

ZnO Nanostructures for Gas Sensing Applications: From Tetrapods-Based Chemoresistive Devices to Carbon Fiber Integration [†]

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1. Introduction

Zinc oxide (ZnO) nanostructures can be grown in different morphologies by means of a wide range of techniques. Although the strong evidence of their gas sensing capabilities has been reported in several papers, not all of them are suitable for a large-scale or industrial scale production of gas sensor devices.

Among the several ZnO nanostructures that have been grown so far at IMEM-CNR Institute, we focused our attention on tetrapods (TPs), because a vapour phase growth process that can produce grams of these nanostructures have been designed and optimized in our laboratories. This quantity of nanostructures, produced in a small lab-scale reactor, is enough to prepare several thousands of gas sensing devices. Moreover, the produced ZnO-TPs are free-standing and not constrained to a growth substrate, and can be easily suspended in a liquid media.

The highly-porous entangled network of ZnO-TPs, which can be obtained by direct deposition on sensor substrate, demonstrated to efficiently work as chemoresistor, while its sensing properties (sensitivity, selectivity, ...) can be tuned or modified through the functionalization of TPs surface with other materials (noble metals, inorganic semiconductor nanoparticles, organic semiconductor layers).

At the same time, ZnO nanostructures and their multifunctional properties can be used to functionalize the surface of other materials and, eventually, add to them sensing capabilities. As a meaningful example, we can illustrate the adding of ZnO nanorods (ZnO-NRs) to the surface of carbon fibers with a wet chemical process that is easily scalable to a larger scale.

It has been recently demonstrated that two crossing ZnO-functionalized carbon fibers can be used to sense and transduce a piezoelectric signal or UV light, as well as a chemoresistive information.

2. Gas Sensors Based on ZnO Tetrapods

ZnO-TPs are obtained by evaporating cheap metallic zinc powders in a controlled stream of inert gas and oxygen. At the end of the process, a large veil of electrostatically bonded nanostructures can be easily collected from the growth reactor. By suspending these nanostructures in an alcoholic solution, it is possible then to deposit the nanostructures on different substrates with contacts for collecting the electric signal and heaters to control the sensing element temperature. Proper methods have been optimized and successfully tested for both simple alumina substrates and micromachined MEMS micro-membrane substrates. Dynamic responses are reported both for not-functionalized ZnO-TPs and ZnO-TPs functionalized with cadmium sulphide (CdS) and titanyl-phthalocyanine (TiO-PC) to show and compare the original and modified sensing properties of these nanostructures.

3. Sensing by ZnO Nanorods Integrated in Carbon Fibers

Carbon fibers have been functionalized with a brush-like layer of ZnO-NRs, aligned perpendicularly to the fiber surface. The functionalization has been obtained thanks to a two-steps process. The first one is for the deposition of a ZnO seed layer by Silar-technique. The second one is for the growth of 1–2 μm long NRs by chemical bath deposition, dipping them in a closed reactor containing equimolar zinc acetate and hexamethylenetetramine aqueous solution (20 mM) at 90 °C for 4 h, during which NWs grew.

To demonstrate the working principle, two 4 cm long carbon fibers, functionalized with ZnO-NWs only in their central part, were placed in a crossing configuration, touching each other in a single point in the middle. Electrically conductive carbon fibers were used to transduce the signal from that point, while ZnO-NRs were self-heated by Joule effect thanks to the flowing electrical current. A very fast response and high response is observed towards the testing volatile organic (ethanol). The peculiar response dynamic is a combination of resistance variation and temperature variation, because of the different current flowing through the intersection point.

These results can be then considered as the basis to turn a carbon fiber texture into a “smart” array of different micron-scale sensors.



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