

Decorated single- and multi-walled carbon nanotubes aiming H₂S sensing

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ABSTRACT

A novel hybrid material comprised of single- or multi-walled carbon nanotubes decorated with cerium-praseodymium mixed oxide nanoparticles was synthesized. The intrinsic redox characteristics of CePr-oxides make this chemical system promising for applications in gas sensing and catalysis. In this work, carbon nanotubes were first pre-oxidized followed by the in situ growth of oxide nanoparticles on the nanotube walls. Hydrolysis reactions of the metal precursors under appropriate conditions led to the formation of crystalline mixed oxide nanoparticles on the nanotube walls. Composition and structural characteristics of particles were analyzed using electron microscopy and EELS techniques. Decorated carbon nanotubes were explored for gas sensing in a chemi-resistor configuration, and preliminary results show high potential of this new hybrid material for sensing applications.

Keywords: carbon nanotubes, nanoparticles, metal oxide, gas sensing devices

1 INTRODUCTION

Carbon nanotubes (CNTs) have received great attention due to unique combination of interesting electrical, thermal, mechanical, and chemical properties. The gas sensing capability of CNTs was also demonstrated by adsorption of electron-withdrawing or donating molecules on the nanotubes surface resulting in a charge transfer between CNTs and gas molecules that can be detected [1,2]. However, CNTs do not show appreciable sensitivity to many gases, e.g. hydrogen and carbon monoxide [3,4]. In order to promote or increase sensitivity and selectivity in gas sensing, CNTs surface can be modified using various chemical or physical approaches aiming the introduction of functional groups or active species.

Nanostructured metal particles, metal oxides, and especially mixed oxides grown or deposited on nanotube walls are promising candidates for gas sensing applications [5]. Cerium-praseodymium mixed oxide is in particular an interesting material presenting electrical properties that strongly depend on the oxide composition. The existence of two different valence states for both metals, Ce⁺³/Ce⁺⁴ and Pr⁺³/Pr⁺⁴, enables the synthesis of a number of different CePr-oxides, some of them demonstrating mixed valence

[6]. Preparation method influences the characteristics of CePr-oxides making possible to obtain different structures and stoichiometries. The ability to exchange the oxide lattice oxygen with the environment, called oxygen storage capacity (OSC), is critical for technological applications. This ability is related to the non-stoichiometry and changeable Ce and Pr valence states. Introduction of Pr in the cerium oxide structure is important for creation of oxygen vacancies, providing high levels of non-stoichiometry and enhancing the oxygen ions mobility through the oxide lattice and thus improving the system's OSC. Praseodymium oxide presents high electron mobility due to hopping mechanism between the mixed valence states of Pr, which makes it very sensitive to chemical species from the environment and, consequently, a suitable material for sensor devices. Praseodymium oxide also has the highest oxygen ion mobility compared to the others lanthanide oxides due to the fast changes in the praseodymium oxidation state and, thus changes in the number of oxygen vacancies. According to the literature, improved characteristics have been observed for cerium-praseodymium mixed oxides in catalysis and sensing applications [6-8]. In a nanostructured form, CePr mixed oxides may demonstrate improved performance in different technological applications due to a high area-volume ratio and a high density of interfaces with significant variations in transport properties [6-8].

Different experimental procedures have been reported to obtain thin film and bulk CePr mixed oxide materials, including chemical co-precipitation followed by calcinations, impregnation of a substrate using solutions of the metal precursors followed by calcinations, and pulsed laser deposition. In this work, we present for the first time the preparation of cerium-praseodymium oxide nanoparticles grown directly on single- and multi-walled carbon nanotubes (SWCNTs and MWCNTs, respectively). Herein, we describe the preparation method to obtain SWCNTs/CePr-oxide nanoparticles and MWCNTs/CePr-oxide nanoparticles hybrid materials which shows promising gas sensitivity due to the favorable combination of carbon nanotubes and oxide nanoparticles properties. Preliminary experiments showed the possibility of H₂S detection with high sensitivity using this hybrid material in a simple chemi-resistor configuration.

2 EXPERIMENTAL

MWCNTs were purchased from Iljin Nanotech Co., Ltd. (Seoul, Korea) and Elicarb P925 SWCNTs were purchased from Thomas Swan & Co., Ltd. (County Durham, UK). The nanotubes were first heated for 2 h under air at 330 °C to reduce the content of amorphous carbonaceous material and then refluxed in nitric acid for 12 h. The acid-treated nanotubes were washed with distilled water until pH 7 and dried at 80 °C for 6 h.

Cerium-praseodymium mixed oxide nanoparticles were grown directly on the surface of acid-treated nanotubes by using praseodymium and cerium carbonates or nitrates as precursors in a hydrolysis reaction, under controlled pH value, assisted by ultrasonic bath. In a typical synthesis, appropriate molar ratios of Ce and Pr precursors were added to a suspension of 1 mg acid treated MWCNTs in 40 mL of distilled water, followed by 10 minutes of ultrasonication to achieve maximum dispersion. The pH value of the solution was adjusted to 3 by using HCl. The mixture was stirred for 60 minutes and the precipitate was filtered and dried at 80 °C for 6 h.

The samples were characterized by thermogravimetric analysis (TGA) carried out using a TA equipment, model SDT Q600, over the 25-1000 °C temperature range with a heating rate of 10 °C min⁻¹ under nitrogen flow of 100 mL min⁻¹. Attenuated Total Reflection - Fourier Transform Infrared (ATR-FTIR) spectra were recorded with IlluminatIR equipment, Smiths Detection. Scanning electron microscopy (SEM) images were obtained using Nova™ NanoLab 200 DualBeam™ system, FEI Co; high-resolution transmission electron microscopy (HRTEM) images were obtained using HR-TEM JEM-3010 URP, Jeol. Electron energy loss spectroscopy (EELS) was performed using 80 keV Carl Zeiss CEM-902 transmission electron microscope (TEM) equipped with a Castaing-Henry-Ottensmeyer filter spectrometer within the TEM column.

Decorated nanotubes were used for fabrication of test devices using thermally oxidized silicon substrates. Initially, they were suspended in aqueous or dimethylformamide solutions using ultrasonication and centrifuged at 8,000 rpm to remove agglomerated material from the solution. Further, decorated nanotubes were deposited between metal electrodes by ac dielectrophoresis (DEF) technique. A drop of the nanotube solution was placed over the pairs of metal electrodes and then ac field (100 kHz, peak to peak voltage of 3 V) was applied to the electrodes for 1 minute; after this the drop was blown away by dry nitrogen. Gold metal electrodes (100 nm thick) were fabricated by conventional photolithography, electron beam evaporation and lift-off techniques. Inter-electrode gaps with different widths were produced by milling using a focused ion beam (Nova™ NanoLab 200 DualBeam™, FEI Co).

Gas sensing tests were performed by employing a high-vacuum chamber coupled to a N₂ line. A semiconductor

analyser (HP 4145 B) was used to measure the temporal evolution of electric current (I) and voltage (V) during the gas tests.

To evaluate chemical sensitivity of the material to H₂S gas, an aqueous suspension of CNTs/CePr-oxide nanoparticles material was deposited by drop-casting on Si chips with interdigitated gold electrodes, followed by drying at 70 °C. These devices were used for H₂S sensing tests in the range of 1-40 ppm in a custom-built gas flow chamber and the electrical conductance was measured using Keithley Dual SourceMeter 2602 and Keithley Switching Matrix 708A. The measurements were conducted at ambient temperature with a drain-source bias voltage of 500 mV.

3 RESULTS AND DISCUSSION

Infrared spectroscopy (ATR-FTIR) results clearly showed the oxidation of carbon nanotubes after the acid treatment. Spectra for pristine carbon nanotubes present an intense absorption in the 4000-700 cm⁻¹ spectral region, without well defined absorption bands, characteristic for dark materials (not shown). After chemical oxidation, a broad absorption around 3290 cm⁻¹ appears in the ATR-FTIR spectrum (Fig. 1) revealing the presence of hydroxyl groups on the nanotubes surface. Weak bands observed around 3054 and 2889 cm⁻¹ can be assigned to C-H stretching vibrations of sp² and sp³ bonded carbons, respectively. The band around 1390 cm⁻¹ can be related to C-H and O-H vibrations whereas the split bands between 1170-1105 and 1065-970 cm⁻¹ are related to the presence of C-O bonds on the nanotubes surface. The absence of absorption near 1700 cm⁻¹ indicates a mild oxidation without a significant formation of carboxylic groups. A mild oxidation is important to keep the structural integrity and electrical properties of the nanotubes aiming gas sensing applications. Meanwhile, the presence of oxygen-containing functional groups, such as hydroxyl (-OH), carbonyl (-C=O), and carboxylic (-COOH) groups, on the surface of nanotubes are believed to act as initiator sites for the nanoparticles formation.

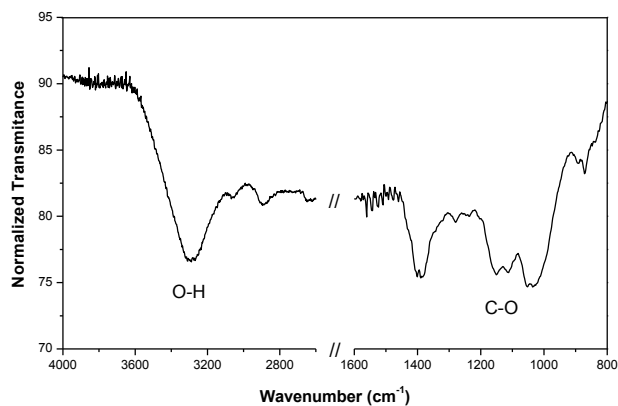


Figure 1: Infrared spectrum of MWCNTs after chemical oxidation.

HRTEM images show the successful *in situ* synthesis of nanoparticles directly on the MWCNTs outermost walls. Figure 2 illustrates the decoration of MWCNTs by well-dispersed nanoparticles, with particle diameters varying between 2-6 nm. High-resolution TEM micrograph also reveals a high crystallinity of nanoparticles. HRTEM images also allow observing the maintenance of the graphitic structure of MWCNTs after the acid treatment and oxide nanoparticles growth.

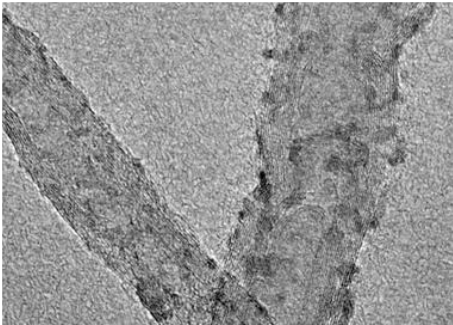


Figure 2: HRTEM image of CePr-oxide nanoparticles attached on MWCNTs outermost wall.

Due to the chemical characteristics of CePr-oxides allowing redox reactions at relatively low temperatures, this novel hybrid material constituted by carbon nanotubes decorated with cerium-praseodymium mixed oxide nanoparticles was used here for H₂S gas sensing tests, in a chemi-resistor configuration. This sensing element is constituted basically by a film of nanotubes decorated with mixed CePr-oxide nanoparticles deposited between metal electrodes. The gas sensing capabilities of the decorated nanotubes were evaluated here using different gases, concentrations and chamber configurations. For this, a constant voltage between electrodes was applied and the current evolution was measured during the gas injection.

The sensor array based on MWCNTs/CePr-oxide nanoparticles was exposed to air and H₂S/synthetic air mixtures at atmospheric pressure, room temperature (~25 °C) and 500 mV bias. A significant conductance decrease was detected when parts per million (ppm) concentrations of H₂S were introduced inside the gas chamber at a constant flow rate of 400 standard cm³/min (sccm). An abrupt decrease in the conductance value was observed when 40 ppm of H₂S was introduced inside the chamber. A sensing test using a smaller concentration of H₂S is presented in Fig. 3. In this case, 10 ppm of H₂S was introduced inside the chamber for 3 min. Once more, an abrupt decrease in the conductance is observed suggesting fast interaction of the hybrid material under study with chemically active (redox) gases.

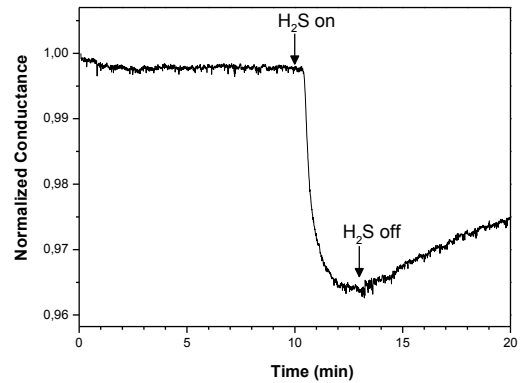


Figure 3: Network conductance of MWCNT/CePr-oxide upon exposure to 10 ppm hydrogen sulfide in air (arrows indicates the beginning and the end of the exposure).

Tests using SWCNTs/PrCe-oxide hybrid material have being also performed. Figure 4 shows the sensing tests in the range of 2-10 ppm.

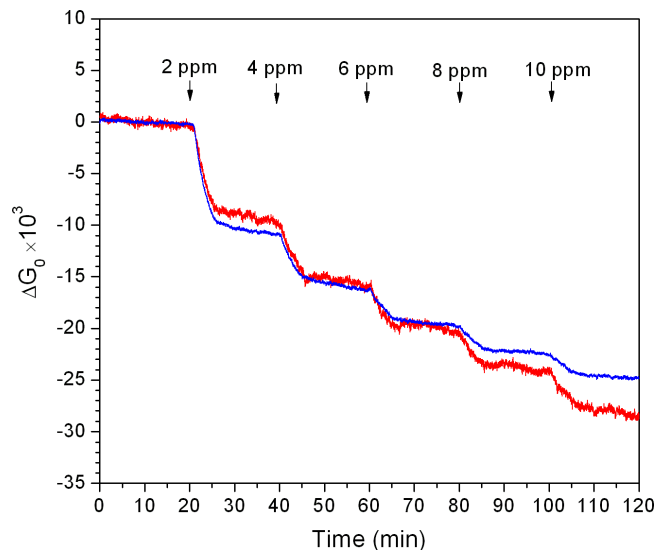


Figure 4: Network conductance of SWCNT/CePr-oxide upon exposure to 2-10 ppm hydrogen sulfide in N₂.

The device based on decorated SWCNTs had achieved responses toward H₂S in ppb level, indicating the high potential of this nanocomposite material.

4 CONCLUSION

The preparation of a novel hybrid material constituted by carbon nanotubes decorated with cerium-praseodymium mixed oxide nanoparticles directly grown on the nanotubes outermost walls was successfully achieved. Sensor devices in a chemi-resistor configuration were tested toward H₂S under room temperature and atmospheric pressure conditions showing the chemical nature of the sensor response, characterized by a fast response of the system.

Such CePr-oxides grown directly on the nanotube walls can also be potentially interesting in the area of catalysis and field-effect transistors devices based on semiconducting single-wall nanotubes, as this is a high-k material suitable for the FET insulating layer.

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