Supporting Information

Enhanced sensitivity towards hydrogen by a TiN interlayer in Pd-decorated SnO_2 nanowires

Clémence Badie,[1†] Jae-Hyoung Lee,[2†] Ali Mirzaei,[3] Hyoun Woo Kim,[4#] Syreina Sayegh,[5§] Mikhael Bechelany,[5,6#] Lionel Santinacci,[1#] and Sang Sub Kim[7#]

[1]*Aix Marseille Univ, CNRS, CINaM, Marseill 13009, France*

[2]*Electronic Materials Research Center, Korea Institute of Science and Technology, Seoul 02792, Republic of Korea*

[3]*Department of Materials Science and Engineering, Shiraz University of Technology, Shiraz 715557-13876, the Islamic Republic of Iran*

[4]*Division of Materials Science and Engineering, Hanyang University, Seoul 04763, Republic of Korea*

[5]*Institut Européen des Membranes, IEM – UMR 5635, University of Montpellier, CNRS, ENSCM, Place Eugène Bataillon, Montpellier 34095, France.*

[6] *Gulf University for Science and Technology, GUST, Kuwait*

[7]*Department of Materials Science and Engineering, Inha University, Incheon 22212, Republic of Korea.*

[†] *Co-first Authors*

[#] *Corresponding authors*

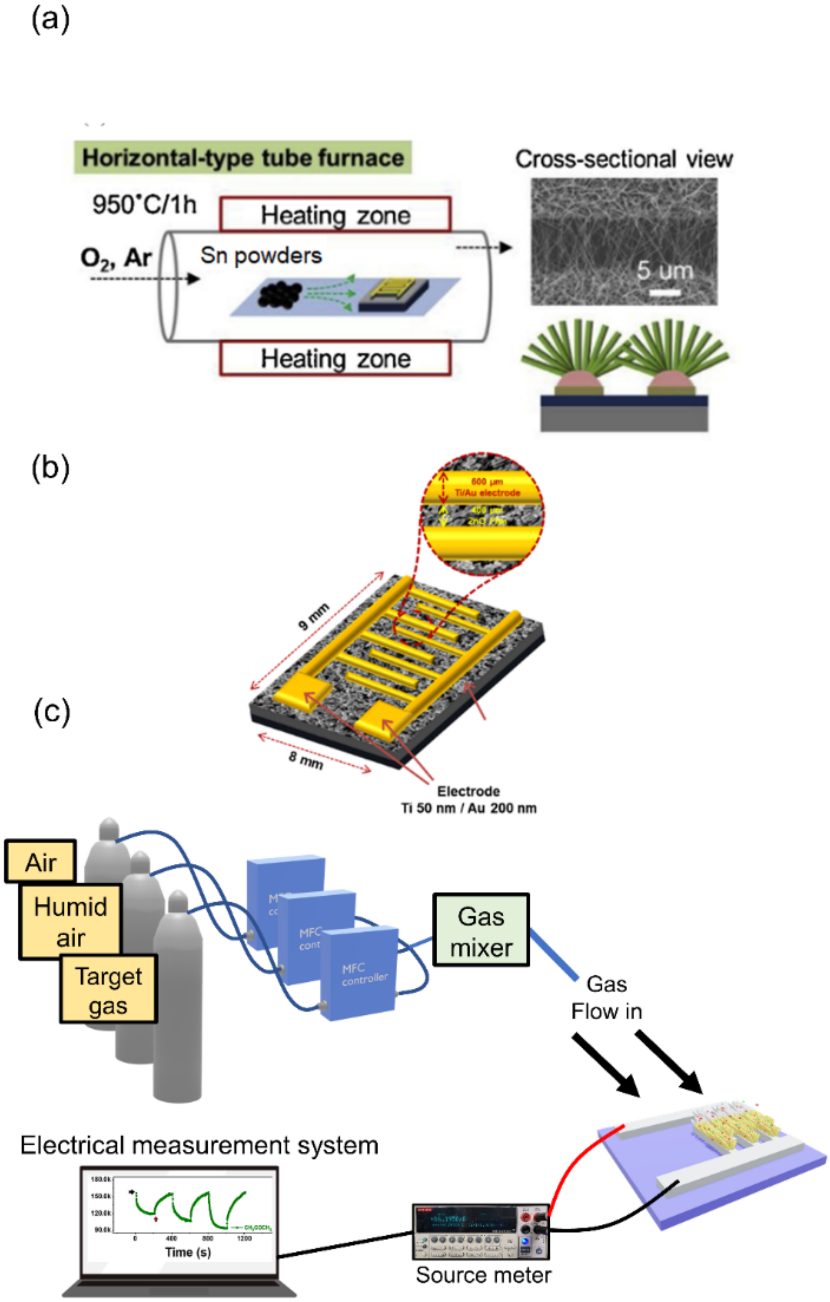


Fig. S1. (a) Growth of SnO_2 NWs by VLS growth method. (b) Schematic of a typical gas sensing device and (c) gas sensing measurement setup.

TiN deposition proceeds according to a transamination reaction proposed earlier[1,2] in which TDMAT can react with up to three active sites (here TDMAT reacts with two $-NH_x$ surface groups).

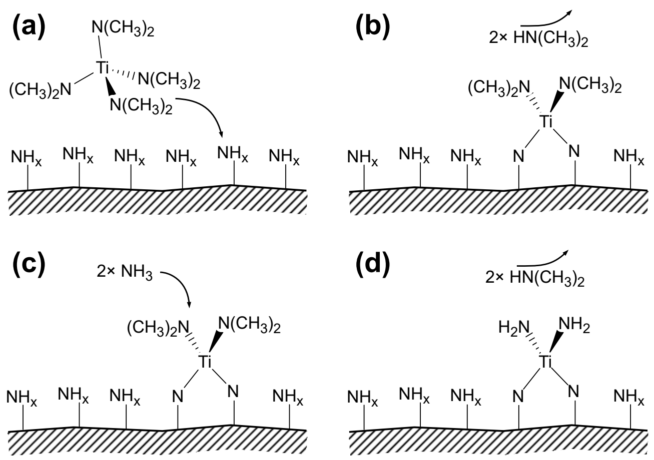


Fig. S2. Schematic description of the TiN deposition mechanism from TDMAT and NH_3: (a) Injection of TDMAT, (b) transamination reaction, (c) injection of NH_3, and (d) removal of ligands.

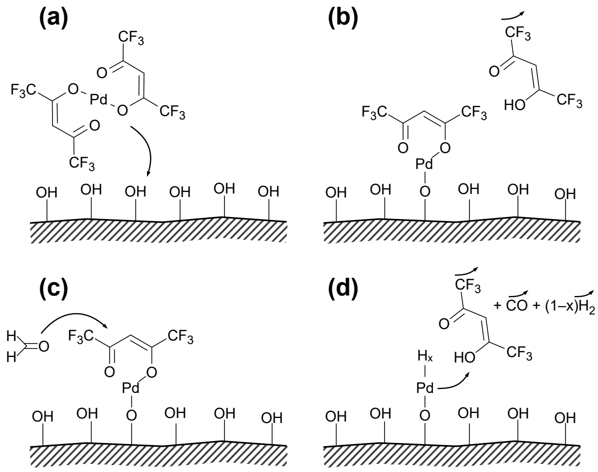


Fig. S3. ALD sequence during Pd deposition from $Pd(hfac)_2$ and formaldehyde. The steps are described in the text.

Steps 1 and 2 consist of the adsorption of the $Pd(hfac)_2$ precursor onto the surface and its reaction with the hydroxyl surface sites and a subsequent Hhfac release (**Fig. S2a, b**). After the exposition of the surface to the second precursor (step 3), Pd(hfac) is reduced by formaldehyde (**Fig. S2c**). A $-Pd-H_x$ termination is created at the active site and Hhfac, CO and H_2 are released during step 4 (**Fig. S2d**)

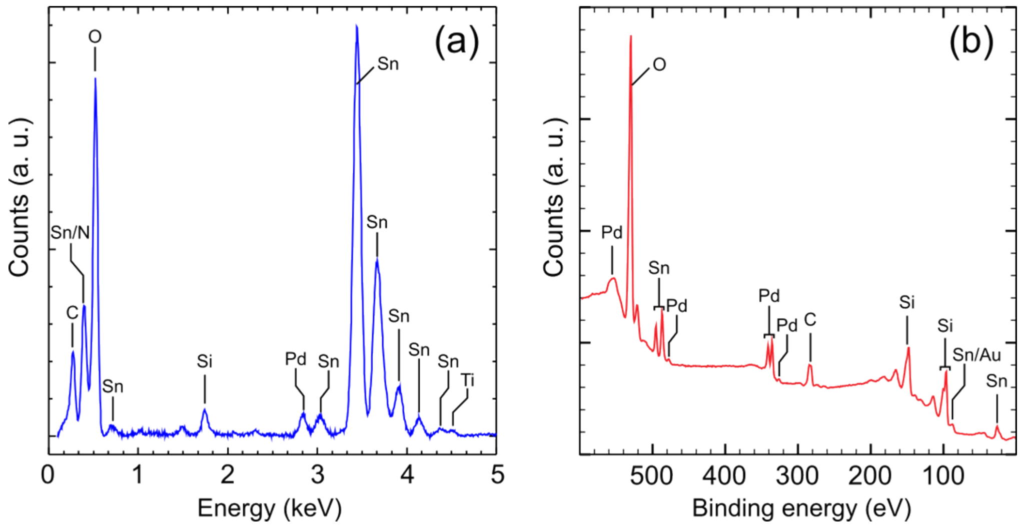


Fig. S4. EDS spectra (a) and XPS survey (b) of SnO_2 NWs covered by TiN and Pd. The detected elements are indicated on the corresponding peaks.

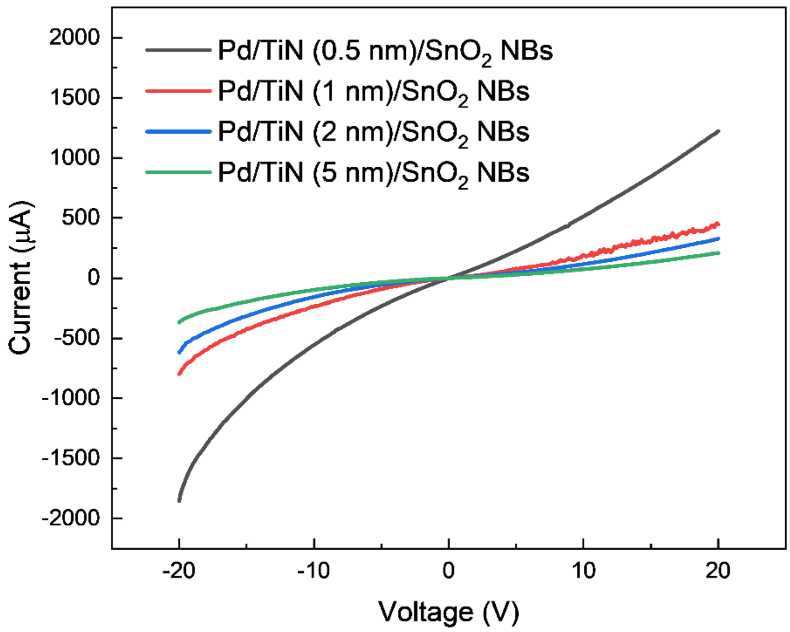


Fig. S5. I-V curves of Pd/TiN (0.5, 1, 2, 5 nm)/SnO_2 NWs gas sensors

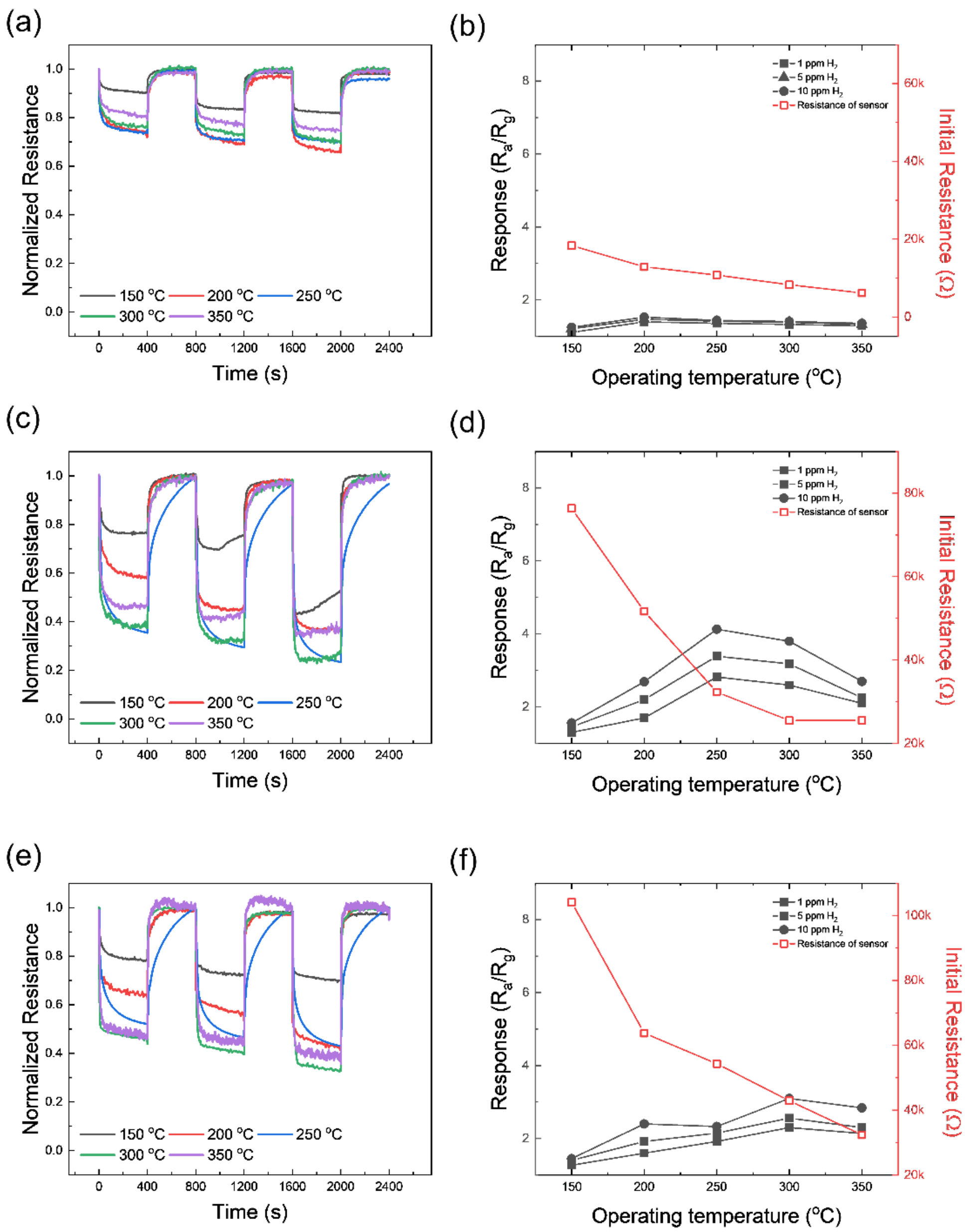


Fig. S6. Transient resistance curves and response plots of (a), (b) Pd/TiN (0.5 nm)/ SnO_2 NWs (c), (d) Pd/TiN (2 nm)/ SnO_2 NWs and (e), (f) Pd/TiN (2 nm)/ SnO_2 NWs, respectively.

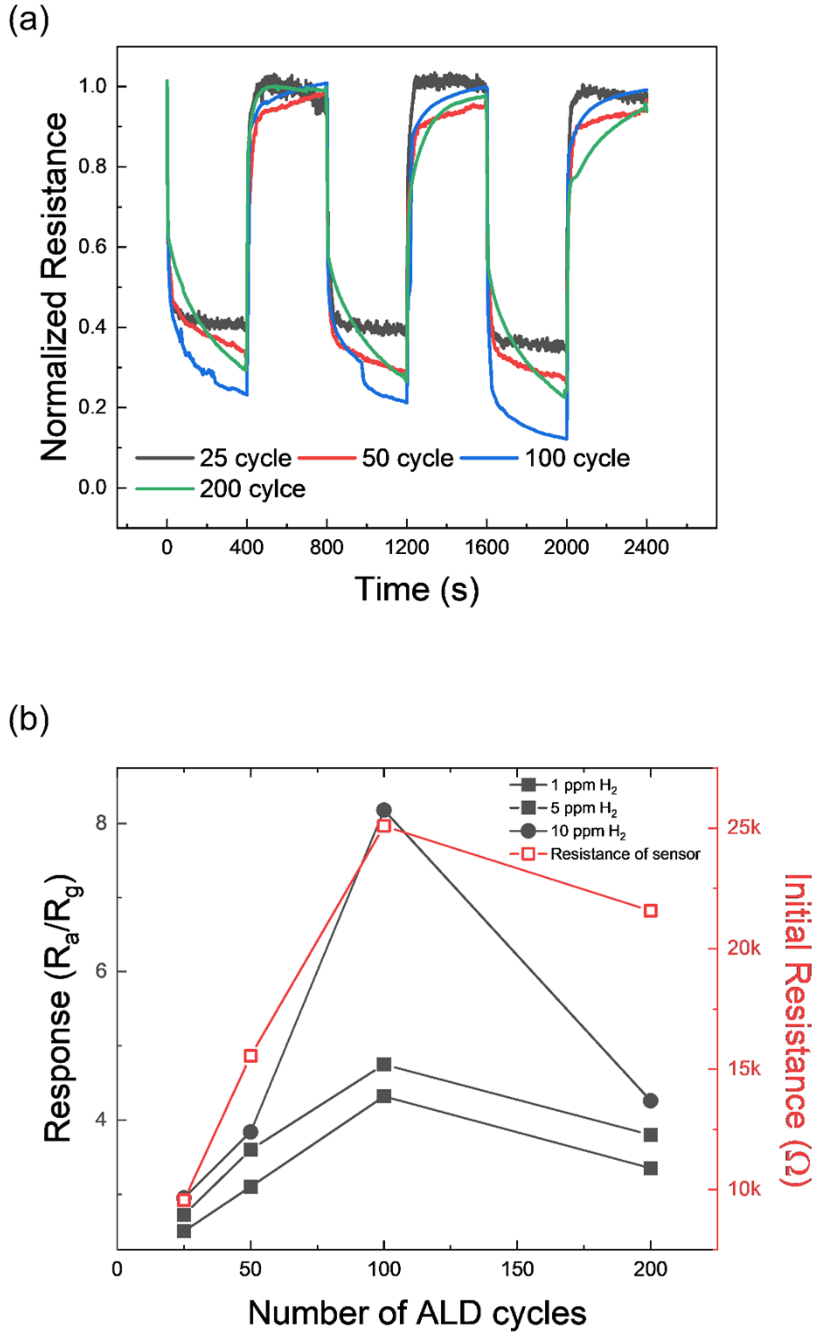
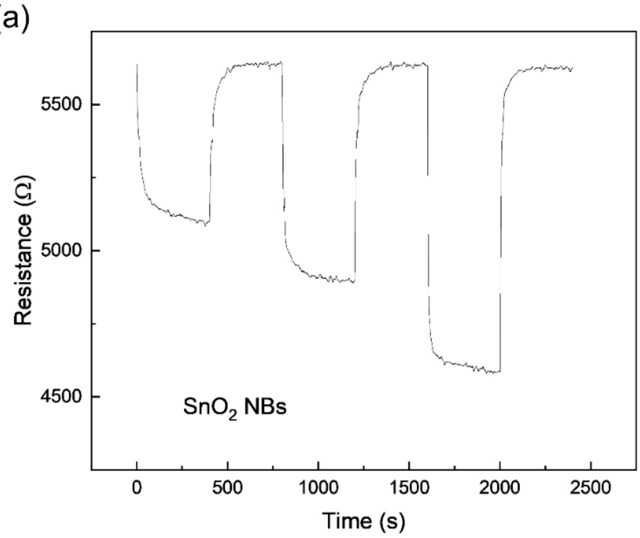


Fig. S7. (a) Transient resistance curves of Pd (25, 50, 100, 200 cycles)/TiN (1 nm)/ SnO_2 NWs and (b) response plots to 1-10 ppm of H_2 gas.

(a)



(b)

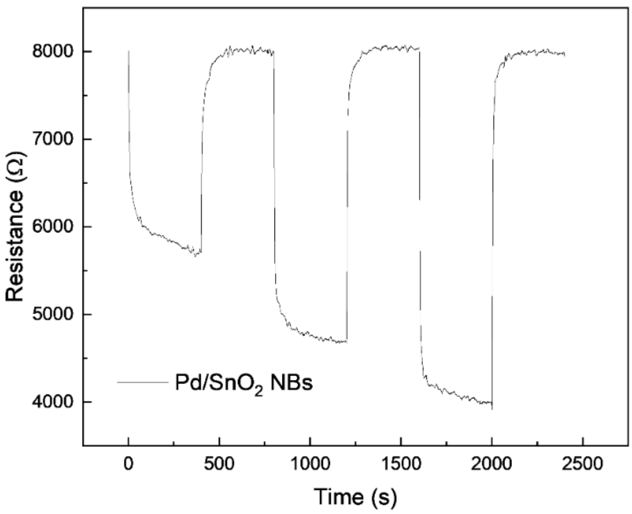


Fig. S8. (a) Transient resistance curves of SnO_2 NWs and (b) Pd/SnO_2 NWs gas sensors to 1-10 ppm of H_2 gas.

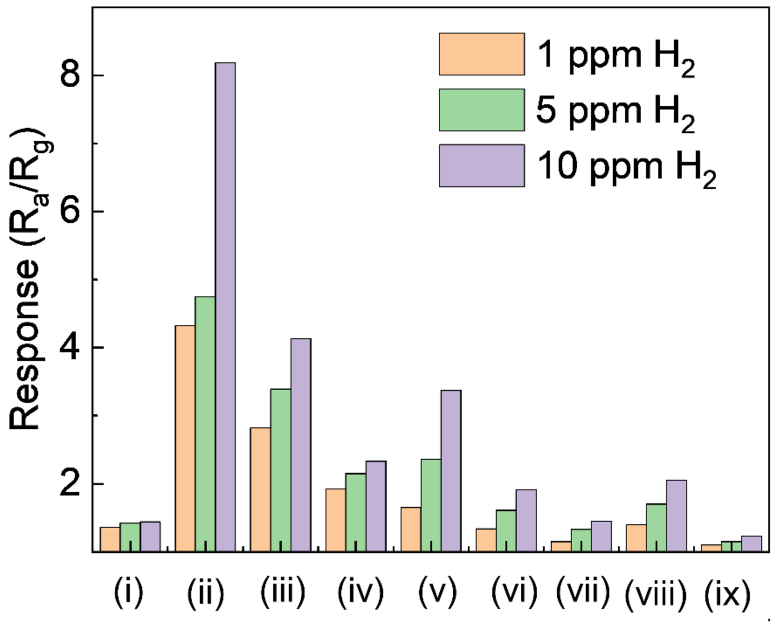


Fig. S9: Comparison of response of different gas sensors (i) Pd/TiN (0.5 nm)/SnO_2 NWs (ii) Pd/TiN (1 nm)/SnO_2 NWs (iii) Pd/TiN (2 nm)/SnO_2 NWs (iv) Pd/TiN (5 nm)/SnO_2 NWs (v) TiN (1 nm)/SnO_2 NWs (vi) TiN (2 nm)/SnO_2 NWs (vii) TiN (5 nm)/SnO_2 NWs (viii) Pd/SnO_2 NWs (ix) pristine SnO_2 NWs to 1, 5 and 10 ppm H_2 gas.

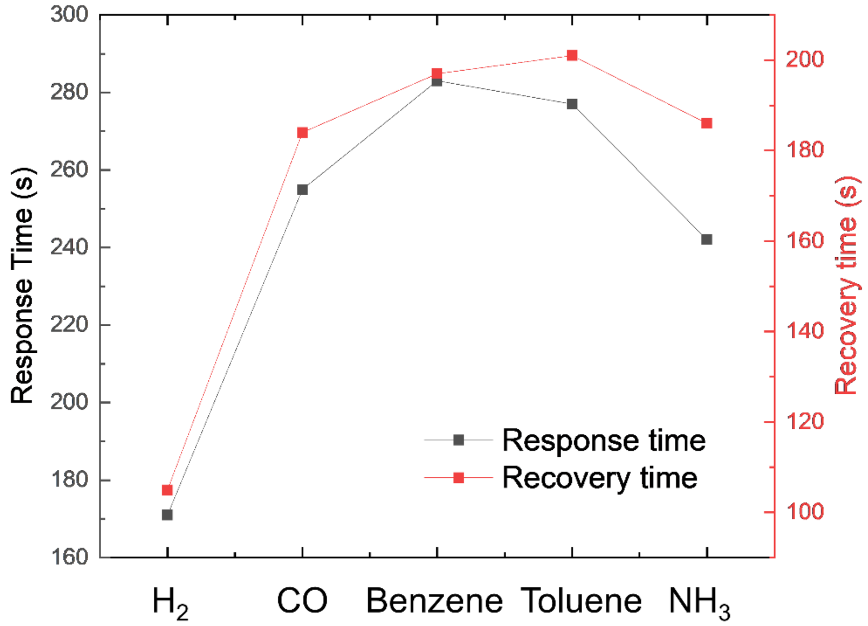


Fig. S10. Response and recovery time of Pd/TiN (1 nm)/SnO_2 NWs and to 10 ppm of tested gases.

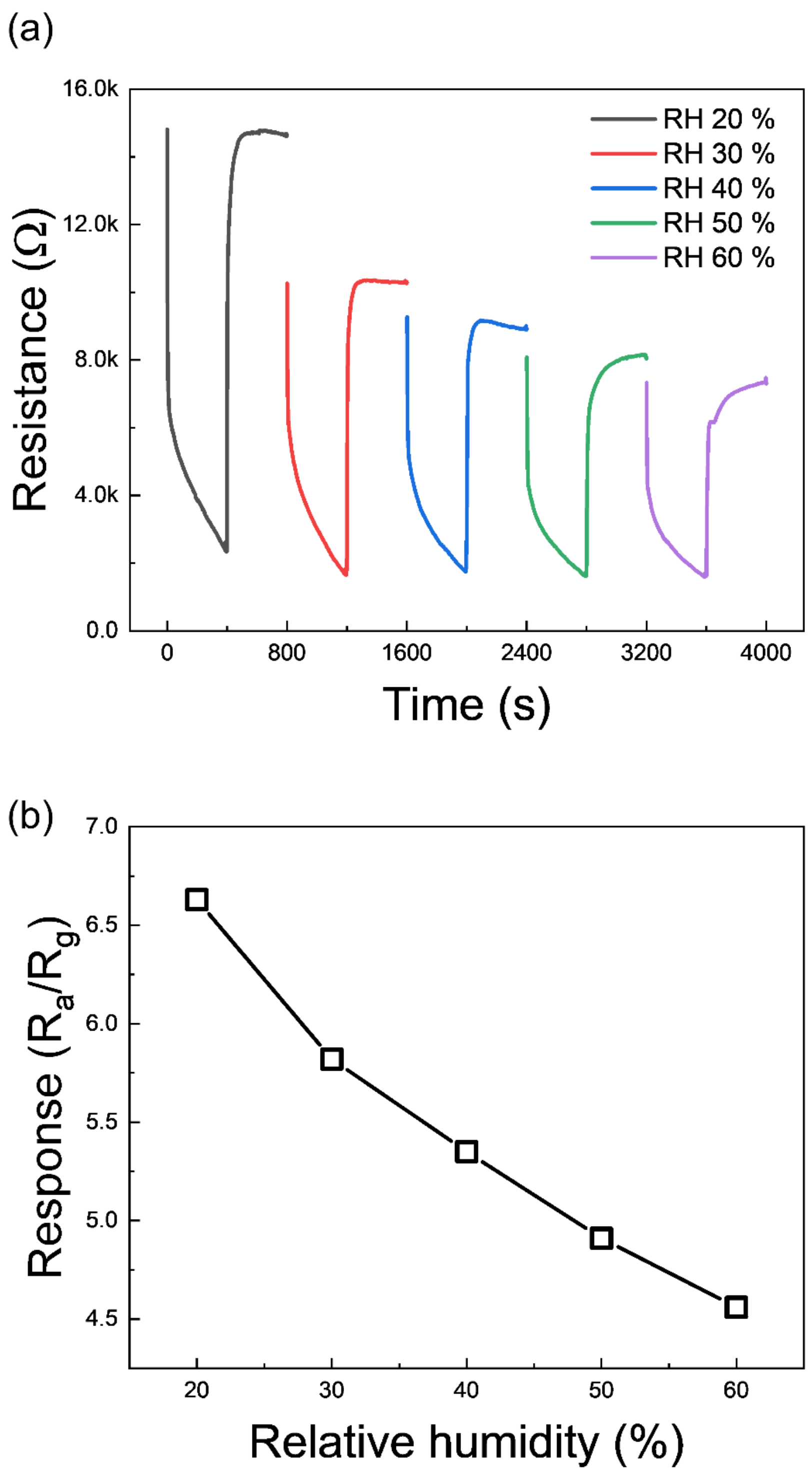


Fig. S11. (a) Transient resistance curves of Pd/TiN (1 nm)/ SnO_2 NWs and (b) response plots to 10 ppm of H_2 gas in the presence of relative humidity.

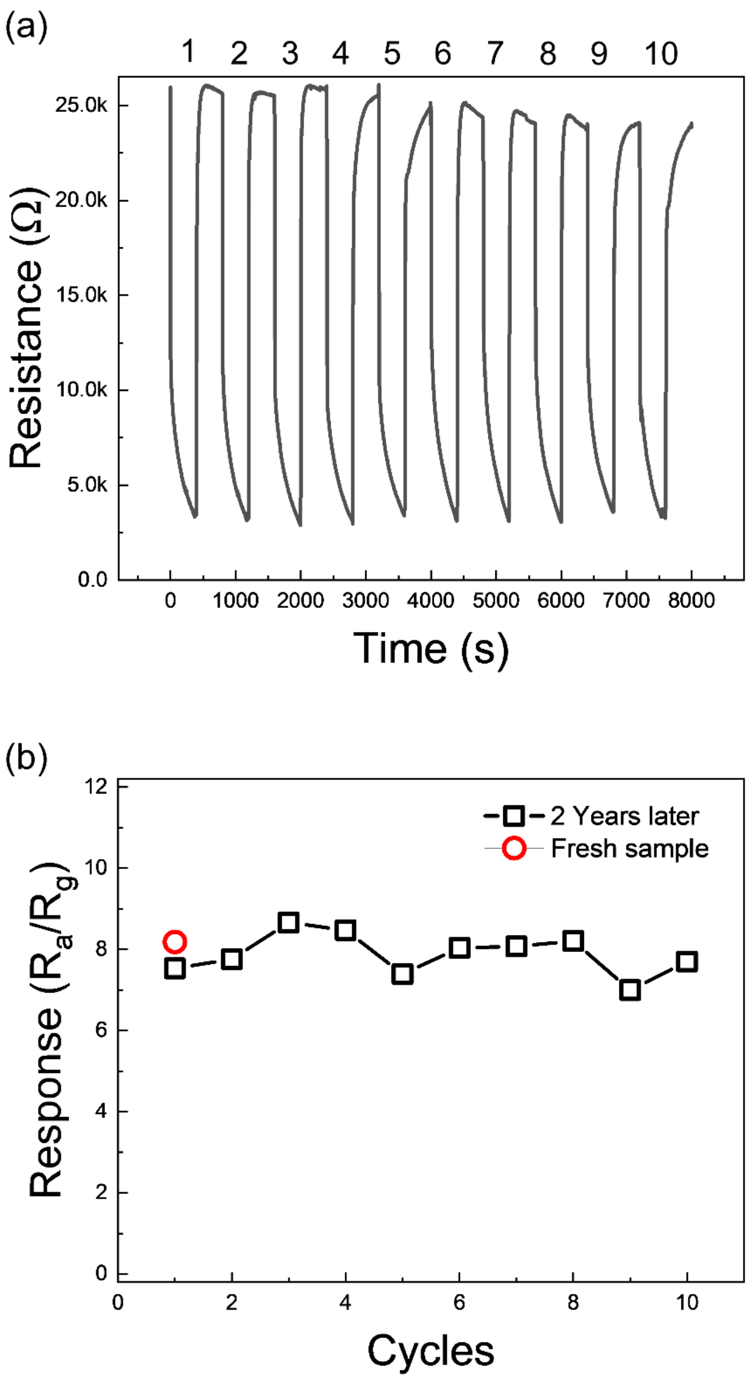


Fig. S12. (a) Transient resistance curves of 2 years aged Pd/TiN (1 nm)/ SnO_2 NWs and (b) response comparison between fresh and 2 years aged s to 10 ppm of H_2 gas.

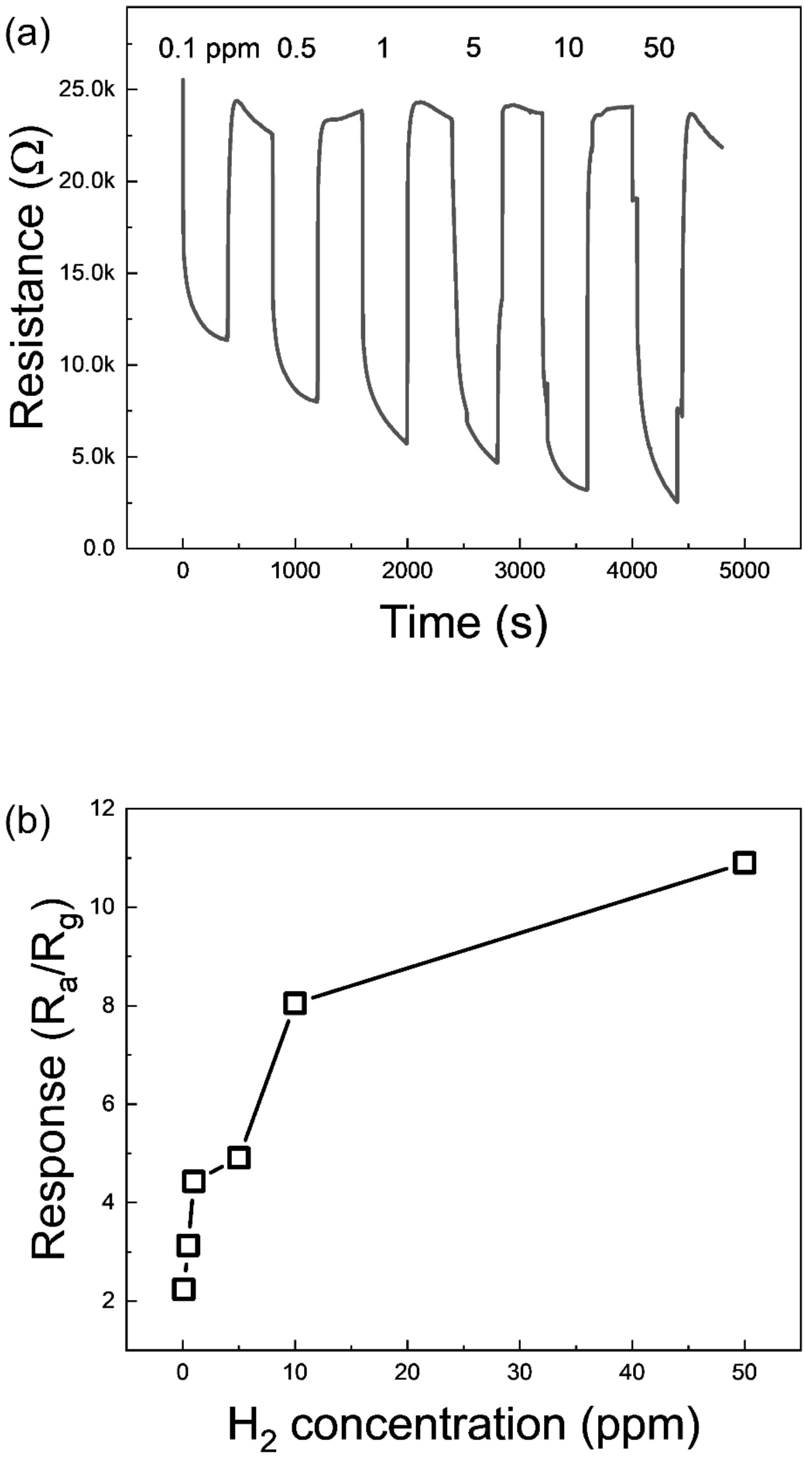


Fig. S13. (a) Transient resistance curves of Pd/TiN (1 nm)/ SnO_2 NWs to various concentration of H_2 gas and (b) correspond response plots.

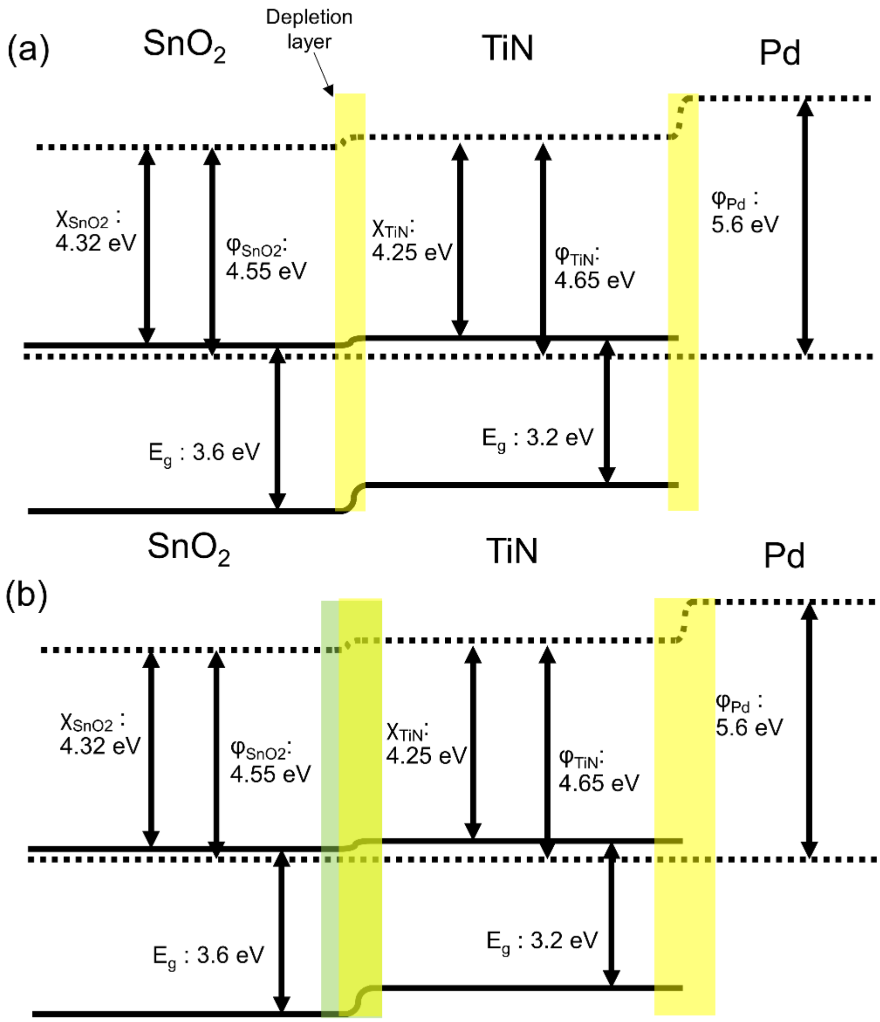


Fig. S14. Band diagram of Pd, SnO_2 and (a) TiN 1 nm, (b) 2, 5 nm.

REFERENCES

1. J. W. Elam, M. Schuisky, J. D. Ferguson and S. M. George, Thin Solid Films, 2003, 436, 145-156.
2. J. C. F. Rodríguez-Reyes and A. V. Teplyakov, *J. Phys. Chem. C*, 2007, **111**, 16498-16505.