Gas sensing with ultrafine and micro-scale ZnO powders: shape matters

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In this study, we investigate the effect of crystal habit (shape) and surface termination of exposed crystal facets on the gas sensing behaviors of ultrafine ZnO grains. Morphology-controlled and size-controlled bottom-up syntheses were used to make ZnO particles with a well-defined hexagonal pyramid shape. This type of crystal habit exhibits facets that are all polar planes of ZnO, whereas the more commonly observed rod-like or plate-like habits for ZnO expose predominantly non-polar planes. The aim of this work is to establish the relationship between crystal habit, surface polarity, and gas-surface reactivity for ZnO crystal when interacting with target gases that are relevant for fugitive and flare emissions in petrochemical industries.

Metal oxide micro-scale and nano-scale particles have been frequently utilized in electrical gas sensor applications because they show high sensitivities to many gases as well as low fabrication costs. Gas detection is achieved by measuring a change in conductance or capacitance upon exposure to certain target gases. The high sensitivity of these fine particles is often attributed to the large effective surface area due to small particle sizes. However, recent efforts show that changes in particle morphology (crystal habit) can dramatically alter electrical characteristics and reactivity when interacting with foreign gaseous species [1]. The links between morphology, surface termination, electrical response are complex and not yet well understood at a predictive level. Thus, experimental studies that build connections between particle morphology, surface reactivity and bulk electrical properties can provide crucial insights to develop robust strategies to improve the sensitivity and selectivity of metal-oxide gas sensors.

In this study, ZnO hexagonal pyramids were made by a molten salt assisted synthesis [2], in which a zinc acetate precursor is heated at 400 °C in a $LiNO_3$ salt melt for 30 minutes. A representative example of this pyramidal crystal habit is shown in Figure 1a. The formation of this shape is attributed to the presence of excess Li^+ that inhibits the growth rate of the polar facets. For comparison, ZnO rods (Figure 1b) were prepared by a different, two-step method. First, polycrystalline ZnO polycrystalline with irregular shapes were synthesized by a solid state metathesis reaction, mixing $ZnCl_2$ and NaOH powders in 1:2 molar ratios at room temperature. Rod-shaped crystallites were obtained after annealing this product at 400 °C for 30 minutes.

The gas sensing responses of these and other ZnO crystal shapes have been examined when exposed to volatile organic compounds such as ethanol vapor. Enhanced gas desorption rates occur for pyramids relative to rods, based on our measurements of capacitance changes (Figure 1c). This finding is consistent with the higher reactivity of polar faces of ZnO[1], and persists even when results are normalized for surface area effects. We also describe how the AC and DC electrical properties, through impedance spectroscopic data, provide further insights.

Acknowledgments

This work was supported by NSERC (Canada), the Canada Foundation for Innovation, and Petroleum Research Atlantic Canada.

References

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Figures:

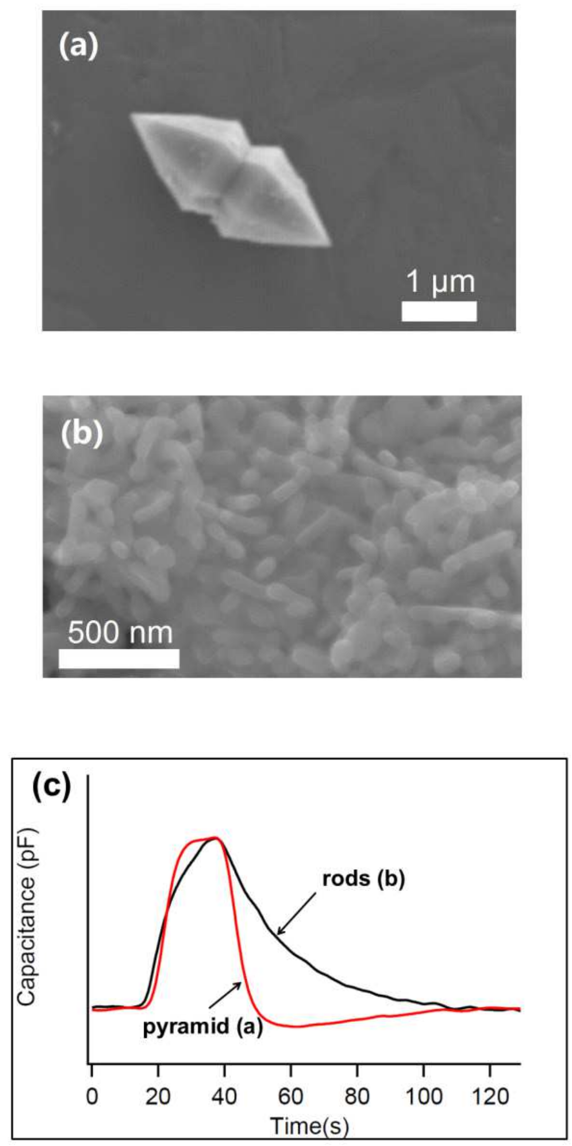

Figure 1: Scanning electron micrographs of ZnO in the form of (a) an hexagonal bipyramid and (b) rods. (c) Representative gas sensing responses of synthetic ZnO particles when exposed to 5000 ppm ethanol vapor at room temperature. Faster signal recovery occurs for ZnO pyramids, indicating a higher gas desorption rate.