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Effect of pyrene substitution on the formation and sensor properties of phthalocyanine-single walled carbon nanotube hybrids

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ABSTRACT

The hybrids of single walled carbon nanotubes (SWCNTs) with symmetrically octasubstituted zinc phthalocyanine (**2**) bearing eight polyoxyethylene groups and asymmetrically substituted zinc phthalocyanine (**1**) bearing one pyrene and six polyoxyethylene groups as side chains have been prepared and characterized by Raman and fluorescence emission spectroscopies, scanning electron and transmission electron (SEM and TEM) microscopies, and thermogravimetric analysis. The pyrene group was chosen to enhance the interaction of phthalocyanine molecules with SWCNTs. Thin films of pristine SWCNTs and SWCNT/ZnPc hybrids were prepared by drop casting onto interdigitated electrodes and employed as active layers to detect ammonia vapour (1–200 ppm) by measuring electrical resistance changes. A comparative analysis of sensors' response of pristine SWCNTs and SWCNT/ZnPc hybrid films to ammonia vapour was carried out to demonstrate the synergic effect between SWCNTs and ZnPc derivatives. Influence of pyrene substituent in the phthalocyanine ring on the hybrid formation and their sensor response has also been discussed.

1. Introduction

Hybrid and composite materials play more important role in nanoelectronics due to the synergic effects on the electrical, optical, or mechanical properties of two or more components [1–3]. The use of carbon nanotubes (CNTs) and their hybrids in sensing has been extensively studied in recent years and progress in CNT-based sensor development for gas detection has been the subject of several reviews [4–6]. The use of nanostructured materials for gas sensing has been of great interest due to their unique and interesting properties including high surface-to-volume ratio and sensitive electronic structures [7–10]. Upon exposure to gas molecules, the electrical resistance of single-walled carbon nanotubes (SWCNTs) changes and the threshold voltage is shifted due to charge transfer between the semiconducting SWCNT and electron-withdrawing and electron-donating molecules.

It is well known that defect sites on SWCNTs play an important role in the electrical response for the binding of chemical vapor molecules [11]. It was found that the chemical sensitivity of SWCNTs could be significantly increased by controllably introducing a low density of defects along the sidewalls of the tubes [11,12]. The other way to increase sensitivity of SWCNTs is achieved through introduction of some functional groups [13] or by producing hybrids with different compounds [14,15].

As ammonia is a low boiling point compound and volatile, it is very important to develop sensitive devices to detect the gaseous NH_3 molecules. Chemical sensing application of SWCNTs for NO_2 and NH_3 gases was first reported by Kong et al. [16]. Other studies have revealed that semiconducting SWCNTs could detect small concentrations of NH_3 and NO_2 with high sensitivity at room temperature [17].

On the other hand, metal phthalocyanine derivatives possess high sensitivity, fast response, ease of processability, as well as a scope of operation at room temperature; they have therefore been studied extensively as thin films for chemical detection [18]. Jiang et al. have described the process of interaction between copper tetra-4-(2,4-di-*tert*-amylphenoxy)phthalocyanine (tapCuPc) and

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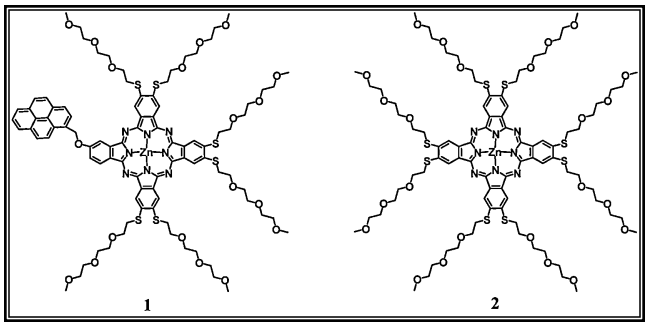

Fig. 1. Asymmetrical (**1**) and symmetrical (**2**) zinc phthalocyanine derivatives.

NH_3 [19]. Two different types of amphiphilic phthalocyanines have been compared for their sensing properties to NH_3 [20]. Sensor response of spin-casted films of copper, lead and nickel 1,8,15,22-tetra-iso-pentyloxyphthalocyanine (Cu, Pb and NiPc(iso-PeO)$_4$) to ammonia vapour was studied by Wang et al. [21].

The combined excellent properties of carbon nanotubes and phthalocyanines were demonstrated for the development of sensitive NH_3 sensors based on CNT/phthalocyanine hybrids [22,23]. The evidence so far has shown that these hybrids are expected to be more efficient in improving the relative response of hybrid films compared to the pristine CNT or phthalocyanine species. There are two different routes for hybridising metal phthalocyanines and carbon nanotubes; in the first type CNT are functionalized with metallophthalocyanine derivatives through formation of covalent bonding [24–26] while in the second type the hybrid can be formed through non-covalent interaction between the two materials [27–29].

In this work, hybrids of SWCNTs with symmetrically octa-substituted ZnPc bearing eight polyoxyethylene groups (**2**) and asymmetrically substituted ZnPc bearing one pyrene and six polyoxyethylene groups (**1**) as substituents (Fig. 1) were prepared and characterized. The pyrene group was chosen to enhance the interaction of the phthalocyanine molecules with the CNTs. This class of organic molecules is known to interact strongly with SWCNTs via π-stacking interactions [30–33]. To demonstrate the potential applications of the SWCNT/ZnPc hybrids in gas sensing, a conductometric gas sensor device based on these hybrid materials has been fabricated. A comparative analysis of sensor response of pristine SWCNTs and SWCNT/ZnPc hybrid films to ammonia vapour (1–200 ppm) was carried out to demonstrate the synergic effect between SWCNTs and ZnPc derivatives. Influence of pyrene group as substituent in the phthalocyanine ring on the hybrids formation and their sensor response is discussed.

2. Experimental

2.1. Materials

Synthesis and characterization of zinc(II) phthalocyanine derivatives **1** and **2** (Fig. 1) have already been described in an earlier publication [34]. SWCNTs were purchased from Sigma-Aldrich and used without further purification and chemical treatment.

2.2. Equipment

Optical spectra in the UV–visible region were recorded with Shimadzu UV–vis-3101 and 2101 spectrometers using 1 cm path length cuvette at room temperature. Fluorescence emission spectra were recorded on a Varian Eclipse spectrofluorometer. Thermogravimetric analysis (TGA) was carried out on a Mettler Toledo STARe Thermal Analysis System at a rate of 10 °C min^{-1} in nitrogen flow of 50 mL min^{-1}.

Raman spectra were recorded with a Triplemate, SPEX spectrometer equipped with CCD detector in back-scattering geometry. The spectral excitation was achieved using 488 nm line Ar laser with the power of 40 mW.

Scanning electron microscopy (SEM) images were obtained using FEI-nova nanosem 200. Transmission electron microscopic (TEM) images were obtained using JEM-2010 instrument at an accelerating voltage of 200 kV. A thin film sample was prepared by dispensing a droplet of the hybrids dispersed in dichloromethane on a 200 mesh copper grid covered with a "holey" carbon film and allowing the solvent to evaporate.

Spectroscopic ellipsometry measurements were carried out to determine the thickness of the films using a Woolam *M-2000V*™ rotating analyser spectroscopic ellipsometer in the spectral range of 400–800 nm. DC-conductivity measurements were carried out using Keithley 236 semiconductors characterization system.

2.3. Preparation of SWCNT-phthalocyanine hybrids

5 mg of zinc phthalocyanines (**1** or **2**) have been dissolved in 1 mL DMF and sonicated for 15 min. At the same time 1.0 mg SWCNTs was suspended in 3 mL DMF and sonicated for 30 min. After sonication the suspension was stirred and the solution of phthalocyanines **1** or **2** was added drop wise to the SWCNTs suspension during stirring to obtain the hybrids **SWCNT/1** and **SWCNT/2**, respectively. Addition of zinc phthalocyanine solution was stopped when the green phthalocyanine solution became colorless due to phthalocyanine adsorption onto the SWCNT. The stirring was continued for another 1 h before the mixture was centrifuged. The obtained solid was washed with DMF several times, centrifuged again and finally dried in vacuum.

2.4. Sensor properties study

The sensing performance was studied at the relative humidity of 50% RH under exposures to low-concentration of NH_3 in the range 1–200 ppm. Pure commercial NH_3 gas ("Dioksid", Russia) was used as the NH_3 source. Air was used as the diluent gas, and NH_3 was diluted by a syringe static volumetric method. Diluted NH_3 was injected into the container using a microsyringe. The test chamber was degassed by turning a heating element on at 80 °C immediately after the removal of NH_3 gas.

Thin films of hybrids SWCNT/**1** and SWCNT/**2** were deposited by drop-casting their solutions in DMF (0.5 mg/mL) onto interdigitated electrodes which were used as substrates for the electrical characterization of the films. The electrical resistance of the sensors was measured using a Keithley 236 electrometer by applying a constant DC voltage of 3 V. The response and recovery times of the films were defined as the times needed to reach 90% of the steady state resistance.

3. Result and discussion

3.1. Characterization of SWCNT/phthalocyanine hybrids

3.1.1. Raman spectra

The non-covalent attachment of phthalocyanine molecules to SWCNTs can be confirmed by Raman spectroscopy. Raman spectra for pristine SWCNTs and both hybrids are shown in Fig. 2. The radial breathing modes (RBM), disorder (D) mode and tangential/graphite mode (G-band) are monitored as indicators of functionalization with phthalocyanine molecules [35]. The spectra were normalized to the tangential G band at ~1590 cm^{-1}. Both spectra of pristine SWCNTs before and after hybridization contained the following