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Fe_3O_4–MWCNT—PhCOOH composites for ammonia resistive sensors

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ABSTRACT

Hybrid composites of Fe_3O_4 and multiwalled carbon nanotubes (MWCNT) chemically functionalized with the benzoic acid group (—PhCOOH) are described as novel sensing materials for resistive-type ammonia gas sensors. Fe_3O_4/MWCNT—PhCOOH composites have been synthesized by a simple procedure. The morphological and microstructural characterization has been performed by using TGA, FT-IR, XRD and TEM. TGA and FT-IR confirmed the covalent attachment of the benzoic acid groups, thus creating highly localized sites with high affinity toward ammonia molecules. Fe_3O_4 nanoparticles, about 7 nm in diameter, were found homogeneously distributed on the functionalized MWCNT—PhCOOH surface.

The ammonia sensing characteristics of samples synthesized with different Fe_3O_4 loading have been investigated at low temperature. Sensor devices fabricated with the hybrid Fe_3O_4/MWCNT—PhCOOH composites have shown more higher variation of resistance upon exposure to NH_3 compared to pristine MWCNT and functionalized MWCNT—PhCOOH ones, indicating a combined effect between the organic group and metal oxide in improving the response toward the target gas. The reversibility of the sensor was improved operating under UV irradiation.

1. Introduction

The development of CNTs-based gas sensors has attracted intensive interest in the last several years because of their high and prompt response, low power consumption, small size and low operating temperature [1]. In order to enhance their potentiality, hybrid composites of carbon nanostructures with transition metal oxides have been successfully exploited, leading to the development of more sensitive and selective chemo-sensors [2]. As the nature, microstructure, size and morphology of the metal oxide particles determine their performances, many studies on such composite materials are devoted to find the optimal composition for specific sensing applications and the more suitable synthesis method.

Here, we report a study focused to the development of Fe_3O_4/MWCNT composites and to apply them as sensing layer in low-temperature NH_3 resistive sensors. Owing the importance of ammonia monitoring in many advanced applications, including clinical diagnostics, automotive, environmental and food industry, carbon nanotubes-based NH_3 sensors have been largely described in the literature [3–6]. Pristine SWCNT, MWCNT and polymer/CNT and metal oxide/CNT composites have been reported. Hoa et al. developed a CNT-based NH_3 gas sensor, detecting ammonia gas in the range of 0.1–6% [4]. Nguyen et al. [5] developed a MWCNT-based device exhibiting a fast response and a high response to NH_3 from 2500 to 7500 ppm. Van Hieu et al. fabricated a SnO_2/MWCNT composite sensor showing, at room temperature, much higher response to ammonia at concentrations from 60 to 800 ppm in comparison with the CNT-based sensor [6].

We applied a novel approach, combining functionalization and metal oxide nanoparticles deposition on the MWCNT. So far, both covalent and non-covalent functionalizing agents have been used to modify the carbon nanotubes. Covalent chemical modification of CNT is an important tool for introducing new functional groups with specific properties [7–9]. It can be achieved by (i) oxidation of defect sites and (ii) addition reactions, such as fluoride addition, free radical addition, cycloaddition, and aryl diazonium salt addition. The oxidative process under harsh conditions utilizing strong acids simultaneously cuts the CNT into small pieces decreasing the nanotube aspect ratio and weakening their outstanding electronic and mechanical properties. The functionalization process using the diazonium protocol with p-aminomethyl benzoate on MWCNT, followed by basic ester hydrolysis allows to MWCNT decorated with benzoic acids groups maintaining an high aspect ratio. Then, nanoparticles of Fe_3O_4 have been subsequently dispersed on the surface of MWCNT.

The covalent functionalization of the MWCNT has the primary function to insert the binding sites for ammonia, providing an effective way to detect this gaseous molecule [10]. Indeed, the adsorption of ammonia gas onto specific sites on the nanotubes modifies the induced localized states, which subsequently alter the electronic conductance [11].

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The outermost walls functionalization is also an important step to the direct synthesis of metal oxide nanoparticles on the MWCNT surface since these oxygen-containing groups act as sites for nucleation of nanoparticles [2]. The synthesis of Fe_3O_4–CNT composites has been largely reported in literature, for preparing magnetic carbon nanomaterials due to the potential of these as-modified CNT in applications such as electrical devices, magnetic data storage and heterogeneous catalysis [12–15]. Qu et al. first took the combined advantages of MWCNT and nano-Fe_3O_4 preparing a magnetic composite by co-precipitation for electrochemical sensing in solution. The composite developed exhibited high electro-catalytic activity toward the redox processes of H_2O_2 [16].

As, at the best of our knowledge, no literature data has been so far reported on Fe_3O_4/MWCNT—PhCOOH composites gas sensing properties, we investigated here their characteristics for ammonia sensing at low temperature and the related results have been reported and discussed. MWCNT—PhCOOH, MWCNT—COOH and Fe_3O_4/MWCNT composites were also tested for comparison. Fe_3O_4/MWCNT—PhCOOH hybrid composites combine the binding property of the organic functional group and semiconducting metal oxide, thereby possessing unique gas sensing properties unavailable from single component-sensors [17].

2. Experimental

2.1. Preparation of functionalized MWCNT—PhCOOH sample

MWCNT were purchased from Sigma–Aldrich (95 + %C purity, diameter of 20–30 nm). All reagents and solvents were purchased from different commercial suppliers and used as received. 200 mg of multiwalled carbon nanotubes were dispersed in o-dichlorobenzene (50 mL), sonicated for 15 min at room temperature; then a solution of ethyl 4-aminobenzoate (1 g dissolved in 100 mL of dry acetonitrile) was added, and the mixture was sonicated for 30 min at room temperature (RT, 25 °C). The reaction mixture was stirred for 10 min under helium flow, added with 1.48 mL of isoamyl nitrite and stirred at 60 °C for 24 h under helium flow. The mixture was then cooled, diluted with ethanol (100 mL) and filtered under vacuum on Millipore membrane of 0.1 μm. The solid residue was washed with ethanol, acetonitrile, chloroform and ethyl acetate (3 × 50 mL) and each time sonicated for 10 min. The solid residue was treated with NaOH (1 M, 20 mL) at 80 °C for 8 h, neutralized with an aqueous solution of hydrogen chloride, filtered and washed with water under vacuum on Millipore membrane of 0.1 μm. The residue was dried under vacuum at 60 °C to give MWCNT—PhCOOH.

A reference MWCNT—COOH sample was also prepared by oxidation of pristine MWCNT using a mixture of nitric acid and sulfuric acid (1:1), according to our previously reported procedure [18].

2.2. Preparation of Fe_3O_4/MWCNT—PhCOOH hybrids

The preparation of Fe_3O_4/MWCNT—PhCOOH hybrids was conducted as follows. First, functionalized MWCNT—PhCOOH were ultrasonicated in ultra-pure water for few minutes, and then kept at 60 °C, under a constant stream of inert gas and subjected to mechanical stirring throughout the synthesis. Then, $FeCl_3$ and $FeCl_2$ (2:1 molar ratio) were sequentially added to the suspension, waiting about 30 min between the two additions. An excess of 6% ammonium hydroxide was added drop-wise and the whole mixture was left to react for 2 h. The solid was filtered under vacuum on a 0.1 μm Millipore membrane and washed with deionized water until the pH was neutral. The samples were dried under vacuum at 50 °C overnight.

Reference samples Fe_3O_4/MWCNT and Fe_3O_4/MWCNT—COOH were also prepared following the above reported procedure.

2.3. Samples characterization

The determination of the concentration of acidic sites present on the MWCNT after the functionalization was carried out according to literature method [19]. Briefly, the sample was heated at 100 °C to remove carbon dioxide and water and was added into 100 mL of 0.01 N sodium hydroxide and stirred for 48 h. The sample was centrifuged at 10,000 rpm for 15 min. Unreacted NaOH was titrated with 0.01 N hydrochloridric acid.

The morphology of samples was analyzed using an JEOL JEM 2010 TEM microscope operating at 200 kV. The formation of the carboxylic functional groups on CNT was verified by FT-IR (Nicolet FTIR Impact 400D). XRD data were collected with an Ital Structures diffractometer (Mod. APD 2000) using CuKα radiation source. Thermogravimetric studies were performed on a TA Instruments Q500 under nitrogen at 10 °C/min in temperature range from 30 to 700 °C. The Fe content was determined by Atomic Absorption Spectrometry (AAS) using a Perkin-Elmer model 4000 spectrometer. A known amount of solid was dissolved in an aqueous solution of HCl and the absorbance of the solution was measured at 248.3 nm.

2.4. Sensing tests

The sensing device consists of an alumina substrate with Pt interdigitated electrodes, on which the sensing layer was deposited by screen printing. The deposited sensing films have a thickness around 10–20 μm. An Agilent 34970A multimeter data acquisition unit and a Keithley 2400 source meter were used to acquire the sensor signal while an Agilent E3632A dual-channel power supplier instrument was used to bias the UV LED (model HUVL400-320B produced by Hero with a typical peak emission wavelength (λ) of 400 nm). An Agilent E3632A dual-channel power supply was used to set the operating temperature of the sensor by biasing the platinum heater, and to illuminate the sensing film with UV radiation by biasing the UV LED. Sensing tests were carried out in dry synthetic air (20% oxygen in He). Dry ammonia gas in helium (0.5%) coming from certified bottles was used, after diluting it with dry helium and oxygen, to convey the desired NH_3 concentration in the test chamber. The sensor response is given by $[(R - R_0)/R_0] \times 100$, where R_0 is the resistance baseline in dry synthetic air and R is the resistance recorded under different NH_3 concentrations.

3. Results and discussions

3.1. MWCNT functionalization

It is well known that exposure to NH_3 can change the electronic properties of pristine MWCNT inducing a resistance variation [20]. The chemical and structural modifications of carbon nanotubes can greatly improve the sensing performance. Previous reports focused the attention on the oxidative functionalization procedure which provides the suitable binding sites for ammonia at the side-walls of the MWCNT [4–6]. This approach, based on the treatment with strong oxidizing agents such as HNO_3 [21] or using oxygen plasma [22], has shown great utility to create bulk carboxylic acid (—COOH) functionalized MWCNT. However, the strong acid treatment necessary for functionalization can lead to the partial damage of the nanotube structure. Further, this treatment is not only selective toward the formation of carboxylic groups, but also some other chemical groups with acidic properties can be formed on the sidewall of CNT [23].

Here, we implemented a functionalization of the MWCNT for inserting the COOH group, by using p-aminobenzoic acid as