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Carbon nanotube-based ethanol sensors

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Abstract

Sensors containing metal–carbon nanotube (CNT) hybrid materials as the active sensing layer were demonstrated for ethanol vapor detection at room temperature. The metal–CNT hybrid materials were synthesized by infiltrating single wall carbon nanotubes (SWNTs) with the transition metals Ti, Mn, Fe, Co, Ni, Pd or Pt. Each sensor was prepared by drop-casting dilute dispersions of a metal–CNT hybrid onto quartz substrate electrodes and the impedimetric responses to varying ethanol concentration were recorded. Upon exposure to ethanol vapor, the ac impedance (Z') of the sensors was found to decrease to different extents. The sensor containing pristine CNT material was virtually non-responsive at low ethanol concentrations ($<$50 ppm). In contrast, all metal–CNT hybrid sensors showed extremely high sensitivity to trace ethanol levels with 100-fold or more gains in sensitivity relative to the starting SWNT sensor. All hybrid sensors, with the exception of Ni filled CNT, exhibited significantly larger sensor responses to ethanol vapor up to 250 ppm compared to the starting SWNT sensor.

S Supplementary data are available from stacks.iop.org/Nano/20/235502

1. Introduction

Carbon nanotubes (CNTs), due to their attractive and unique chemical and physical properties, are excellent materials for gas/vapor sensing [1–9]. Ironically, one main disadvantage towards the successful use of these materials in commercial sensors is the very fact of this high response to a spectrum of gases and organic vapors, i.e. the relatively poor selectivity offered by pristine CNTs in discriminating among gases. Consequently, though the use of CNTs for gas sensing holds much promise, several key issues remain to be resolved, such as inhomogeneity (mixture of metallic and semiconducting nanotubes) of CNT samples, and selectivity of sensing. These factors will ultimately determine the usefulness of CNT-based devices in practical sensing applications.

With this in mind, we recently reported on a strategy to tune the chemical properties (electronic density of states (DOS), chemical potential) of pristine CNTs for gas/vapor sensing [10]. Our intrinsic approach involved infiltrating commercial arc discharge single wall carbon nanotubes (SWNTs) with various transition metals (Ti, Mn, Fe, Co, Ni, Pd, and Pt) to create metal–CNT hybrids (referred to as M@CNT where M is metal and @ indicates infiltrated inside CNT). This intrinsic modification to the *interior* of the CNT means that virtually all surface C atoms are preserved and thus available for gaseous molecular adsorption. This is in direct contrast to extrinsic schemes involving introduction of foreign groups, functionalities or materials onto the CNT surface which naturally reduce the available surface area for gaseous adsorption. Analytical characterization techniques of high-resolution TEM, XRD, SEM/EDX and Raman spectroscopy provided evidence of metal predominantly infiltrating SWNT bundles as opposed to coating the CNT outer surface. Sensors fabricated from these metal–CNT hybrids showed dramatically different resistive and capacitive responses to NO_2 gas [10]. All hybrid sensors showed enhanced capacitive responses over the pristine SWNT sensor. More differentiation in resistive response was observed among the hybrid sensors, with SWNT infiltrated with Ti, Mn, Fe, Co and Ni showing enhanced sensitivity to NO_2 detection while CNT material containing TiH_x, Pd and Pt exhibited reduced sensitivity compared to the starting SWNT sensor at room temperature.

The detection and sensing of ethanol vapor is important for a variety of purposes including ethanol production, industrial chemical processing, fuel processing and use, societal applications, and physiological research on alcoholism. A large number of commercial ethanol measurement systems are available for several of these applications, but in general, these systems are designed exclusively for vapor

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