ACS APPLIED MATERIALS & INTERFACES

www.acsami.org

Research Article

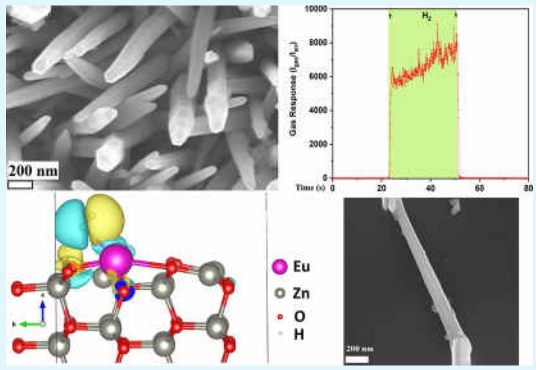
Nanosensors Based on a Single ZnO:Eu Nanowire for Hydrogen Gas Sensing

Cristian Lupan,* Abhishek Kumar Mishra,* Niklas Wolff, Jonas Drewes, Helge Krüger, Alexander Vahl,* Oleg Lupan,* Thierry Pauporté, Bruno Viana, Lorenz Kienle, Rainer Adelung, Nora H de Leeuw, and Sandra Hansen*

Cite This: *ACS Appl. Mater. Interfaces* 2022, 14, 41196–41207

Read Online

ACCESS | Metrics & More | Article Recommendations | Supporting Information



ABSTRACT: Fast detection of hydrogen gas leakage or its release in different environments, especially in large electric vehicle batteries, is a major challenge for sensing applications. In this study, the morphological, structural, chemical, optical, and electronic characterizations of ZnO:Eu nanowire arrays are reported and discussed in detail. In particular, the influence of different Eu concentrations during electrochemical deposition was investigated together with the sensing properties and mechanism. Surprisingly, by using only 10 μM Eu ions during deposition, the value of the gas response increased by a factor of nearly 130 compared to an undoped ZnO nanowire and we found an H_2 gas response of ~7860 for a single ZnO:Eu nanowire device. Further, the synthesized nanowire sensors were tested with ultraviolet (UV) light and a range of test gases, showing a UV responsiveness of ~12.8 and a good selectivity to 100 ppm H_2 gas. A dual-mode nanosensor is shown to detect UV/H_2 gas simultaneously for selective detection of H_2 during UV irradiation and its effect on the sensing mechanism. The nanowire sensing approach here demonstrates the feasibility of using such small devices to detect hydrogen leaks in harsh, small-scale environments, for example, stacked battery packs in mobile applications. In addition, the results obtained are supported through density functional theory-based simulations, which highlight the importance of rare earth nanoparticles on the oxide surface for improved sensitivity and selectivity of gas sensors, even at room temperature, thereby allowing, for instance, lower power consumption and denser deployment.

KEYWORDS: *Eu_2O_3, ZnO, sensor, hydrogen, electrochemical deposition*

REFERENCES

(1) Saeedmanesh, A.; Mac Kinnon, M. A.; Brouwer, J. Hydrogen Is Essential for Sustainability. *Curr. Opin. Electrochem.* **2018**, *12*, 166–181.

(2) Arshad, F.; Haq, T.; Hussain, I.; Sher, F. Recent Advances in Electrocatalysts toward Alcohol-Assisted, Energy-Saving Hydrogen Production. *ACS Appl. Energy Mater.* **2021**, *4*, 8685–8701.

(3) Ohsaki, T.; Kishi, T.; Kuboki, T.; Takami, N.; Shimura, N.; Sato, Y.; Sekino, M.; Satoh, A. Overcharge Reaction of Lithium-Ion Batteries. *J. Power Sources* **2005**, *146*, 97–100.

(4) Essl, C.; Golubkov, A. W.; Fuchs, A. Comparing Different Thermal Runaway Triggers for Two Automotive Lithium-Ion Battery Cell Types. *J. Electrochem. Soc.* **2020**, *167*, 130542.

(5) *Guide for the Ventilation and Thermal Management of Batteries for Stationary Applications*; IEEE, 2018.

(6) Chen, Y.; Kang, Y.; Zhao, Y.; Wang, L.; Liu, J.; Li, Y.; Liang, Z.; He, X.; Li, X.; Tavajohi, N.; Li, B. A Review of Lithium-Ion Battery Safety Concerns: The Issues, Strategies, and Testing Standards. *J. Energy Chem.* **2021**, *59*, 83–99.

(7) Sundén, B. Battery Technologies. *Hydrogen Batter. Fuel Cells* **2019**, 57–79.

(8) Hosseini, S. E.; Wahid, M. A. Hydrogen from Solar Energy, a Clean Energy Carrier from a Sustainable Source of Energy. *Int. J. Energy Res.* **2020**, *44*, 4110–4131.

(9) Essl, C.; Golubkov, A. W.; Gasser, E.; Nachtnebel, M.; Zankel, A.; Ewert, E.; Fuchs, A. Comprehensive Hazard Analysis of Failing Automotive Lithium-ion Batteries in Overtemperature Experiments. *Batteries* **2020**, *6*, 30.

(10) Golubkov, A. W.; Scheikl, S.; Planteu, R.; Voitic, G.; Wiltsche, H.; Stangl, C.; Fauler, G.; Thaler, A.; Hacker, V. Thermal Runaway of Commercial 18650 Li-Ion Batteries with LFP and NCA Cathodes - Impact of State of Charge and Overcharge. *RSC Adv.* **2015**, *5*, 57171–57186.

(11) International Code Council. *2018 International Fire Code*; International Code Council, 2017.

(12) Carcassi, M. N.; Fineschi, F. Deflagrations of H_2-Air and CH_4-Air Lean Mixtures in a Vented Multi-Compartment Environment. *Energy* **2005**, *30*, 1439–1451.

(13) Lupan, O.; Cretu, V.; Postica, V.; Ahmadi, M.; Cuenya, B. R.; Chow, L.; Tiginyanu, I.; Viana, B.; Pauporté, T.; Adelung, R. Silver-Doped Zinc Oxide Single Nanowire Multifunctional Nanosensor with a Significant Enhancement in Response. *Sens. Actuators, B* **2016**, *223*, 893–903.

(14) Gorup, L. F.; Amorin, L. H.; Camargo, E. R.; Sequinel, T.; Cincotto, F. H.; Biasotto, G.; Ramesar, N.; de La Porta, F. A. Methods for Design and Fabrication of Nanosensors: The Case of ZnO-Based Nanosensor. *Nanosensors Smart Cities* **2020**, 9–30.

(15) Hastir, A.; Kohli, N.; Singh, R. C. Comparative Study on Gas Sensing Properties of Rare Earth (Tb, Dy and Er) Doped ZnO Sensor. *J. Phys. Chem. Solids* **2017**, *105*, 23–34.

(16) Lupan, O.; Postica, V.; Pauporté, T.; Viana, B.; Terasa, M. I.; Adelung, R. Room Temperature Gas Nanosensors Based on Individual and Multiple Networked Au-Modified ZnO Nanowires. *Sens. Actuators, B* **2019**, *299*, 126977.

(17) Lupan, O.; Postica, V.; Wolff, N.; Su, J.; Labat, F.; Ciofini, I.; Cavers, H.; Adelung, R.; Polonskyi, O.; Faupel, F.; Kienle, L.; Viana, B.; Pauporté, T. Lowerature Solution Synthesis of Au-Modified ZnO Nanowires for Highly Efficient Hydrogen Nanosensors. *ACS Appl. Mater. Interfaces* **2019**, *11*, 32115–32126.

(18) Postica, V.; Vahl, A.; Santos-Carballal, D.; Dankwort, T.; Kienle, L.; Hoppe, M.; Cadi-Essadek, A.; De Leeuw, N. H.; Terasa, M. I.; Adelung, R.; Faupel, F.; Lupan, O. Tuning ZnO Sensors Reactivity toward Volatile Organic Compounds via Ag Doping and Nanoparticle Functionalization. *ACS Appl. Mater. Interfaces* **2019**, *11*, 31452–31466.

(19) Han, D.; Yang, J.; Gu, F.; Wang, Z. Effects of Rare Earth Element Doping on the Ethanol Gas-Sensing Performance of Three-Dimensionally Ordered Macroporous In_2O_3. *RSC Adv.* **2016**, *6*, 45085–45092.

(20) Dash, D.; Panda, N. R.; Sahu, D. Photoluminescence and Photocatalytic Properties of Europium Doped ZnO Nanoparticles. *Appl. Surf. Sci.* **2019**, *494*, 666–674.

(21) Pauporté, T.; Pellé, F.; Viana, B.; Aschehoug, P. Luminescence of Nanostructured Eu3+/ZnO Mixed Films Prepared by Electrodeposition. *J. Phys. Chem. C* **2007**, *111*, 15427–15432.

(22) Zhao, S.; Shen, Y.; Li, A.; Chen, Y.; Gao, S.; Liu, W.; Wei, D. Effects of Rare Earth Elements Doping on Gas Sensing Properties of ZnO Nanowires. *Ceram. Int.* **2021**, *47*, 24218–24226.

(23) Lupan, C.; Khaledialidusti, R.; Mishra, A. K.; Postica, V.; Terasa, M. I.; Magariu, N.; Pauporté, T.; Viana, B.; Drewes, J.; Vahl, A.; Faupel, F.; Adelung, R. Pd-Functionalized ZnO:Eu Columnar Films for Room-Temperature Hydrogen Gas Sensing: A Combined Experimental and Computational Approach. *ACS Appl. Mater. Interfaces* **2020**, *12*, 24951–24964.

(24) Lupan, O.; Pauporté, T.; Viana, B.; Aschehoug, P.; Ahmadi, M.; Cuenya, B. R.; Rudzevich, Y.; Lin, Y.; Chow, L. Eu-Doped ZnO Nanowire Arrays Grown by Electrodeposition. *Appl. Surf. Sci.* **2013**, *282*, 782–788.

https://doi.org/10.1021/acsami.2c10975
ACS Appl. Mater. Interfaces 2022, 14, 41196–41207

(25) Moulder, J. F.; Stickle, W. F.; Sobol, P. E.; Bomben, K. D. *Handbook of Photoelectron Spectroscopy*. Phys. Electron. Inc.: Eden Prairie, Minnesota 1992.
(26) Kohlmann, N.; Hansen, L.; Lupan, C.; Schu, U.; Reimers, A.; Schu, F.; Adelung, R.; Kersten, H.; Kienle, L. Fabrication of ZnO Nanobrushes by H 2 − C 2 H 2 Plasma Etching for H 2 2 Sensing Applications. 2021, *13* (51), 61758−61769, DOI: 10.1021/acsami.1c18679.
(27) Lupan, O.; Magariu, N.; Khaledialidusti, R.; Mishra, A. K.; Hansen, S.; Krüger, H.; Postica, V.; Heinrich, H.; Viana, B.; Ono, L. K.; Cuenya, B. R.; Chow, L.; Adelung, R.; Pauporté, T. Comparison of Thermal Annealing versus Hydrothermal Treatment Effects on the Detection Performances of ZnO Nanowires. *ACS Appl. Mater. Interfaces* **2021**, *13*, 10537−10552.
(28) Lupan, O.; Chai, G.; Chow, L. Fabrication of ZnO Nanorod-Based Hydrogen Gas Nanosensor. *Microelectron. J.* **2007**, *38*, 1211−1216.
(29) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, *77*, 3865−3868.
(30) Blöchl, P. E. Projector Augmented-Wave Method. *Phys. Rev. B* **1994**, *50*, 17953−17979.
(31) Kresse, G.; Joubert, D. From Ultrasoft Pseudopotentials to the Projector Augmented-Wave Method. *Phys. Rev. B* **1999**, *59*, 11−1775.
(32) Kresse, G.; Furthmüller, J. Efficiency of Ab-Initio Total Energy Calculations for Metals and Semiconductors Using a Plane-Wave Basis Set. *Comput. Mater. Sci.* **1996**, *6*, 15−50.
(33) Postica, V.; Gröttrup, J.; Adelung, R.; Lupan, O.; Mishra, A. K.; de Leeuw, N. H.; Ababii, N.; Carreira, J. F. C.; Rodrigues, J.; Sedrine, N. B.; Correia, M. R.; Monteiro, T.; Sontea, V.; Mishra, Y. K. Multifunctional Materials: A Case Study of the Effects of Metal Doping on ZnO Tetrapods with Bismuth and Tin Oxides. *Adv. Funct. Mater.* **2017**, *27*, 1604676.
(34) Lupan, O.; Postica, V.; Gröttrup, J.; Mishra, A. K.; De Leeuw, N. H.; Carreira, J. F. C.; Rodrigues, J.; Ben Sedrine, N.; Correia, M. R.; Monteiro, T.; Cretu, V.; Tiginyanu, I.; Smazna, D.; Mishra, Y. K.; Adelung, R. Hybridization of Zinc Oxide Tetrapods for Selective Gas Sensing Applications. *ACS Appl. Mater. Interfaces* **2017**, *9*, 4084−4099.
(35) Pack, J. D.; Monkhorst, H. J. "Special Points for Brillouin-Zone Integrations"-a Reply. *Phys. Rev. B* **1977**, *16*, 1748−1749.
(36) Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. A Consistent and Accurate Ab Initio Parametrization of Density Functional Dispersion Correction (DFT-D) for the 94 Elements H-Pu. *J. Chem. Phys.* **2010**, *132*, 154104.
(37) Henkelman, G.; Arnaldsson, A.; Jónsson, H. A Fast and Robust Algorithm for Bader Decomposition of Charge Density. *Comput. Mater. Sci.* **2006**, *36*, 354−360.
(38) Lupan, O.; Chai, G.; Chow, L. Novel Hydrogen Gas Sensor Based on Single ZnO Nanorod. *Microelectron. Eng.* **2008**, *85*, 2220−2225.
(39) Lupan, O.; Ursaki, V. V.; Chai, G.; Chow, L.; Emelchenko, G. A.; Tiginyanu, I. M.; Gruzintsev, A. N.; Redkin, A. N. Selective Hydrogen Gas Nanosensor Using Individual ZnO Nanowire with Fast Response at Room Temperature. *Sens. Actuators, B* **2010**, *144*, 56−66.
(40) Hocking, W. H.; Matthew, J. A. D. Electron Spectroscopy of Europium. *J. Phys. Condens. Matter.* **1990**, *2*, 3643−3658.
(41) Tizei, L. H. G.; Nakanishi, R.; Kitaura, R.; Shinohara, H.; Suenaga, K. Core-Level Spectroscopy to Probe the Oxidation State of Single Europium Atoms. *Phys. Rev. Lett.* **2015**, *114*, 197602.
(42) Mundy, J. A.; Hodash, D.; Melville, A.; Held, R.; Mairoser, T.; Muller, D. A.; Kourkoutis, L. F.; Schmehl, A.; Schlom, D. G. Hetero-Epitaxial EuO Interfaces Studied by Analytic Electron Microscopy. *Appl. Phys. Lett.* **2014**, *104*, No. 091601.
(43) Mairoser, T.; Mundy, J. A.; Melville, A.; Hodash, D.; Cueva, P.; Held, R.; Glavic, A.; Schubert, J.; Muller, D. A.; Schlom, D. G.; Schmehl, A. High-Quality EuO Thin Films the Easy Way via Topotactic Transformation. *Nat. Commun.* **2015**, *6*, 1−7.
(44) Postica, V.; Vahl, A.; Strobel, J.; Santos-Carballal, D.; Lupan, O.; Cadi-Essadek, A.; De Leeuw, N. H.; Schütt, F.; Polonskyi, O.; Strunskus, T.; Baum, M.; Kienle, L.; Adelung, R.; Faupel, F. Tuning Doping and Surface Functionalization of Columnar Oxide Films for Volatile Organic Compound Sensing: Experiments and Theory. *J. Mater. Chem. A* **2018**, *6*, 23669−23682.
(45) Lupan, O.; Emelchenko, G. A.; Ursaki, V. V.; Chai, G.; Redkin, A. N.; Gruzintsev, A. N.; Tiginyanu, I. M.; Chow, L.; Ono, L. K.; Roldan Cuenya, B.; Heinrich, H.; Yakimov, E. E. Synthesis and Characterization of ZnO Nanowires for Nanosensor Applications. *Mater. Res. Bull.* **2010**, *45*, 1026−1032.
(46) Rumble, J. R.; Bickham, D. M.; Powell, C. J. The NIST X-ray Photoelectron Spectroscopy Database. *Surf. Interface Anal.* **1992**, *19*, 241−246.
(47) Lupan, O.; Chai, G.; Chow, L.; Emelchenko, G. A.; Heinrich, H.; Ursaki, V. V.; Gruzintsev, A. N.; Tiginyanu, I. M.; Redkin, A. N. Ultraviolet Photoconductive Sensor Based on Single ZnO Nanowire. *Phys. Status Solidi Appl. Mater. Sci.* **2010**, *207*, 1735−1740.
(48) Rashid, T. R.; Phan, D. T.; Chung, G. S. A Flexible Hydrogen Sensor Based on Pd Nanoparticles Decorated ZnO Nanorods Grown on Polyimide Tape. *Sens. Actuators, B* **2013**, *185*, 777−784.
(49) Khan, R.; Ra, H. W.; Kim, J. T.; Jang, W. S.; Sharma, D.; Im, Y. H. Nanojunction Effects in Multiple ZnO Nanowire Gas Sensor. *Sens. Actuators, B* **2010**, *150*, 389−393.
(50) Zhou, J.; Gu, Y.; Hu, Y.; Mai, W.; Yeh, P. H.; Bao, G.; Sood, A. K.; Polla, D. L.; Wang, Z. L. Gigantic Enhancement in Response and Reset Time of ZnO UV Nanosensor by Utilizing Schottky Contact and Surface Functionalization. *Appl. Phys. Lett.* **2009**, *94*, 191103.
(51) Sihar, N.; Tiong, T. Y.; Dee, C. F.; Ooi, P. C.; Hamzah, A. A.; Mohamed, M. A.; Majlis, B. Y. Ultraviolet Light-Assisted Copper Oxide Nanowires Hydrogen Gas Sensor. *Nanoscale Res. Lett.* **2018**, *13*, 4−9.
(52) Yamazoe, N.; Fuchigami, J.; Kishikawa, M.; Seiyama, T. Interactions of Tin Oxide Surface with O2, H2O AND H2. *Surf. Sci.* **1979**, *86*, 335−344.
(53) Lenaerts, S.; Roggen, J.; Maes, G. FT-IR Characterization of Tin Dioxide Gas Sensor Materials under Working Conditions. *Spectrochim. Acta Part A* **1995**, *51*, 883−894.
(54) Chang, S. C. Oxygen Chemisorption on Tin Oxide: Correlation Between Electrical Conductivity and Epr Measurements. *J. Vac. Sci. Technol.* **1979**, *17*, 366−369.
(55) Cooke, D. J.; Marmier, A.; Parker, S. C. Surface Structure of (1010) and (1120) Surfaces of ZnO with Density Functional Theory and Atomistic Simulation. *J. Phys. Chem. B* **2006**, *110*, 7985−7991.
(56) Wander, A.; Harrison, N. M. Ab-Initio Study of ZnO(1120). *Surf. Sci.* **2000**, *468*, 851−855.
(57) Grimme, S. Semiempirical GGA-Type Density Functional Constructed with a Long-Range Dispersion Correction. *Comput. Chem.* **2006**, *27*, 1787−1799.

https://doi.org/10.1021/acsami.2c10975
ACS Appl. Mater. Interfaces 2022, 14, 41196−41207