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# Ultrasensitive Chemiresistors Based on Electrospun $TiO_2$ Nanofibers

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**ABSTRACT**

**Nanostructured semiconducting metal oxides and particularly single nanowire devices offer exceptional gas sensitivity but at the expense of statistical variations and excessive noise levels. In this study $TiO_2$/poly(vinyl acetate) composite nanofiber mats were directly electrospun onto interdigitated Pt electrode arrays, hot pressed at 120 °C, and calcined at 450 °C. This resulted in a novel multiple nanowire network composed of sheaths of 200–500 nm diameter cores filled with readily gas accessible ∼10 nm thick single-crystal anatase fibrils. $TiO_2$ nanofiber sensors tested for $NO_2$, in dry air, exhibited exceptional sensitivity showing with, for example, a 833% increase in sensor resistance when exposed to 500 ppb $NO_2$ at 300 °C, consistent with a detection limit estimated to be well below 1 ppb. Unusual response patterns were observed at high $NO_2$ concentrations (>12.5 ppm), consistent with n to p inversion of the surface-trap limited conduction facilitated by the high surface-to-volume ratio of this material.**

Increasing demands for ever more sensitive chemical sensors for air-quality control,[1] environmental monitoring,[2] healthcare,[3] defense and security,[4] and other applications have led to an upsurge of interest in nanostructured semiconducting metal oxides such as $SnO_2$, $TiO_2$, ZnO, $In_2O_3$, and $WO_3$. These materials and other wide band gap metal oxides are known for their ability to detect trace concentrations, typically in the parts per million (ppm) levels and above,[5] of various gases in air via charge-transfer interactions between the sensor and chemisorbed species that modify the sensor's resistance.[6] With the need for ever broader sensor deployment, these so-called chemiresistors provide many attractive features including simple device structure and operation, inherent stability, and compatibility with microfabrication processes. Cross-sensitivity to interfering species, a common problem for nearly all sensor types, can be circumvented by use of arrays of different chemiresistors yielding characteristic response patterns ("fingerprints") to different species enabling multianalyte gas analysis by means of pattern recognition and classification methods (so-called electronic nose).[7,8] Recent efforts have been focused on the development of nanostructured sensors[9−11] to achieve increased surface-to-volume ratios and reduced cross sections, offering more effective gas modulation of device resistance.[12−14] Most efforts are based on conventional three-dimensional (3D) and two-dimensional (2D) material architectures comprising thick (∼1−20 $\mu$m) mesoporous layers or thin films (∼100−200 nm), respectively.

Inspired by the exceptional sensing properties of carbon nanotubes[15,16] and silicon nanowires,[17−19] new types of architectures were recently introduced comprising one-dimensional (1D) and quasi-1D metal oxide nanostructures.[20] These have included networks of $SnO_2$ nanobelts[21,22] and ZnO nanowires[23] synthesized by thermal evaporation of the respective metal oxide powders,[24] quasi-ordered arrays of $TiO_2$ nanotubes produced by anodization,[25] and individual $SnO_2$ and $In_2O_3$ nanowires carefully assembled by combining top-down and bottom-up nanofabrication strategies.[26−28] Recent advances in this field are reviewed by Kolmakov and Moskovits.[20] 1D sensing architectures provide unparalleled advantages in terms of facilitating fast mass transfer of the analyte molecules to and from the interaction region as well as requiring charge carriers to traverse any barriers introduced by molecular recognition events along the entire wire. Under favorable conditions, this can lead to significant gain in the sensing signal in a manner similar to chemical sensors based on conducting polymer chains (so-called molecular wires).[29] Furthermore, in contrast to films, the interfacial area between the active sensing region of the nanofibers and the underlying substrate is greatly reduced. This substantially reduces stability problems connected with chemical interactions between substrate and sensor material as well as interferences

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