

1. Designing Selectivity: A Chemists Perspective

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Abstract (style "IMCS2018_Headline"):

A discussion of how materials design considerations, from a chemists perspective, can be used to design gas sensor materials with exquisite sensitivity towards particular (classes of) analytes.

Key words: metal oxide, heterojunction, selectivity, materials design

Titles and Headings

In a particulate-based sensor (as opposed to, for instance, a single nanowire-based sensor) charge transport is thought to be controlled by Schottky barriers at grain junctions formed by electron transfer from bulk donor states to surface acceptor states, commonly ascribed to the presence of chemisorbed oxygen species. There are therefore a number of ways one could consider trying to *design* selectivity in such a metal oxide-based gas sensor device based on nano-sized particles. For instance synthesizing metal oxide nanocrystals with specific exposed (high-index) crystal planes [1]. Alternatively, if the particle size is sufficiently small, i.e. on the nanoscale, and the bulk donor density is sufficiently low, i.e. an n-type material modified with acceptor dopants, the sensing response mediated *via* the surface acceptors (presumed to be chemisorbed oxygen) can be minimized and hence sensitivity based on specific analyte/surface site reactions may be observed [2]. Neither of these methods of imparting selectivity in gas sensitive materials have been extensively exploited in literature, possibly due to the difficulty of controlling the synthesis (i.e. controlling the exposed facets or controlling the dopant level in the required range) to produce the desired materials.

Work in my group focuses on development of high performance gas sensing materials. We have been particularly interested in the opportunities for designing selectivity by using heterojunctions, synthesized at the nanoscale. Perhaps the most frequently reported heterojunction is that formed with noble metal particles. Noble metals may enhance selectivity

by various mechanisms, including 'spill-over' (i.e. the enrichment of the surface of the sensing body by active sensing species) and also by modification of the electronic properties of the sensing body. Certainly when we decorate nanorods of tungsten oxide with small (< 10 nm) gold or platinum particles we observe significant changes in sensor response, e.g. a ten-fold improvement in sensitivity towards H₂ for Pt-decorated WO₃ (Figure 1). However Au-decoration has little effect and the origin of the improvement by Pt-decoration may not be immediately obvious. For instance we see changes in baseline resistance (Figure 1), i.e. electronic properties, consistent with electron transfer from the sensing body (tungsten oxide) to the decorating particles, e.g. an increase in resistance for Pt particles (the Pt work function is larger than that for WO₃). For Au particles a decrease in resistance is observed (the Au work function is smaller than that for WO₃). Therefore there is clearly a difference in bulk electronic properties for decoration of WO₃ with Pt or with Au, and this could give rise to the differentiation of response *via* a similar mechanism to that described previously for bulk doping of small particles. However, we also observe changes in response time towards analytes (Figure 1), although perhaps against expectation these are not always faster than for the non-functionalised material, which is perhaps an indication that presence of the noble metal particles have altered the 'receptor' part of the sensor function. Whilst it is certainly possible to apply chemistry principles to guide the direction of materials design for highly selective materials, for instance adsorption

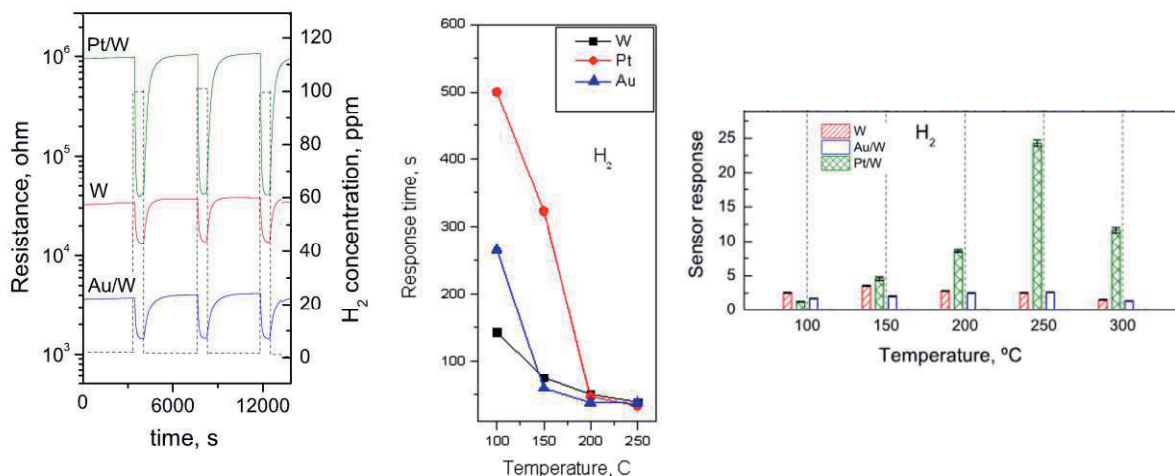


Fig. 1. Baseline resistance, response time and sensor response towards H₂ of tungsten oxide nanorods either non-functionalized or decorated with Pt- or Au- nanoparticles.

strengths benzene and toluene differ significantly over metal surfaces and hence use of different metal nanoparticles potential offers a route to differentiation of these analytes.

An alternative approach for a heterojunction material is to adopt the so-called Fermi level control, or catalytic spill-over approach. An example of this has been described by Hernandez-Ramirez et al (REF), who used a heterojunction formed between CuO (decorating particle) and SnO₂ (bulk sensing body). In this structure a p-n junction is initially formed, but under the action of H₂S, p-type CuO is converted to 'metallic' CuS and a metal-semiconductor interface is formed, causing a net effect on the electrical properties of the sensor orders of magnitude higher than that caused by standard redox surface reactions. This approach now provides a readily understandable route to *designing* sensor materials with high selectivity towards particular (classes of) analytes. In work we carried out with Llobet (REF) we took this approach and applied it to the design of a highly selective H₂ sensor. In our design we decorated tungsten oxide nanorods with Pd nanoparticles. The oxidation of the Pd nanoparticles at the normal operating temperature of the sensors causes oxidation of the Pd to PdO (in ambient air) forming a p-n junction. Exposure of the PdO/WO₃ sensor to H₂ causes reduction of the PdO to metallic Pd (PdH_x), again forming a metal-semiconductor junction and giving orders of magnitude increased sensitivity towards H₂ than found in the bulk WO₃ sensing body alone (Figure 2).

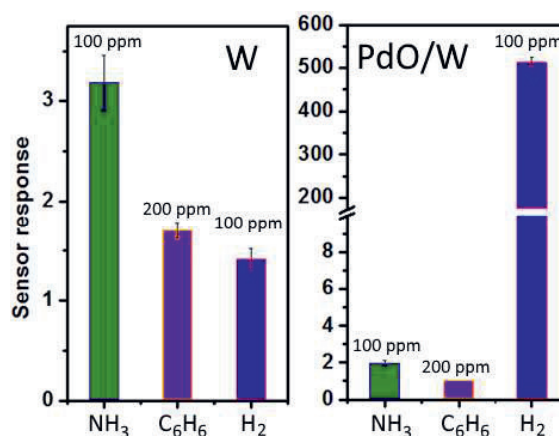


Fig. 2. Graph of sensor response towards NH₃, C₆H₆ and H₂ or tungsten oxide nanorods either non-functionalized or decorated with PdO nanoparticles.

In my view this approach offers the best opportunity for designing highly selective gas sensitive materials. The key is understanding the potential chemistry taking place and identifying decorating materials that produce a significant change in electronic properties on exposure to a particular analyte.

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