Fluorinated and chlorinated double-walled carbon nanotubes for gas sensing

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Carbon nanotubes (CNTs), possessing a high surface area and electrical conductivity, are very sensitive to surface adsorbates. This make them attractive for development of gas sensors. Detection of NO_2 and H_2O molecules is important for industrial purposes and ordinary people environment. Double-walled CNTs (DWCNTs) consisted of two cylindrical tubes have been shown to be a good sensor material, where the inner nanotube transfer a signal from the outer nanotube electrostatically interacting with adsorbates. In this work, we demonstrate that covalent functionalization of DWCNTs by fluorine or chlorine allows substantially increase performance of the DWCNT-based sensor.

DWCNTs, purified from the synthesis by-products, have been fluorinated using a mixture of BrF_3 and Br_2 at room temperature. Chlorination of DWCNTs and holey-DWCNTs (produced by sample boiling in concentrated sulfuric acid) has been carried out using CCl_4 vapor at 650°C. The films of initial DWCNTs and halogenated DWCNTS weredeposited on SiO_2/Si substrates, which were used for device fabrication. Two silver electrodes of a width 5 mm were formed by a silver glue on the top of the film at a distance of ~ 1 mm from each other. The device was mounted in a test chamber and investigation of gas sensor properties was carried out under nearly practical conditions (atmospheric pressure and room temperature) against NO_2 or H_2O diluted by argon. A change in electrical resistance of the device was monitored when the sensor was periodically exposed to an analyte gas and pure Ar.

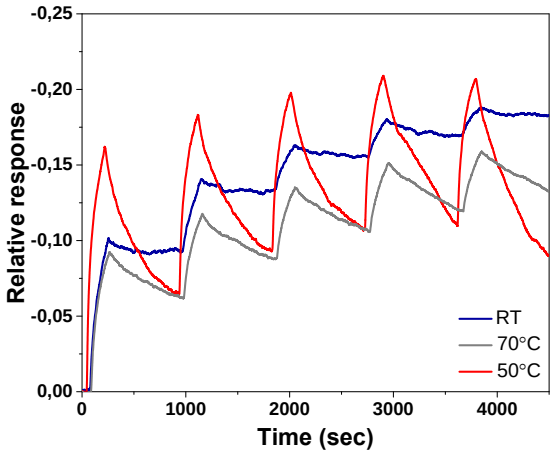

Fig. 1. Cycle-by-cycle response of fluorinated DWCNTs against 100 ppm of NO_2, measured at room temperature (RT) and enhanced temperatures.

Covalent attachment of chlorine to the DWCNTs allowed preparing more uniform and thin film for gas sensing as compared to non-modified DWCNTs. This provided a higher change in electrical resistivity of the chlorinated holey-DWCNT sample under exposure to H_2O vapor. Moreover, we showed that this sensor fully recovers after the heating at 115°C in argon flow. A comparative study of initial DWCNTs and fluorinated DWCNTs against to 100 ppm of NO_2 detected a higher relative response for the former sensor and better recovery of the latter sensor. The response and recovery of the fluorinated DWCNTs increased with a rise of the sensor temperature (see Fig.1).

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