



# Editorial: Nano-Hetero-Structures for Chemical Sensing: Opportunities and Challenges

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## Editorial on the Research Topic

### Nano-Hetero-Structures for Chemical Sensing: Opportunities and Challenges

Developing novel materials with desired microstructure and active surfaces can bring about significant advances in the field of gas sensors. Nanostructured materials such as metal oxides, graphene and its derivatives, and metal sulfides have been established to have great potentials for use in gas sensing due to their high specific surface area, abundant surface active sites, large surface-to-volume ratio, and availability of crystal facets with high surface reactivity. Lately, there is a clear and steady tendency to explore the opportunities available from 1D, 2D, and 3D nanostructured materials for fabrication of high-performance gas sensors for a wide variety of applications. Chemical gas sensors based on nano-hetero-structures provide novel opportunities to design sensors with improved performance in different applications such as agriculture, safety and security, environmental monitoring, and in medical applications to predict, monitor, and diagnose a wide range of diseases. However, there are still many challenges in the field of chemi-resistive gas sensors such as relatively poor sensitivity and selectivity to the low concentration especially at low operating temperature limiting their commercial viability.

This Frontiers in Materials Research Topic aims to present recent advances in the development of nano-hetero-structure-based chemical gas sensors which integrate experimental and theoretical resources and cutting-edge expertise in the fields of thin films, chemistry, physics, materials science, nanotechnology, and biotechnology.

This Research Topic contains a collection of 21 contributions: 1 review article and 20 original articles. Note that the web-page number count is 22, because one article appears twice: one is referred to as “original article” and the other “correction article.” The title of the review article is “Gas Sensing by Microwave Transduction: Review of Progress and Challenges” by Li et al. The original articles include “Improved Gas Selectivity Based on Carbon Modified SnO<sub>2</sub> Nanowires” by Tonezzer et al., “Synthesis, Characterization and Ethanol Sensing Properties of Nanocrystalline  $\alpha$ -MoO<sub>3</sub>” by Sau et al., “A Simple Flow Injection Sensing System for the Real-Time On-Line Determination of Chemical Oxygen Demand Based on 3D Au-NPs/TiO<sub>2</sub> Nanotube Arrays” by Si et al., “Detection of Semi-volatile Plasticizers as a Signature of Early Electrical Fire” by Han et al., “Flame Spray Synthesis of VOPO<sub>4</sub> Polymorphs” by Jodhani et al., “Light-Activated Sub-ppm NO<sub>2</sub> Detection by Hybrid ZnO/QD Nanomaterials vs. Charge Localization in Core-Shell QD” by Chizhov et al., “Metal Decoration and Magnetic Field Effect on the Electrical Breakdown Voltage for ZnO Nanorods Gas Ionization Sensor” by Liu et al., “Three-Dimensional Fe<sub>3</sub>O<sub>4</sub>@Reduced Graphene Oxide Heterojunctions for High-Performance Room-Temperature NO<sub>2</sub> Sensors” by Zou et al., “Improvement of NO<sub>2</sub> Sensing Properties in Pd Functionalized Reduced Graphene Oxides by Electron-Beam Irradiation” by Choi et al., “Silver Nanoparticle-Decorated Tin Oxide Thin Films: Synthesis, Characterization, and Hydrogen Gas Sensing”

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by Mohamedkhair et al., “UV Light Activated SnO<sub>2</sub>/ZnO Nanofibers for Gas Sensing at Room Temperature” by Li et al., “Heating Method Effect on SnO Micro-Disks as NO<sub>2</sub> Gas Sensor” by Masteghin et al., “Highly Sensitive and Selective Ethanol Sensor Based on ZnO Nanorod on SnO<sub>2</sub> Thin Film Fabricated by Spray Pyrolysis” by Tharsika et al., “Sol-gel Synthesis of TiO<sub>2</sub> With p-Type Response to Hydrogen Gas at Elevated Temperature” by Xie et al., “Improving Hydrogen Sensing Performance of TiO<sub>2</sub> Nanotube Arrays by ZnO Modification” by Yu et al., “Improvement in NO<sub>2</sub> Sensing Properties of Semiconductor-Type Gas Sensors by Loading of Au Into Porous In<sub>2</sub>O<sub>3</sub> Powders” by Ueda et al., “Effect of Zinc Oxide Modification by Indium Oxide on Microstructure, Adsorbed Surface Species, and Sensitivity to CO” by Marikutsa et al., “Kinetic Insight on Improved Chemi-Resistive Response of Hydrothermal Synthesized Pt Loaded TiO<sub>2</sub> Nano-rods Toward Vapor Phase Isopropanol” by Das et al., “High-Performance Non-enzymatic Glucose Sensors Based on CoNiCu Alloy Nanotubes Arrays Prepared by Electrodeposition” by Gong et al., and “Enhanced Acetone-Sensing Properties of PEI Thin Film by GO-NH<sub>2</sub> Functional Groups Modification at Room Temperature” by Zhao et al.

The review of Li et al. summarizes the recent progress of microwave gas sensors including the characteristic of the various nanostructured materials, and propagative structures (non-resonator and resonator). Original articles in this Research Topic can be classified according to the target gas into four groups: nitrogen dioxide gas sensors (5 articles), hydrogen gas sensors (3 articles), volatile gas sensors (ethanol, isopropanol, and acetone) (4 articles), and other gas sensors (8 articles).

Multiple types of chemical gas sensors to detect NO<sub>2</sub> gas have been demonstrated in this special issue. The paper by Choi et al. reports the effect of electron-beam irradiation on the NO<sub>2</sub> gas-sensing properties of Pd-functionalized rGO. The so-fabricated sensors are subjected to different irradiation doses (0, 100, and 500 kGy) and their NO<sub>2</sub> gas-sensing performance are measured and compared. Their results show that the response of the fabricated sample increases with increasing the irradiation doses which is attributed by the authors to the formation of high energy defects. Zou et al. report the fabrication of a core-shell 3D Fe<sub>3</sub>O<sub>4</sub>@rGO p-n heterojunctions using self-assembly method for NO<sub>2</sub> gas sensor. The contribution from Chizhov et al. demonstrates that the illumination of ZnO/CdSe, ZnO/CdS@CdSe, and ZnO/ZnSe@CdS nanocomposites fabricated by the immobilization of nanocrystals colloidal quantum dots by a green light ( $\lambda_{\text{max}} = 535 \text{ nm}$ ) changes the population of surface states, which strongly affects the response of the fabricated materials toward NO<sub>2</sub>. Masteghin et al. compare the response of SnO micro-disks toward NO<sub>2</sub> using two different heating methods: (1) self-heating in which the heater circuit deposited on the back side of the interdigitated electrode, and (2) external heating such as a tube furnace. According to their results, the external heating method shows higher sensor response and lower recovery time, which is ascribed by the authors to the lack of a temperature gradient between the SnO micro-disks and the sensor chamber atmosphere. In the study of Ueda et al., porous In<sub>2</sub>O<sub>3</sub> powders loaded with noble metals (Pd, Au, or Pt) fabricated using ultrasonic spray pyrolysis and their

NO<sub>2</sub> sensing properties are examined. The Au nanoparticles loading on the In<sub>2</sub>O<sub>3</sub> show higher response toward NO<sub>2</sub> than that of Pd or Pt loaded In<sub>2</sub>O<sub>3</sub>.

Furthermore, there are four papers focused on H<sub>2</sub> sensing applications. Mohamedkhair et al. report the formation of well-dispersed Ag nanoparticles over the surface of SnO<sub>2</sub> thin films via DC reactive sputtering and a subsequent heat treatment process for detecting low concentration of H<sub>2</sub> at low operating temperature. The so-fabricated sensor shows better response compared to that of pristine and heated SnO<sub>2</sub> films. They propose that the depletion layer caused by Ag, Ag<sub>2</sub>O, and SnO<sub>2</sub> played a vital role in the improvement of H<sub>2</sub> sensing properties. In another paper, Xie et al. discuss H<sub>2</sub> sensing properties of Cr doped TiO<sub>2</sub> nanoparticles fabricated by sol-gel method and investigates the effect of doping concentration (1–10 at.%) on the gas sensing performance. Yu et al. investigate the hydrogen gas sensing behavior based on ZnO decorated onto the surface of TiO<sub>2</sub> nanotubes, where anodization and facile impregnation synthesis methods are employed to fabricate TiO<sub>2</sub> nanotubes and ZnO decorated TiO<sub>2</sub>.

The contribution from Sau et al. reports the fabrication of  $\alpha$ -MoO<sub>3</sub> nanoparticles fabricated via facile sol-gel technique and their gas sensing properties for breath diagnostics applications. Although, the sensor is highly sensitive toward ethanol, it is insensitive toward the main interfering agent of exhaling human breath. The paper by Tharsika et al. reports the preparation of mixed structure of ZnO nanorod on SnO<sub>2</sub> thin film via spray pyrolysis followed by thermal annealing and their gas sensing properties toward ethanol. In the study of Ueda et al., flower like architecture consisting of innumerable numbers of TiO<sub>2</sub> nanorods are fabricated hydrothermally and subsequently modified chemically with platinum nanoparticles. The isopropanol gas sensing properties of the fabricated materials are examined at different temperatures and concentrations of isopropanol. In another paper, Zhao et al. focuses on fabrication of PEI/GO-NH<sub>2</sub> composite film on quartz crystal microbalance using a spraying and drop coating method. Furthermore, the acetone-sensing performance is explored at room temperature. PEI/GO-NH<sub>2</sub> composite film sensor shows an enhancement in acetone sensitivity compared with the pristine PEI film.

Tonezzer et al. demonstrate that carbon modified SnO<sub>2</sub> nanowires fabricated by chemical vapor deposition can be used as a sensing material to detect different gases (carbon monoxide, ammonia, acetone, ethanol, toluene, and hydrogen). Furthermore, machine learning algorithms are employed in their work to distinguish various gases based on the obtained data. Si et al. propose a real-time on-line sensing system combining with 3D Au nanoparticles/TiO<sub>2</sub> nanotube sensing electrode and photoelectrochemical reactor for the determination of chemical oxygen demand. The proposed sensing system displays a linear range from about 2 to more than 3,000 mg/L with low detection limit of 0.18 mg/L. The paper by Han et al. reports the detection of semi-volatile Diethyl phthalate and 2-Ethylhexanol released from over-heated PVC cables for early warning of electrical fire using SnO<sub>2</sub> nanofibers synthesized via electrospinning followed by calcination at 600°C for 3 h. The contribution from Jodhani et al. introduces a novel method

to fabricate different VOPO<sub>4</sub> polymorphs using two different organic compounds as precursors via flame spray pyrolysis. The article by Liu et al. focuses on the fabrication of ZnO nanorod arrays with sharp tips via chemical vapor deposition and use them as the anode for gas ionization sensor. The authors also explore the effects of metal (Ni, Fe, Mn, and Au) decoration and magnetic field on the electrical breakdown voltage. The synthesis of SnO<sub>2</sub>/ZnO nanocomposites composed of SnO<sub>2</sub> nanofiber and ZnO nanorods is reported by Li et al. The so-prepared sensor shows a good response to various concentrations of formaldehyde gas and a good selectivity against many possible interferents such as methanol, ethanol, acetone, toluene, and benzene at room temperature under UV irradiation. Marikutsa et al. focus on nanostructured ZnO modified by 1–7 at.% of indium synthesized via coprecipitation and annealing at 450°C and their CO gas sensing properties are tested at temperatures ranging from room temperature to 450°C. Finally, the article by Gong et al. reports the preparation of CoNiCu alloy nanotube arrays using a template-assisted electrodeposition method. The glucose sensing performance of CoNiCu alloy nanotube arrays exhibits wider linear range, higher sensitivity, high selectivity to glucose, and low operation potential compared to that of single or binary alloy electrodes reported in literature.

While rapid progress in new synthesis routes has made it possible to engineer and optimize specific types of nano-hetero-structures for a given application, the largely trial-and-error approach has failed to effectively understand and model the response behavior of these nano-hetero-structures in a way that could otherwise advance the field toward bottom-up design for

specific applications. It is hoped that this Research Topic on nanostructured chemical gas sensors will be of great interest to the *Frontiers in Materials* readers and will inspire considerable future R&D activities and progress in the field.

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