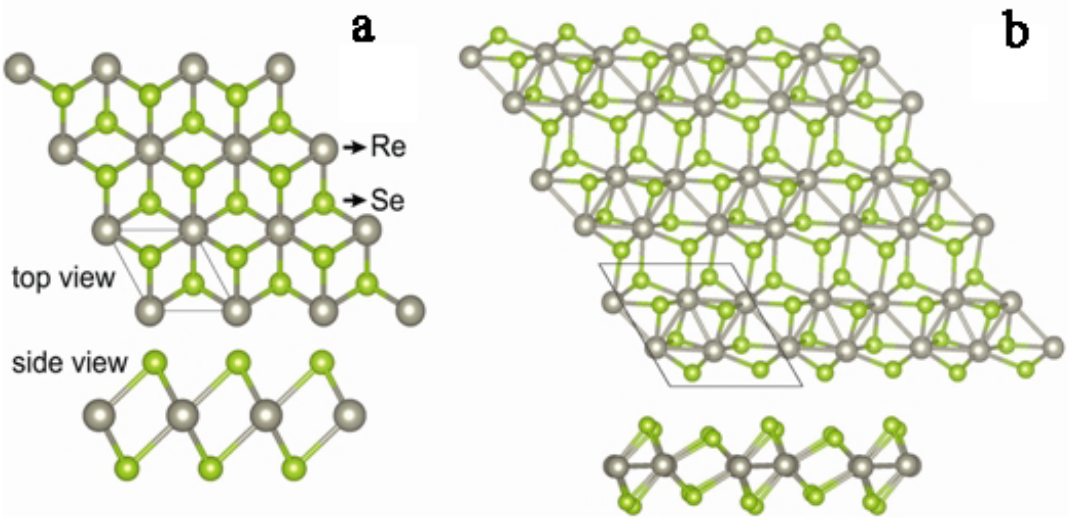


Figure S1. The structure of $ReSe_2$. a. Undistorted $ReSe_2$, **b.** distorted $ReSe_2$.

In order to verify the stability of the distorted structure of $ReSe_2$, we have constructed an undistorted model of $ReSe_2$ with the honeycomb structure, as shown in Fig. S1, similar to other transition metal dichalcogenides. The total energy of the undistorted one is -17.395 eV per molecular, while that of the distorted one is -18.473 eV per molecular, which is more stable than the undistorted one by 1.078 eV per molecular.

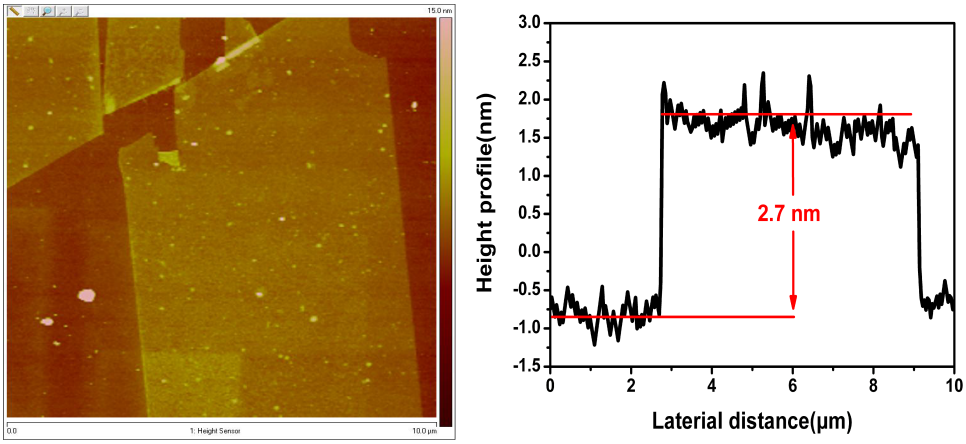


Figure S2. AFM height image of few-layer $ReSe_2$.

The thickness of few-layer $ReSe_2$ is about 2.7nm, corresponding to four layer.

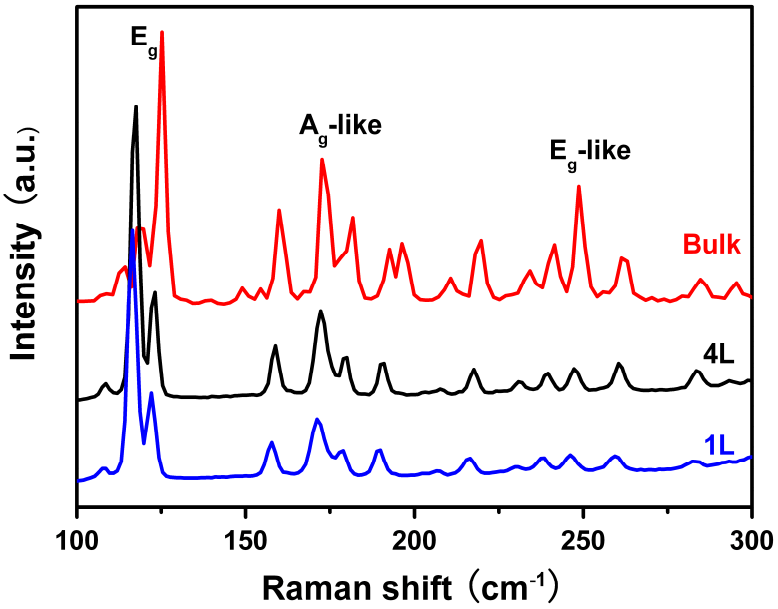


Figure S3. Raman spectra of $ReSe_2$ nanosheets.

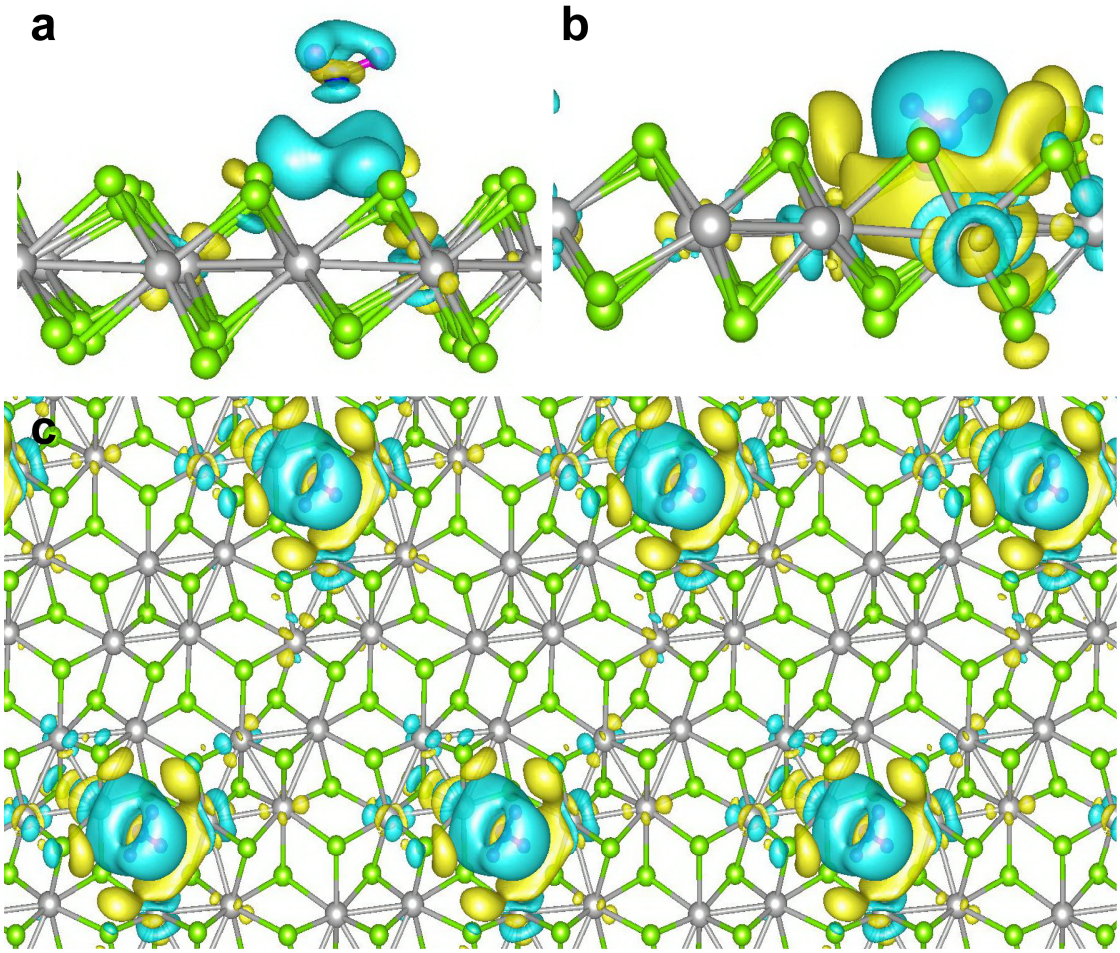
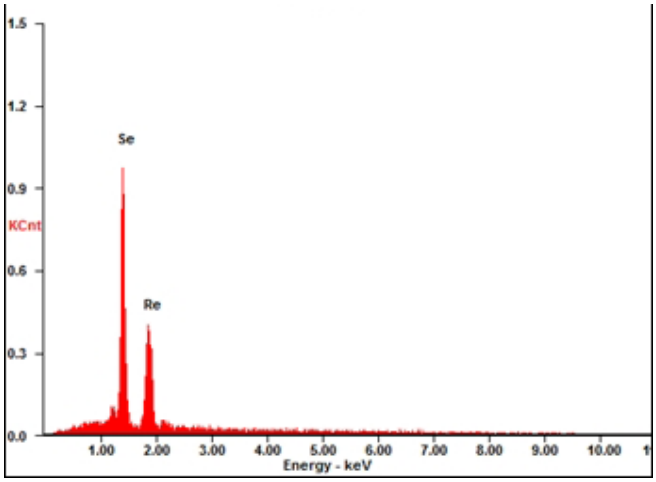


Figure S4. Single NH_3 molecule adsorbed on the $ReSe_2$ monolayer. Charge density difference plots for **a,** without defects and **b,** with defects for side view and **c,** with defects for top view on monolayer $ReSe_2$. The isosurface value without defects is set to be 5×10^{-4} e/Å^3 and that with defects is 1×10^{-3} e/Å^3 . Yellow and blue distributions correspond to charge accumulation and depletion, respectively.

For NH_3 molecules, the adsorption energies are determined to be -203 meV, indicating the physisorption of NH_3 on the pristine $ReSe_2$ monolayer. A NH_3 molecule acts as a charge donor and donates 0.024 electrons to the $ReSe_2$ nanosheet, reducing hole carrier density in the p-type monolayer $ReSe_2$ (Fig. S3a). For system with Se vacancies, such as those generated by annealing, more electrons (0.049) are

transferred from gas molecule to the $ReSe_2$ nanosheet, leading to more significant reduction of carrier density of $ReSe_2$ monolayer (Figs. S3b and 3c).



Element	*Wt%*	*At%*
SeL	45.07	65.93
ReM	54.93	34.07
Matrix	Correction	ZAF

Figure S5. EDX of $ReSe_2$ nanosheet.

Table S1 The related parameters measured in different gas environment.

	O_2	Air	NH_3
I_{dark}(A)	2.1×10^{-8}	9×10^{-9}	7.7×10^{-9}
I_{light}(A)	4×10^{-7}	8×10^{-8}	5×10^{-8}
$R_\lambda(AW^{-1})$	95	17.8	10.5
EQE(%)	18,645	3,484	2,061
On/Off ratio	20	9	6

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