Electronic Supplementary Material (ESI) for RSC Advances.


# Supporting Information's

# Hierarchical ZnO/Zeolite Nanostructures: Synthesis, Growth Mechanism and Hydrogen Detection

*Ahsanulhaq Qurashi [a,b] Mohiuddin Haffar[b] Z.H. Yamani[a,c]*

Nanomaterials hydrogen sensor were largely investigated in the recent times. Some of the recent work is summarized in table 1 [1-11]. However the response of our sensors based on ZnO/Zeolite hierarchical structures is swift and highly promising. Also, Ra. et al studied hydrogen sensing of ZnO nanowires fabricated by top-down approach [12]. The sensor response and recovery time was found to be slow. Navale et al studied hydrogen and liquefied petroleum gas sensor response using ZnO nanostructures [13]. Nevertheless ZnO nanostructures selectivity towards liquefied petroleum gas. Kaciulis et al investigated hydrogen sensing performance of $SnO_2$ nanowires at high temperature of 530°C. However the response and recovery of hydrogen gas was slow at higher operating temperature [14]. Mubeen et al, studied the palladium (Pd) nanoparticles decorated carbon nanotubes (CNT) for hydrogen gas sensors [15, 16]. The response and recovery time of hydrogen gas was more than 10 min. Jeon et al lately reported the single Pd nanowire based hydrogen gas sensors [17]. The Pd nanowires were fabricated by top-down approach (electron beam lithography). The hydrogen sensors made from single Pd nanowire showed fast response when the thickness of nanowire was kept 20 nm. Contrariwise by modifying the thickness of nanowire the response time and recovery changed. When the nanowires thickness increased to 400 nm the resistance of the sample did not return to the initial value. Also electron beam lithography is costly and time consuming method. We earlier investigated synthesis of $In_2O_3$, nanowires, nanoneedles and nanopushpins by vapor transport technique and then studied hydrogen sensing using In2O3 nanostructures devices (9-11). However the devices showed response in from 30-60 seconds. In this work we observed quite ***interesting and fast response (10 s) of hydrogen gas***.

| Material | diameter | Shape | Response time | Working temperature | Detection limit | Synthesis method | References |
|---|---|---|---|---|---|---|---|
| $TiO_2$ | 46 nm | Nanotubes | 150 (s) | 300°C | 1000 ppm | Electrochemical deposition | 1 |
| $SnO_2$ | ~50 nm | Nanowires | 5 min. | 200°C | 0.5% | Vapor transport | 2 |
| ZnO | 100-150 nm | Nanorods | 20 (s) | 350°C | 2500 ppm | Chemical approach | 3 |
| $SnO_2$ | 200 nm | Nanoholes | 2 min. | 350°C | 1000 ppm | Liquid phase deposition | 4 |
| ZnO | 10 nm | Nanobelts | 100 (s) | 50°C | 250ppm | Electrochemical deposition | 5 |
| $TiO_2$ | 75 nm | Nanosponges | ~500 (s) | 275°C | 4000 ppm | PECVD | 6 |
| $Al_2O_3$ | 60 nm | Nanowells | ~ 60 (s) | RT | 500 ppm | Anodization | 7 |
| ZnO | 500 nm | Microrod | 100 (s) | RT | 200 ppm | Chemical approach | 8 |
| ZnO | 70-80 nm | Nanowires | 65 (s) | 200°C | 500 ppm | Microwave evaporation | 9 |
| $In_2O_3$ | | Nanopushpins | 35 (s) | 250°C | 500 ppm | Vapor transport | 10 |
| $In_2O_3$ | 70 nm | Nanowires | 31 (s) | 200°C | 500 ppm | Vapor transport | 11 |
| **ZnO/Zeolite nanocrystals** | **200 nm** | **nanospheres** | **10 (s)** | **400°C** | **1000 ppm** | **Chemical approach** | **Present Study** |

**Table 1:** Summary of hydrogen sensors response built on metal oxide nanostructures

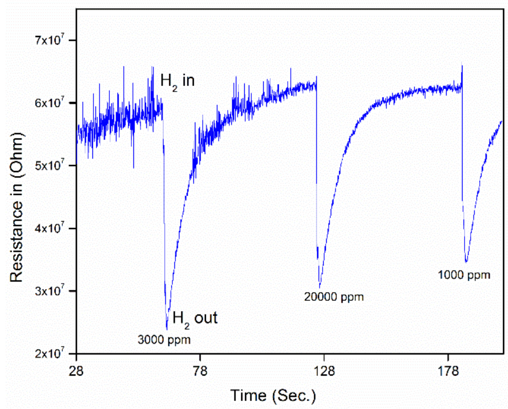


**Figure 1:** Gas sensor response of ZnO/zeolite nanocrystals for different hydrogen gas concentrations.

## References


[1] O. Varghese, D.Gong, M. Paulose, K.G. Ong, C.A. Grimes "Hydrogen sensing using titania nanotubes" Sensors and Actuators B 93 (2003) 338–344.

[2] R.L. Vander Wal, G.W. Hunter, J.C. Xu, M.J. Kulis, G.M. Berger , T.M. Ticich, Metal-oxide nanostructure and gas-sensing performance, Sensors and Actuators B: 138 (2009) 113–119.

[3] L. J. Bie, X. N. Yan, J. Yin, Y. Q. Duan, Zhi-Hao Yuan, Nanopillar ZnO gas sensor for hydrogen and ethanol, Sensors and Actuators B 126 (2007) 604–608.

[4] T. Hamaguchi, N. Yabuki, M. Uno, S. Yamanaka, M. Egashira, Y. Shimizu, T. Hyodo, Synthesis and $H_2$ gas sensing properties of tin oxide nanohole arrays with various electrodes, Sensors and Actuators B 113 (2006) 852–856.

[5] J. Yang, G. Liu, J. Lu, Y. Qiu, S. Yang Electrochemical route to the synthesis of ultrathin ZnO nanorod/nanobelt arrays on zinc substrate" Appl. Phys. Lett. 90 (2007) 103109.

[6] Abu Samah Zuruzi, Noel C. MacDonald, Martin Moskovits, and Andrei Kolmakov,

Metal Oxide "Nanosponges" as chemical sensors: highly sensitive detection of hydrogen with nanosponge titania, Angew. Chem. 119, (2007) 4376 –4379.

[7] F. Rumiche, H.H.Wang, W.S. Hu, J.E. Indacoche, M.L.Wang, Anodized aluminum oxide (AAO) nanowell sensors for hydrogen detection, Sensors and Actuators B 134 (2008) 869–877.

[8] O. Lupana, G. Chaic, L. Chow, Fabrication of ZnO nanorod-based hydrogen gas nanosensor, Microelectronics Journal 38 (2007) 1211-1216.

[9]. **Ahsanulhaq. Qurashi** N. Tabet M. Faiz T.Yamazaki, Ultra-fast microwave synthesis of ZnO nanowires and their dynamic response toward hydrogen gas, Nanoscale Res. Lett. 4 (2009) 948-954.

[10]. **Ahsanulhaq Qurashi,** El Maghraby, Toshinari Yamazaki and Toshio Kikuta **"**Fabrication and Gas Sensing Properties of $In_2O_3$ Nanopushpins" Appl. Phys Lett. **95**, 153109 (2009)

[11]. **Ahsanulhaq Qurashi,** El Maghraby, Toshinari Yamazaki and Toshio Kikuta "Catalyst Supported Growth of $In_2O_3$ Nanostructures and Their Hydrogen Gas Sensing" Sensors and actuators B**.** 147, (2010), 48-54

[12] H.W. Ra, K.S. Choi, J.H. Kim, Y.B. Hahn, and Y. H. Im, Fabrication of ZnO Nanowires Using Nanoscale Spacer Lithography for Gas Sensors, Small 4, (2008) 1105-1109.

[13] C. S. C. Navale, S.W. Gosavi , I.S. Mulla, Controlled synthesis of ZnO from nanospheres to micro-rods and its gas sensing studies, Talanta 75 (2008) 1315-1319.

[14] S.Kaciulis, L. Pandolfi, E. Comini, G. Faglia, M. Ferroni, G. Sberveglieri, S. Kandasamy, M. Shafieic, and W. Wlodarskic, Nanowires of metal oxides for gas sensing applications, Surf. Interface Anal. 40, (2008) 575-578.

[15] S. Mubeen, T. Zhang, B. Yoo, M. Deshusses, and N.Myung, Palladium Nanoparticles Decorated Single-Walled Carbon Nanotube Hydrogen Sensor, J. Phys. Chem. C**,** 111*,* (2007) 6321-6327.

[16] S. Mubeen, B. Yoo, and N. Myung, Fabrication of nanoelectrodes and nanojunction hydrogen sensor, Appl. Phys. Lett. 93, (2008) 133111.

[17] K.J. Jeon, J.M. Lee, E. Lee and W. Lee, Individual Pd nanowire hydrogen sensors fabricated by electron-beam lithography, Nanotechnology 20, (2009) 135502.