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Editorial

High-Sensitivity and -Selectivity Gas Sensors with Nanoparticles, Nanostructures, and Thin Films

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Advanced gas sensors fabricated with nanoparticles and thin films of semiconductor metal oxides have been widely used for the detection of toxic, hazardous, and combustible gases and as biomarkers for the safety of human beings, environmental control, and breath analysis. This is certainly due to the simplicity of their synthesis, their low fabrication cost, and their advantageous sensor properties such as high sensitivity (even with small gas concentrations) and long-term stability. Despite these advantages, their limited selectivity and cross-sensitivity to a variety of gases remain challenging issues. Other barriers for the implementation of semiconductor metal oxides are their slow adsorption/desorption kinetics both in response to target analytes and their recovery when these cease. Recent progress in the synthesis of novel nanostructures has revealed that these issues can be overcome by the achievement of superior surface area, the tuning of pore size and pore distribution, the control of morphology, doping (in order to promote the reaction to specific gases), and the formation of metal-oxide-based composites and heterostructures, etc. Accordingly, this Special Issue highlights new achievements in the improvement of gas sensor performance by doping and applying p-n and n-n junctions, and by optimizing synthesis methods for the production of nanoparticles, thin films, nanocomposites, and heterostructures.

Consisting of eight original research articles and two review contributions, this Special Issue has successfully proven the relationship between the characteristics of sensing materials and gas sensor properties using these sensing materials.

Ha et al. [1] fabricated micro-scale self-assembles of ultrathin nickel oxysulfide sensing materials. The work demonstrated fully reversible and long-term stable responses at room temperature to hydrogen in concentrations ranging from 0.25% to 1% without the implementation of external stimuli such as light excitation and voltage biasing. The crystal phase and bandgap analysis indicated a transition from original hexagonal to orthorhombic coordination and the expansion of the bandgap by ~0.15 eV compared to that of pure nickel sulfide.

Qin et al. [2] employed two-step fabrication of semiconductor metal oxides based on γ-Fe_2O_3 and SnO_2 nanoparticles and their composites with RGO to assemble the gas sensor devices. They assessed the sensitivities and response and recovery times of the devices manufactured with these materials for the detection of 100 ppm ethanol, methanol, isopropanol, formaldehyde, CO, and NO gases at different temperatures and analyzed the dynamic gas sensitivity of H_2S in different concentrations. The ternary composite of γ-Fe_2O_3/SnO_2/RGO was identified as an ideal candidate, as it responded to all four tested liquids in the gas phase as well as to H_2S with a response value equal to 162.6. Furthermore, only this ternary composite responded to NO gas with a sensor response value equal to 4.09 in 12 s. On the other hand, the binary composite γ-Fe_2O_3/SnO_2 was the only sensing material that responded to CO with a corresponding sensitivity of 1.59 units in 7 s. These results demonstrate the strong relation of chemistry combinations with selectivity to a certain analyte.

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Through the deposition of Au nanoparticles onto the surface of ZnO nanofilms as the active layers, Wang et al. [3] manufactured gas sensors for isopropanol (IPA) detection and showed that the addition of Au nanoparticles on the surface of ZnO nanofilms significantly improved both the response and the response/recovery speed for the detection of IPA. The gas sensor with an optimum content of Au@ZnO nanofilm exhibited the highest responses at 300 °C to 100 ppm and 1 ppm IPA. In addition to high sensitivity and a very low detecting limit, the sensor also displayed very short response/recovery times of 4/15 s, being much shorter than that of the sensor with a pure ZnO nanofilm. The mechanisms of the performance improvement in the sensors are related to the increase in the amount of adsorbed oxygen species on the surfaces. With the strategy proposed in this work, highly sensitive gas sensors for real-time monitoring of IPA can be developed.

For outdoor pollution monitoring, Raivo Jaaniso and coworkers offered wide-area graphene-based chemo-resistive sensors as miniature and low-power gas sensing elements applicable to a portable electronic nose (Lind et al. [4]). The sensing materials were grown via chemical vapor deposition of graphene on Si/Si_3N_4 substrates with interdigitated electrodes and built-in microheaters. The sensors were obtained by functionalizing graphene individually with an ultrathin oxide coating (CuO-MnO_2, In_2O_3, or Sc_2O_3) via pulsed laser deposition. The sensor tests were carried out over the course of 72 h by exposing them to randomly generated low-concentration cycles of 30 ppb NO_2, 30 ppb O_3, 60 ppb NO_2, 60 ppb O_3, and 30 ppb NO_2 + 30 ppb O_3 in synthetic air (21% O_2) and 50% relative humidity. The sensors with the CuO-MnO_2 coating were shown to dominate the selective response to O_3. With the other sensor materials, comparable sensitivity to NO_2 was measured. Considering various response features (such as amplitude, response rate, and recovery rate) as machine learning tools and using the response amplitudes of two complementary sensors, five gas environments with an accuracy of ~85% were distinguished.

Zappi et al. [5] fabricated sensors that consisted of a thin layer of metal oxide (WO_3 and SnO_2) by depositing them over an interdigitated electrode capable of being heated, chosen to maximize the array response toward acetic acid vapors. The signals obtained from the sensor array were mathematically processed to reduce the background signal due to interferent gases produced during the degradation of ancient cinematographic films.

Haidry et al. [6] fabricated a Pt/Cr-TiO_2/Pt-type sensor structure, demonstrating low NO_2 gas detection limits (below 10 ppm) in operating temperatures below 200 °C with fast response (37 s) and recovery (24 s) times. With respect to the dopant effects on the sensor response, the results proved that Cr-doping of TiO_2 alters the semiconductor behavior from n- to p-type and thus enhances sensor performance for the selective detection of low NO_2 concentrations at reduced operating temperatures. Moreover, this work illustrated that as well as the nature of sensing material, the electrode geometry also defines the sensing performance. This work studied NO_2 surface adsorption kinetics by fitting the obtained sensor response curves with Elovich, inter-particle diffusion, and pseudo first-order and pseudo second-order adsorption models toward 7–170 ppm NO_2 gas at 200 °C. This showed that the NO_2 adsorption kinetics are best described with the pseudo first-order reaction model.

Ruiz et al. [7] fabricated mass and resistive sensors based on reduced graphene oxide (RGO) and investigated the functionalization of RGO by tetra tert-butyl phthalocyanine (PcH_2tBu) possessing a macro-ring and tert-butyl peripheral groups. The aim was to demonstrate the gas sensor responses of the functionalized RGO toward benzene, toluene, and xylene (BTX) vapors. The RGO was obtained via the reduction of graphene oxide (GO) using citrate as a reducing agent, while the functionalization was achieved non-covalently by simply using ultrasonic and heating treatment. The sensor devices based on both QCM (quartz crystal microbalance) and resistive transducers were applied simultaneously to understand the reactivity. Both the GO and the RGO showed less sensitivity to BTX vapors, while the RGO/PcH_2tBu presented enhanced sensor responses. These results exhibited that the p-network plays a very important role in targeting BTX vapors. Through the resistive response analysis, it was stated that the RGO is a p-type semiconductor and that the interaction is governed by charge transfer. The QCM response profiles displayed

that the sensor response differs with the type of BTXs. While the weakest sensitivity and reactivity in the higher concentration range (>600 ppm) were obtained with benzene, the sensor response was linear for toluene and xylene in the range of 100–600 ppm.

Jaballah et al. [8] investigated the effect of Al- and Mg-doping on the gas sensing capability of ZnO-based sensors. ZnO, $Mg_{1\%}$-doped ZnO, $Al_{5\%}$-doped ZnO, and ($Al_{5\%}$, $Mg_{1\%}$)-co-doped ZnO nanoparticles (NPs) were synthesized using a modified sol–gel method. All samples had the hexagonal crystalline structure. Morphological characterizations confirmed the nanometric sizes of the NPs (27–57 nm). Gas sensing tests demonstrated that Al and Mg significantly influenced the sensing performances toward H_2 and CO gas, respectively. The sensor manufactured with Al- and Mg-co-doped ZnO NPs exhibited high sensitivity and low detection limits to H_2 (<2 ppm) and CO (<1 ppm), with a response around 70 (at 250 °C) toward 2000 ppm H_2 and 2 (at 250 °C) toward CO.

The review articles of this Special Issue were firstly about magneto-electric hydrogen sensors. Maksymov and Kostylev [9] presented the physical foundations of magneto-electronic hydrogen sensors and critically gave an overview of their advantages and disadvantages for applications in vital safety areas such as hydrogen-powered cars and hydrogen fueling stations, as well as hydrogen concentration meters, including those operating directly inside hydrogen fuel cells. Secondly, the review articles were also about H_2S detection using Cu_xO nanostructures whereby Navale et al. [10] thoroughly discussed the various morphologies of Cu_xO in the pristine form, composites of Cu_xO with other materials, and the decoration/doping of noble metals on Cu_xO nanostructures, for the reliable detection of H_2S gas. Maksymov and Kostylev aimed to facilitate the translation of research results into policy and practice, while Navale et al. emphasized the detection mechanism of Cu_xO-based gas sensors toward H_2S.

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