

Room-Temperature NH₃ Gas Sensor Based on CuO Nanoplatelets Prepared by Sonochemical Method

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Abstract

To enhance the gas-sensing characteristics of semiconductor metal oxides, meticulous control and manipulation of point defects on gas sensing properties is required. Therefore, to elaborate the influence of metal cation defects on the sensing performance, CuO nanoplatelets with various relative concentrations of oxygen vacancies were prepared at various synthesis temperatures. CuO nanostructures prepared at higher synthesis temperature revealed higher selectivity and sensitivity towards NH₃ due to the institution of large number of reactive sites.

Key words: CuO, nanoplatelets, room temperature, gas sensors, sonochemical.

Introduction

CuO are among the most promising *p*-type semiconductor materials for gas sensing applications, showing rapid and reliable detection of various gases including acetone, ethanol, ammonia and hydrogen sulfide etc. [1]. However, a few cases have been reported where pure CuO materials showed good sensing properties at room temperature [2].

Herein we report the enhanced NH₃ sensing response of CuO nanoplatelets based sensor at room temperature, resulting from small crystallites, high point defects and adsorbed oxygen species on the surface of the sensing layer.

Experimental

In a typical experiment, a 0.5 M Cu(NO₃)₂ solution, was placed in the sonication bath, at 35 °C, and modified by urea before the addition of NaOH, for 25 minutes. The resulting black precipitate, denoted as **A-Urea**, was washed with distilled water, and dried in the oven at 100 °C for 24 hours. The experiment was repeated at different preparation temperatures (45 to 85 °C) for 25 minutes, with products denoted as **B-Urea** to **F-Urea**. The set of experiments were repeated under similar preparation conditions, where the aqueous copper solution remained unmodified and where it was modified by NH₄OH, before the addition of NaOH. The

materials were characterized by XRD, TEM, SEM, BET surface analysis, XPS and PL spectroscopy. Sensors were prepared by depositing a mixture of dispersed CuO powders with ethanol onto interdigitated electrodes, and subsequent drying at 100 °C for 1 h. A standard configuration for resistive sensor measurement, with Pt-interdigitated electrodes and a Pt-resistive-type heater printed onto an alumina substrate were carried out for the gas sensing tests.

Results and Discussion

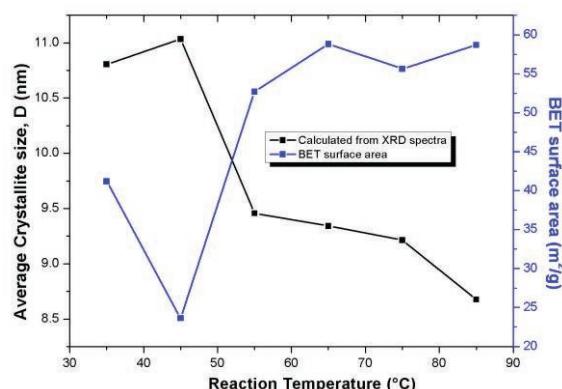


Figure 1: A plot of the average crystallite size and surface area at specific reaction temperatures.

A decrease crystallite size and increase in surface area was observed as the reaction temperature increased, as seen in Figure 1.

The morphology of the as-prepared products was confirmed to be nanoplatelets and the SAED pattern is consistent with the XRD analyses (see Figure 2).

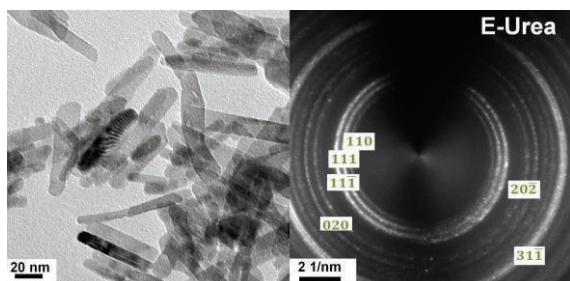


Figure 2: HR-TEM micrograph and SAED pattern of E-Urea.

By observing the gas sensing performance of the as-prepared products to various concentrations of CO, NO₂, NH₃, CH₄ and H₂S gases at room temperature, the effect of the shape and size of the CuO nanomaterials was studied. The **E-Urea**-based sensor showed the highest sensitivity and selectivity to NH₃ gas, whereas **E-NaOH** and **F-NH₄OH**, showed selectivity to NO₂ and CH₄, respectively. The sensitivity observed for **E-Urea** to NH₃ gas and **E-NaOH** to NO₂ gas is higher than previously reported for CuO-based sensors.^[3]

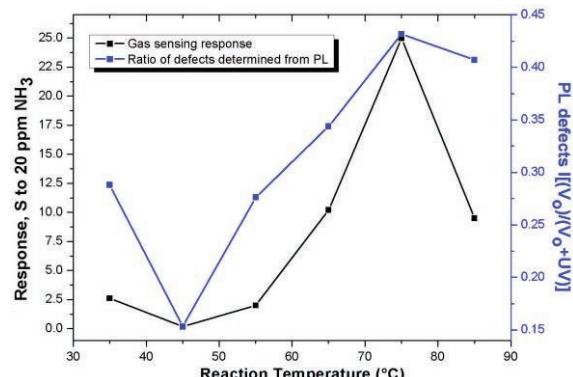


Figure 3: Graph of the room temperature NH₃ gas sensing response and PL defects of CuO products prepared at 35 to 85 °C in the presence of urea, with inserts of HR-TEM and SAED pattern of E-Urea.

The relative concentration of V_O and surface area increased, while the crystallite size decreased for **E-Urea**, leading to enhanced adsorption of oxygen which in turn improved sensing response, as seen in Figure 3. Motaung et al. reported that when the relative concentration of defects decreased the sensing response also decreased.^[4] The simplest mechanism, with the possibility of potential barrier difference for the CuO–CuO homojunctions,^[5] is the due to lattice defects are specified with the Kröger-Vink notation.^[6]

Acknowledgements

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References

- [1] Kim, H.-J. and J.-H. Lee, Highly sensitive and selective gas sensors using p-type oxide semiconductors: Overview, *Sensors and Actuators B: Chemical*, 192, 607-627 (2014); DOI: <http://dx.doi.org/10.1016/j.snb.2013.11.005>
- [2] (a) Li, Z., N. Wang, Z. Lin, J. Wang, W. Liu, K. Sun, Y.Q. Fu, and Z. Wang, Room-Temperature High-Performance H₂S Sensor Based on Porous CuO Nanosheets Prepared by Hydrothermal Method, *ACS Appl Mater Interfaces*, 8, 20962-20968 (2016); DOI: 10.1021/acsmami.6b02893; (b) Bedi, R.K. and I. Singh, Room-Temperature Ammonia Sensor Based on Cationic Surfactant-Assisted Nanocrystalline CuO, *ACS Applied Materials & Interfaces*, 2, 1361-1368 (2010); DOI: 10.1021/am900914h
- [3] (a) Volanti, D.P., A.A. Felix, M.O. Orlandi, G. Whitfield, D.-J. Yang, E. Longo, H.L. Tuller, and J.A. Varela, The Role of Hierarchical Morphologies in the Superior Gas Sensing Performance of CuO-Based Chemiresistors, *Advanced Functional Materials*, 23, 1759-1766 (2013); DOI: 10.1002/adfm.201202332; (b) Lee, J.-S., A. Katoh, J.-H. Kim, and S.S. Kim, Effect of Au nanoparticle size on the gas-sensing performance of p-CuO nanowires, *Sensors and Actuators B: Chemical*, 222, 307-314 (2016); DOI: <http://dx.doi.org/10.1016/j.snb.2015.08.037>; (c) Navale, Y.H., S.T. Navale, M. Galluzzi, F.J. Stadler, A.K. Debnath, N.S. Ramgir, S.C. Gadkari, S.K. Gupta, D.K. Aswal, and V.B. Patil, Rapid synthesis strategy of CuO nanocubes for sensitive and selective detection of NO₂, *Journal of Alloys and Compounds*, 708, 456-463 (2017); DOI: <https://doi.org/10.1016/j.jallcom.2017.03.079>
- [4] Motaung, D.E., I. Kortidis, D. Papadaki, S.S. Nkosi, G.H. Mhlongo, J. Wesley-Smith, G.F. Malgas, B.W. Mwakikunga, E. Coetsee, H.C. Swart, G. Kiriakidis, and S.S. Ray, Defect-induced magnetism in undoped and Mn-doped wide band gap zinc oxide grown by aerosol spray pyrolysis, *Applied Surface Science*, 311, 14-26 (2014); DOI: <http://dx.doi.org/10.1016/j.apsusc.2014.04.183>
- [5] Park, S., S. Kim, G.-J. Sun, W. In Lee, K.K. Kim, and C. Lee, Fabrication and NO₂ gas sensing performance of TeO₂-core/CuO-shell heterostructure nanorod sensors, *Nanoscale Research Letters*, 9, 638 (2014); DOI: 10.1186/1556-276X-9-638
- [6] (a) Yamaguchi, H., T. Ito, and T. Masumi, Large Polarons Photodoped in Pure CuO, *Journal of the Physical Society of Japan*, 67, 1102-1105 (1998); DOI: 10.1143/jpsj.67.1102; (b) Jeong, Y.K. and G.M. Choi, Nonstoichiometry and electrical conduction of CuO, *Journal of Physics and Chemistry of Solids*, 57, 81-84 (1996); DOI: [http://dx.doi.org/10.1016/0022-3697\(95\)00130-1](http://dx.doi.org/10.1016/0022-3697(95)00130-1)