Self-Assembled Nanostructured Tin Oxide Thin Films at the Air-Water Interface for Selective H₂S Detection

Pavithra Bellare,^{†,§} Neha Sakhuja,^{‡,§} Subhajit Kundu,[†] Navakanta Bhat[‡] and N Ravishankar^{†,*}

[†]Materials Research Centre, Indian Institute of Science, Bangalore, 560012, India

[‡]Centre for Nanoscience and Engineering, Indian Institute of Science, Bangalore, 560012, India

*Corresponding author: nravi@iisc.ac.in

Table of Content:	Page No
S1. Schematic and Theory of particle at the air-water interface	-----S-3&4
S2. SEM and XRD of settled SnO ₂ particles	----- S-4
S3. Microstructural characterization of PdO films	----- S-5
S4. Mechanism of growth of PdO thin film	----- S-6
S5. Dynamic sensing characterization of thick film (80 nm)	----- S-7
S6. Dynamic sensing characteristics of SnO ₂ thin film (30 nm) in N ₂ atmosphere	----- S-7
S7. Schematic of Interdigitated Electrodes based chemiresistive device structure	----- S-8
S8. Schematic of Gas Sensing Set up	----- S-8
S9. Supplementary Note: LOD Calculation	----- S-9
S10. Supplementary Table 1	----- S-10
S11. Supplementary Table 2	----- S-11

Figure S1. Schematic of a particle at the air-water interface.

The schematic of a particle trapped at the air- water interface is shown in **Figure S1**.

The free energy of the system when the particle is fully immersed in water is

$$E_B = A_p \gamma_{pw} + A_w \gamma_{wa} \quad (1)$$

The free energy of the system once the particle gets adsorbed at the air- water interface is

$$E_I = A_{pw} \gamma_{pw} + A_{pa} \gamma_{pa} + (A_{wa} - A_c) \gamma_{wa} \quad (2)$$

In equation (1) and (2), γ_{pw} , γ_{pa} , and γ_{wa} are the interfacial energies of the particle-water, particle-air, and water-air, respectively. A_p , A_{pw} , and A_{pa} are the areas of the full particle, the portion of particle that is immersed in water, and that of exposed to the air respectively.

Interfacial energies are related to each other by Young's equation,

$$\gamma_{pa} = \gamma_{pw} + \gamma_{wa} \cos \theta \quad (3)$$

where, θ is the contact angle depicted in the schematic **Figure S1**. After adsorption of a particle to the interface, the interfacial area A_{wa} reduces. Therefore, the energy change associated with moving a fully immersed particle to the interface is

$$\Delta E = E_I - E_B = A_{pa}(\gamma_{pa} - \gamma_{pw}) - A_c \gamma_{wa} \quad (4)$$

Areas A_p , A_c , A_{pw} , A_{pa} are given by

$$A_p = 4\pi r^2 \quad (5)$$

$$A_c = \pi r^2 \sin^2 \theta \quad (6)$$

$$A_{pw} = 2\pi r^2 (1 + \cos \theta) \quad (7)$$

$$A_{pa} = 2\pi r^2 (1 - \cos \theta) \quad (8)$$

Substituting eq (3), (5), (6), (7) and (8) in eq (4), the energy change is finally given by

$$\Delta E = -\pi r^2 \gamma_{wa} (\cos \theta - 1)^2 \quad (9)$$

Figure S2. (a) SEM image and (b) XRD pattern of the heavier SnO₂ particles and rods that settled down in the reaction vessel.

Figure S3. Microstructural characterization of PdO films. (a) SEM image, (b) TEM bright field low magnification image, (c) High magnification image and (d) Diffraction pattern of PdO films.

Figure S4. Mechanism of growth of PdO thin film at the interface. SEM images of PdO sample floating at the interface after (a) 10 min and (b) 30 min of reaction.

Figure S4 represent the SEM images of the sample scooped out from the interface after 10 min and 30 min of reaction respectively. PdO particles come to the interface and start to aggregate at 10 min of the reaction (**Figure S4(a)**); but the complete continuous film formation requires more than half an hour since there are still some pores remaining in the film at 30 min of reaction (**Figure S4(b)**). So, the synthesis of PdO films again confirms the mechanism of formation of the films at the interface.

Figure S5. The dynamic sensing characterization of thick film (80 nm) of SnO₂ towards different concentrations of H₂S at 150°C.

Figure S6. The dynamic gas sensing characteristics of SnO₂ thin film (30 nm) towards H₂S in oxygen free environment (N₂) at 150°C.

Figure S7. Schematic of Interdigitated Electrodes based chemiresistive device structure.

Figure S8. Schematic of Gas Sensing Set up

S9. Supplementary Note: LOD Calculation

We utilized the theoretical approach based on Signal-to-Noise ratio as proposed by International Union of Pure and Applied Chemistry (IUPAC) to quantify the limit of detection (LOD)[a]. The LOD of the sensor can be defined as the minimum detectable amount of H₂S in dry air. It can be statistically computed based on experimentally obtained H₂S sensing results in this work. It is well-known that Signal-to-Noise ratio (SNR) is taken as 3 for accurate LOD calculation¹. Mathematically, it is formulated as Eq. (1)

$$LOD = \frac{3 \sigma}{m}$$

where, σ is root mean square noise (RMS noise) and ‘m’ is the slope of linear regression curve obtained from response v/s concentration plot (fitted with equation $y = mx + c$). Fig. 6(c) shows linear fitting of response (%) versus concentration plot (with $y = 3979x - 97.67$), where 3979 is the slope. The root mean square noise is standard deviation predicted based on relative current variation from average current measured in dry air [52] and can be computed using eq. (2).

$$\sigma = \text{sqrt} \left(\frac{\sum_{i=1}^N (I_i - I)^2}{N} \right)$$

where, I_i is the experimentally measured data point, while I is the value obtained from the curve fitting equation of N (here we used 300) data points taken from experimental data. Using these values and formulas, RMS noise was computed to be 0.216 (Supplementary Data). The LOD was estimated to be 163 ppt by substituting these values in eq. (1).

S10. Supplementary Table 1. Gas flow rates corresponding to different concentrations of H₂S used in the sensing experiments

Concentration (ppm)	Flow rate (sccm)-Dry Air	Flow Rate (sccm)-Target gas (H ₂ S)
0.025	497.92	2.08
0.05	495.83	4.16
0.1	491.67	8.33
0.5	458.33	41.67
1	416.67	83.33
3	250	250
6	0	500

Table 1 depicts the flow rates corresponding to different concentrations of H₂S, keeping total flow constant as 500 sccm.

S11: Supplementary Table 2. Comparison of our work with existing reports in literature

S.No ·	Material	Response (%)	Response Time/ Recovery Time (Seconds)	Operating Temperature (°C)	LOD (ppb)	Ref.
1	In ₂ O ₃	50% @ 20 ppb	1800/300	RT	20 ppb (20ppb - 20 ppm)	2
2	SnO ₂ /RGO/ PANI NC	3.18% @50 ppb	82/78 @ 2 ppm	RT	50 ppb (50 ppb- 1 ppm)	3
3	SnO ₂ /ZnO	175% @ 10 ppb	/513 @ 5ppm	100	10 ppb (10 ppb – 10 ppm)	4
4	PANI nanowires/Au nanoparticles	20% @ 0.1 ppb	120/300	RT	0.1 ppb (0.1 ppb – 1 ppm)	5
5	SWCNT/Au	6% @ 20 ppb	480/1200	RT	3 ppb (20 ppb – 1000 ppm)	6
6	Fe doped SnO ₂ nanoparticles	45% @10 ppm	5-10/95-105 @ 50 ppm	RT	10 ppm (10-50 ppm)	7
7	SnO ₂ nanowire/RGO	50% @ 10 ppm	2/292	RT	10 ppm (10-100 ppm)	8
8	Au functionalized ZnO nanowires	3700% @ 1ppm	-/170 @ 5 ppm	RT	1 and 5 ppm	9
9	ZnO nanowire	2% @ 50 ppb	180/60 @ 2 ppm	150	20 ppb (50 ppb – 5 ppm)	10
10	ZnO nanowire/Cobalt Phthalocyanine Heterojunction	69% @ 5 ppm	26/175 @ 10 ppm	RT	1 ppm (5 – 50 ppm)	11
11	ZnO nanorod (spray pyrolysis)	400% @ 5 ppm	50/20 @ 5 ppm	RT	5 ppm (5 ppm – 500 ppm)	12
12	W-WO _x	387.7% @ 10 ppb	12 /19 @ 1ppm	150	10 ppb (10 ppb – 1 ppm)	13
13	CdS decorated NiO nanofilm	104% @ 0.5 ppb	----	92	0.5 ppb (0.5 – 100 ppb)	14
14	SnO ₂ nanocrystals	100% @ 0.7 ppm	200/150 @ 20 ppm	150	0.7 ppm (0.7-100 ppm)	15
15	CuO-SnO ₂ Core/Shell PN- Junction Nanorods	9.4 x 10 ⁶ @ 10 ppm	30/60 @ 10 ppm	60	10 ppm	16
16	Cu ₂ O functionalized WO ₃ nanoneedles	1.5 @ 0.3 ppm	2/687 @ 5 ppm	380	0.3 ppm (0.3- 5 ppm)	17
	SnO ₂ thin film	19.3% @ 0.025 ppm	22/99 @ 25 ppb	150	0.025 ppm (0.025-6 ppm)	Our work

References

- (1) Asif, M.; Haitao, W.; Shuang, D.; Aziz, A.; Zhang, G.; Xiao, F.; Liu, H. Metal Oxide Intercalated Layered Double Hydroxide Nanosphere: With Enhanced Electrocatalytic Activity towards H₂O₂ for Biological Applications. *Sensors Actuators, B Chem.* **2017**, 239,

- 243–252. <https://doi.org/10.1016/j.snb.2016.08.010>.
- (2) Yao, K.; Caruntu, D.; Zeng, Z.; Chen, J.; O'Connor, C. J.; Zhou, W. Parts per Billion-Level H₂S Detection at Room Temperature Based on Self-Assembled In₂O₃ Nanoparticles. *J. Phys. Chem. C* **2009**, *113* (33), 14812–14817. <https://doi.org/10.1021/jp905189f>.
  - (3) Zhang, D.; Wu, Z.; Zong, X. Flexible and Highly Sensitive H₂S Gas Sensor Based on In-Situ Polymerized SnO₂/RGO/PANI Ternary Nanocomposite with Application in Halitosis Diagnosis. *Sensors Actuators, B Chem.* **2019**, *289* (March), 32–41. <https://doi.org/10.1016/j.snb.2019.03.055>.
  - (4) Fu, D.; Zhu, C.; Zhang, X.; Li, C.; Chen, Y. Two-Dimensional Net-like SnO₂/ZnO Heteronanostructures for High-Performance H₂S Gas Sensor. *J. Mater. Chem. A* **2016**, *4* (4), 1390–1398. <https://doi.org/10.1039/c5ta09190j>.
  - (5) Shirsat, M. D.; Bangar, M. A.; Deshusses, M. A.; Myung, N. V.; Mulchandani, A. Polyaniline Nanowires-Gold Nanoparticles Hybrid Network Based Chemiresistive Hydrogen Sulfide Sensor. *Appl. Phys. Lett.* **2009**, *94* (8). <https://doi.org/10.1063/1.3070237>.
  - (6) Mubeen, S.; Zhang, T.; Mulchandani, A.; Myung, N. V.; Deshusses, M. A. Sensitive Detection of H₂S Using Gold Decorated Single-Walled Carbon Nanotubes. *Anal. Chem.* **2010**, *82* (1), 250–257.
  - (7) Vaishampayan, M. V.; Deshmukh, R. G.; Walke, P.; Mulla, I. S. Fe-Doped SnO₂ Nanomaterial: A Low Temperature Hydrogen Sulfide Gas Sensor. *Mater. Chem. Phys.* **2008**, *109* (2–3), 230–234. <https://doi.org/10.1016/j.matchemphys.2007.11.024>.
  - (8) Song, Z.; Wei, Z.; Wang, B.; Luo, Z.; Xu, S.; Zhang, W.; Yu, H.; Li, M.; Huang, Z.; Zang, J.; et al. Sensitive Room-Temperature H₂S Gas Sensors Employing SnO₂ Quantum Wire/Reduced Graphene Oxide Nanocomposites. *Chem. Mater.* **2016**, *28* (4), 1205–1212. <https://doi.org/10.1021/acs.chemmater.5b04850>.
  - (9) Ramgir, N. S.; Sharma, P. K.; Datta, N.; Kaur, M.; Debnath, A. K.; Aswal, D. K.; Gupta, S. K. Room Temperature H₂S Sensor Based on Au Modified ZnO Nanowires. *Sensors Actuators, B Chem.* **2013**, *186*, 718–726. <https://doi.org/10.1016/j.snb.2013.06.070>.
  - (10) Huang, H.; Xu, P.; Zheng, D.; Chen, C.; Li, X. Sulfuration-Desulfuration Reaction Sensing Effect of Intrinsic ZnO Nanowires for High-Performance H₂S Detection. *J. Mater. Chem. A* **2015**, *3* (12), 6330–6339. <https://doi.org/10.1039/c4ta05963h>.
  - (11) Kumar, A.; Samanta, S.; Singh, A.; Roy, M.; Singh, S.; Basu, S.; Chehimi, M. M.; Roy, K.; Ramgir, N.; Navaneethan, M.; et al. Fast Response and High Sensitivity of ZnO Nanowires - Cobalt Phthalocyanine Heterojunction Based H₂S Sensor. *ACS Appl. Mater. Interfaces* **2015**, *7* (32), 17713–17724. <https://doi.org/10.1021/acsami.5b03652>.
  - (12) Mani, G. K.; Rayappan, J. B. B. Selective Recognition of Hydrogen Sulfide Using Template and Catalyst Free Grown ZnO Nanorods. *RSC Adv.* **2015**, *5* (68), 54952–54962. <https://doi.org/10.1039/c5ra07804k>.
  - (13) Benedict, S.; Bhat, N. Nanodisc Decorated W-WO_x Suspended Nanowire: A Highly Sensitive and Selective H₂S Sensor. *IEEE Sens. J.* **2018**, *PP*, 1. <https://doi.org/10.1109/JSEN.2018.2884703>.
  - (14) Yu, T. T.; Zhang, X. F.; Xu, Y. M.; Cheng, X. L.; Gao, S.; Zhao, H.; Huo, L. H. Low Concentration H₂S Detection of CdO-Decorated Hierarchically Mesoporous NiO Nanofilm with Wrinkle Structure. *Sensors Actuators, B Chem.* **2016**, *230*, 706–713. <https://doi.org/10.1016/j.snb.2016.02.128>.
  - (15) Liu, H.; Gong, S. P.; Hu, Y. X.; Liu, J. Q.; Zhou, D. X. Properties and Mechanism Study of SnO₂ Nanocrystals for H₂S Thick-Film Sensors. *Sensors Actuators, B Chem.* **2009**, *140*

- (1), 190–195. <https://doi.org/10.1016/j.snb.2009.04.027>.
- (16) Xue, X.; Xing, L.; Chen, Y.; Shi, S.; Wang, Y.; Wang, T. Synthesis and H₂S Sensing Properties of CuO - SnO₂ Core / Shell PN-Junction Nanorods. *J. Phys. chem. C* **2008**, *4*, 12157–12160.
- (17) Annanouch, F. E.; Haddi, Z.; Vallejos, S.; Umek, P.; Guttman, P.; Bittencourt, C.; Llobet, E. Aerosol-Assisted CVD-Grown WO₃ Nanoneedles Decorated with Copper Oxide Nanoparticles for the Selective and Humidity-Resilient Detection of H₂S. *ACS Appl. Mater. Interfaces* **2015**, *7* (12), 6842–6851. <https://doi.org/10.1021/acsami.5b00411>.