

**Plasma-Engineered 1T/2H Phases in 3D-Hierarchical WSe₂ Nanoscrews as High
Performance NO Gas Sensors with ppb-level Detection Limit**

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We estimate relative surface areas of nanostructure by electrochemically active surface area method (ECSA). The electrochemically active surface area (ECSA) of samples was usually estimated using cyclic voltammetry measurement. (Refs. 2-3) The surface area of the sample was calculated by the double layer capacitance according to the following formula:

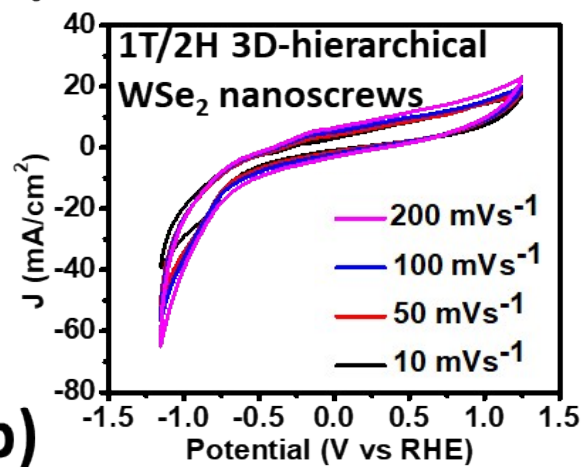
$$ECSA = C_{dl} / C_s$$

However, it is quite challenging to obtain the exact surface area of our material due to the unknown capacitive behavior (C_s) of the WSe_2 , especially in 1D nanostructure. Therefore, we can simply estimate relative surface areas of our two samples, which are flat and nanoscrews since the double layer capacitance (C_{dl}) is expected to be linearly proportional to effective active surface area where the approach to estimate surface area was also commonly employed in previous reports. (Ref 4) The capacitance can be calculated from the scan rate as a function of the current density, which is twice of C_{dl} by extracting slopes from ΔJ versus scan rates as shown in Figure 2c. It is observed that the capacitance obtained from the nanostructured sample (C_{dl} of $14.4 \mu F cm^{-2}$) is approximately two orders of magnitude higher than that of the flat film (C_{dl} of $0.09 \mu F cm^{-2}$). We have added this part into the supporting information.

Table S1. The double layer capacitance (C_{dl}) and the relative surface areas of flat WSe_2 and WSe_2 nanoscrews.

Structure	Capacitance ($\mu F/cm^2$)	Surface area related to flat WSe_2
Flat	0.09	1
Nanoscrews	14.4	160

(a)



(b)

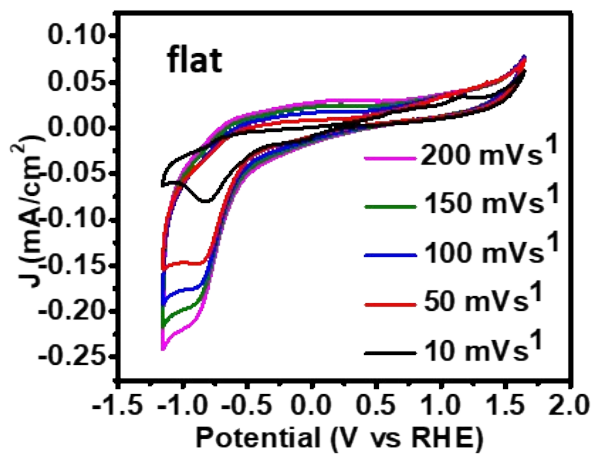


Figure S1 Results of cyclic voltammetry measurement for (a) WSe₂ nanoscrews. (b) flat WSe₂.

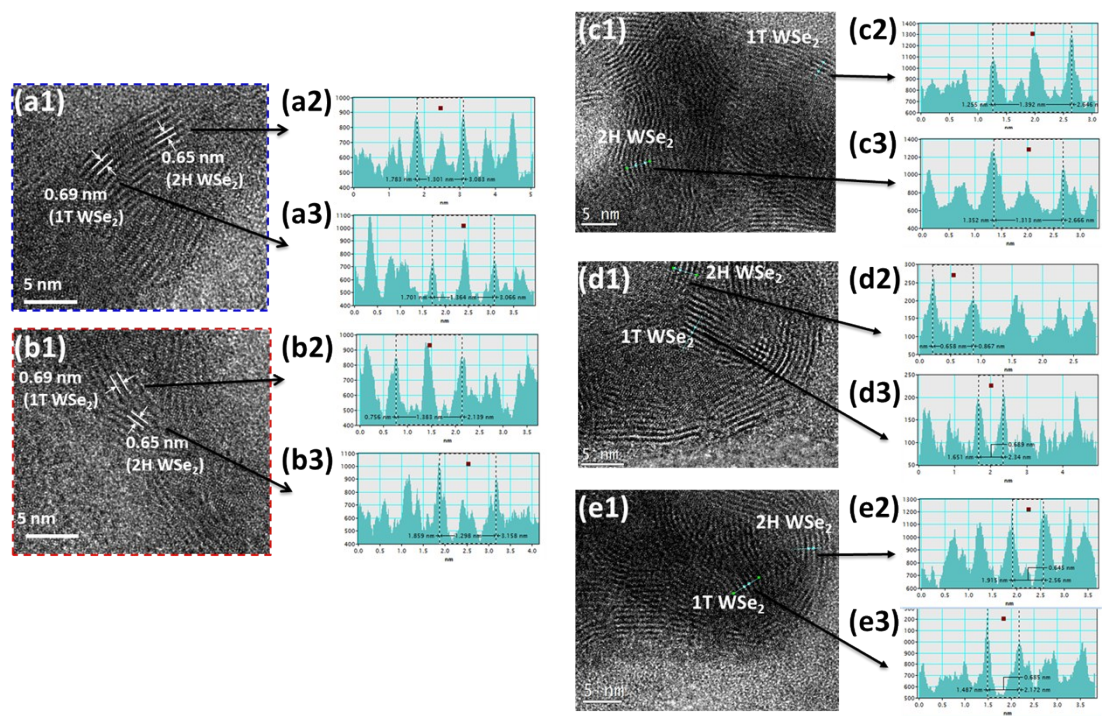


Figure S2 TEM images of 1T/2H of 1T/2H 3D-hierarchical WSe₂ nanoscrews for 5 random area (a1)-(e1) and the corresponded intensity profile for 2H and 1T phase (a2)-(e2), (a3)-(e3), respectively.

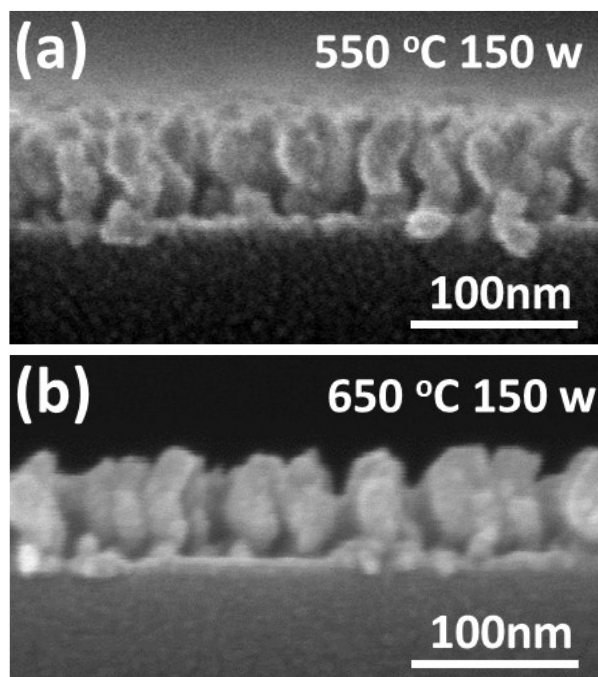


Figure S3 SEM images of 3D-hierarchical WSe_2 nanoscrews synthesized at (a) 550°C (b) 650°C with plasma 150 W.

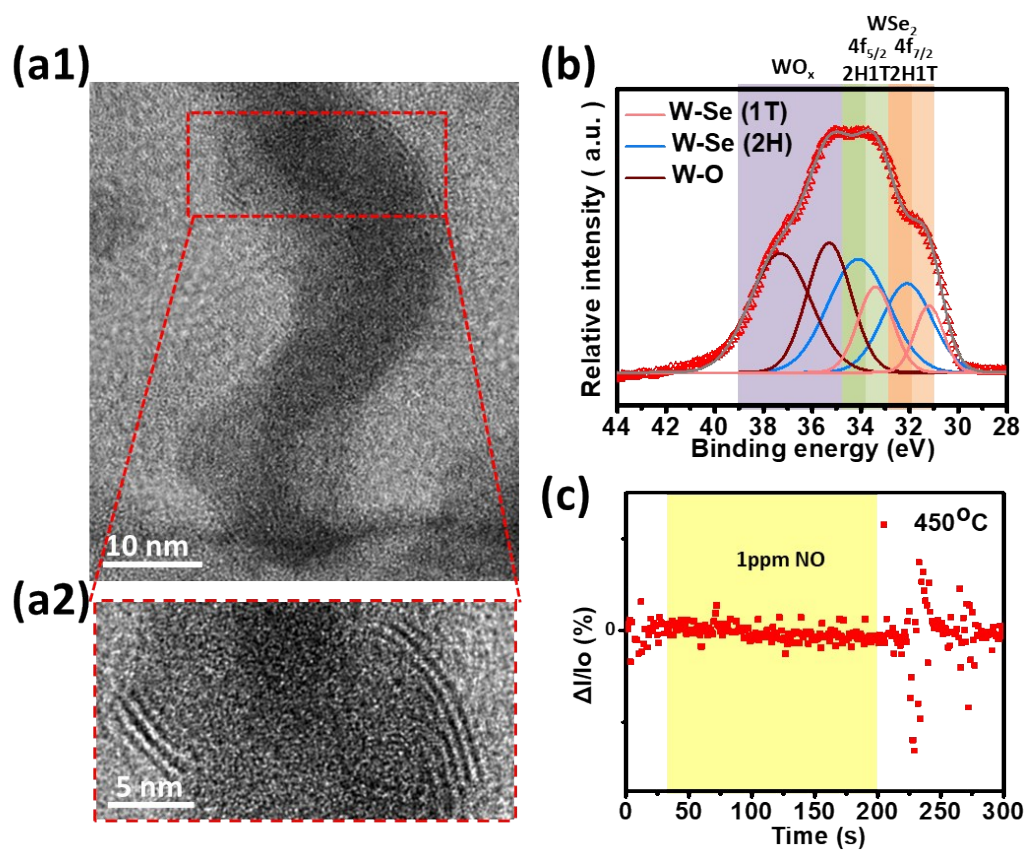


Figure S4 (a1)-(a2) TEM images of 3D-hierarchical WSe₂ nanoscrews selenized without plasma function. (b) XPS results of W 4f (c) Results of gas response upon 1 ppm NO gas.

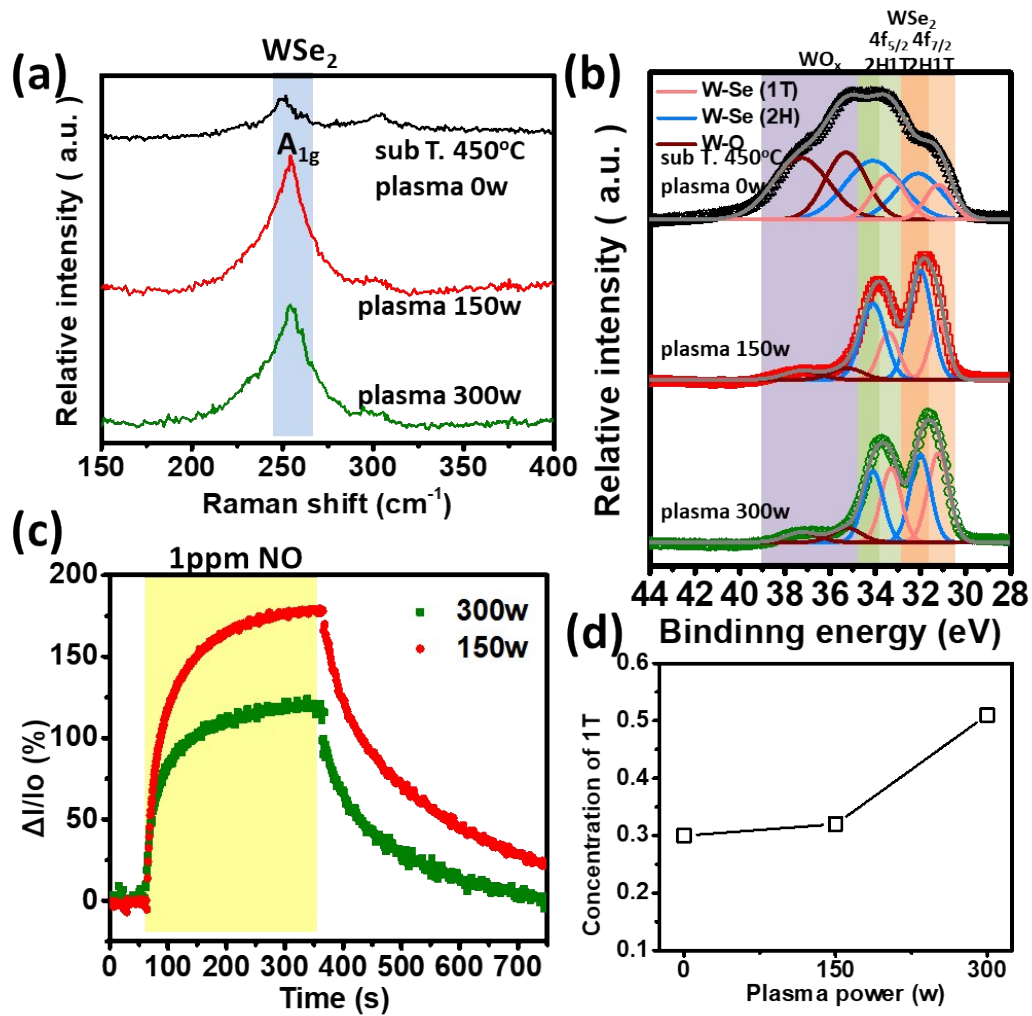


Figure S5 (a) Raman spectra of 3D-hierarchical WSe₂ nanoscrews synthesized at 450 °C with 150 and 300 W. (b) XPS spectra of W 4f of WSe₂ (c) Results of gas response of 3D-hierarchical WSe₂ nanoscrews synthesized at 450 °C with 150 and 300 W upon 1 ppm NO gas. (d) Concentration of 1T as dependence of plasma power.

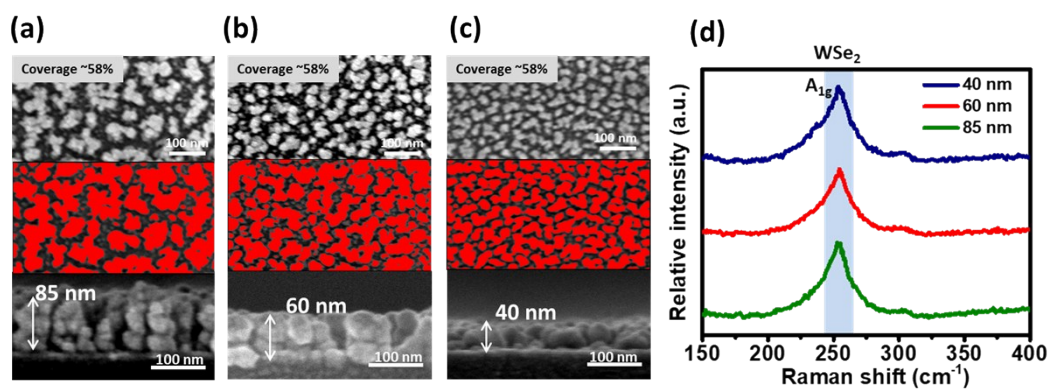


Figure S6 SEM images of 3D-hierarchical WSe₂ nanoscrews with heights of (a) 85 nm (b) 60 nm (c) 40 nm. Note that the coverage was kept as 58 % estimated by software image J. (d) Raman spectra of 3D-hierarchical WSe₂ nanoscrews as a dependence of height.

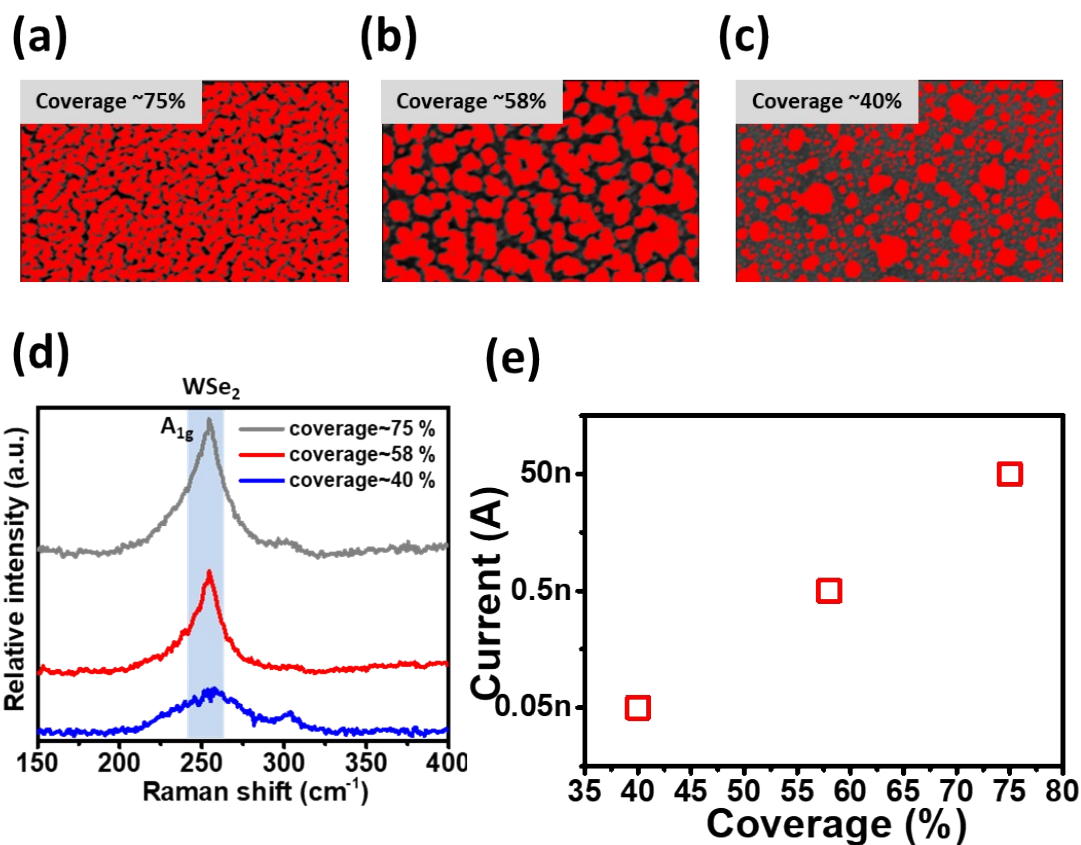


Figure S7 SEM images of 3D-hierarchical WSe₂ nanoscrews with coverages of (a) 75 % (b) 58 % (c) 40 %. Note that the height was kept as 60 nm. (d) Raman spectra of 3D-hierarchical WSe₂ nanoscrews as a dependence of coverages. (e) Base current of 3D-hierarchical WSe₂ nanoscrews as a dependence of coverages.

Reference

- (1) S. Brunauer, P. H. Emmett and E. Teller, Adsorption of Gases in Multimolecular Layers J. Am. Chem. Soc., 60, 309-319 (1938).
- (2) Yang Y., Lun Z.Y., Xia G.L., Zheng F.C., He M.N. & Chen Q.W. Non-precious alloy encapsulated in nitrogen-doped graphene layers derived from MOFs as an active and durable hydrogen evolution reaction catalyst. Energy Environ. Sci. 8, 3563-3571 (2015).
- (3) Lukowski M.A., Daniel A.S., Meng F., Forticaux A., Li L. & Jin S. Enhanced Hydrogen Evolution Catalysis from Chemically Exfoliated Metallic MoS₂ Nanosheets. J. Am. Chem. Soc. 135, 10274–10277 (2013).

(4) Merki, D., Vrabel, H., Rovelli, L., Fierro, S. & Hu, X., Fe, Co, and Ni ions promote the catalytic activity of amorphous molybdenum sulfide films for hydrogen evolution Chem. Sci. 3, 2515-2525 (2015).