Individual hollow and mesoporous aero-graphitic microtube based devices for gas sensing applications

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In this work, individual hollow and mesoporous graphitic microtubes were integrated into electronic devices using a FIB/SEM system and were investigated as gas and vapor sensors by applying different bias voltages (in the range of 10 mV–1 V). By increasing the bias voltage, a slight current enhancement is observed, which is mainly attributed to the self-heating effect. A different behavior of ammonia NH_3 vapor sensing by increasing the applied bias voltage for hollow and mesoporous microtubes with diameters down to 300 nm is reported. In the case of the hollow microtube, an increase in the response was observed, while a reverse effect has been noticed for the mesoporous microtube. It might be explained on the basis of the higher specific surface area (SSA) of the mesoporous microtube compared to the hollow one. Thus, at room temperature when the surface chemical reaction rate (k) prevails on the gas diffusion rate (D_K) the structures with a larger SSA possess a higher response. By increasing the bias voltage, i.e., the overall temperature of the structure, D_K becomes a limiting step in the gas response. Therefore, at higher bias voltages the larger pores will facilitate an enhanced gas diffusion, i.e., a higher gas response. The present study demonstrates the importance of the material porosity towards gas sensing applications. *Published by AIP Publishing.* [http://dx.doi.org/10.1063/1.4989841]

The monitoring of different gaseous and biological species in the atmosphere is of great interest due to intensified industrial emissions and environmental pollution.[1] It has become a severe problem in heavily polluted cities worldwide, such as Beijing.[2] For such purposes, the different bottom-up and top-down methods were combined over the last decade for fabrication of sensing devices based on the individual nano- or microstructures. Such devices are known to be highly sensitive with respect to different gaseous and biological species due to their extremely high surface-to-volume ratio.[3–5] In combination with their ultra-low power consumption, they open new possibilities for the fabrication of miniaturized and portable monitoring devices which can adequately control the air-quality. The most individual used structures for sensing applications are Si nanowires (NWs),[5] carbon nanotubes (CNTs),[3,4] SnO_2 NWs and nanobelts (NBs),[6] ZnO NWs,[7] CuO NWs,[8] and polymer NWs.[9] Among them, the carbon based nanostructured materials have received a great deal of attention for applications in gas sensing due to their excellent sensitivity at room temperature.[10,11] However, less focus has been given to the devices based on individual microtubular structures, especially towards gas sensing applications. Zhang *et al.* reported the gas sensing properties of single porous SnO_2 microtubes demonstrating higher sensing performances compared to non-porous and the filled microtubes.[12] Huang *et al.* fabricated devices on single 3,4,9,10-perylenetetracarboxylic dianhydride (PTCDA) microtubes with different diameters for detection of hydrazine vapors with a concentration down to 5 ppm.[13] Vervacke *et al.* demonstrated the design, realization, and gas sensing properties of rolled-up hybrid nanomembranes with a diameter of $\approx 15\,\mu m$.[14] These results suggested that for sensing applications the microtubular structures may be expected to result in a faster response and regeneration times at room temperature.[12] Moreover, the individual micrometric structures are highly attractive for combined top-down and bottom-up processes because they can be easily handled for further integration on the chip and therefore can reduce the cost of devices. Additionally, the more precise control of parameters can be achieved which determines the higher reproducibility and/or yield of the devices. However, the loss in performances compared to nanoscopic structures is unavoidable. Thus, additional studies are very necessary, especially the investigation of internal porosity of carbon based microtubular structures on gas sensing properties, which has not been reported so far.

In this context, the recently synthesized rolled-up three-dimensional (3-D) framework material with a nanoscale wall thickness, called Aerographite, demonstrated interesting gas sensing properties tunable by the applied bias voltage.[11] The material is composed of hollow microtubular graphitic structures with a nanoscopic wall thickness. In this work, two types of such individual microtubular graphitic structures were integrated into devices using the FIB/SEM system for the further gas sensing investigations. The first type of structure presents the hollow graphitic microtubes with a diameter

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