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Research Paper

Stably dispersed metallophthalocyanine noncovalently bonded to multiwalled carbon nanotubes for ammonia sensing at room temperature☆

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ABSTRACT

Herein, a series of tetra-α-isopentyloxyphthalocyanine copper, nickle, lead (CuPc-3, NiPc-3, PbPc-3) have been successfully bonded on the surface of acidified multi-walled carbon nanotubes (MWCNTs) by using a solution self-assembly method based on π–π stacking interaction facile reaction. The obtained MPc-3/MWCNTs (M = Cu, Ni, and Pb) hybrids display good dispersibility in DMF, which is beneficial to construct uniform sensing devices. The MPc-3/MWCNTs sensors exhibit excellent sensing performance, in terms of sensitivity, reversibility, reproducibility, selectivity and stability, especially CuPc-3/MWCNTs sensor in detail, the response is about 40.5% (80 ppm), the limit of detection is as low as 75 ppb, and the recovery time is about as fast as 180 s at room temperature. The enhanced NH_3-sensing performance is mainly due to the synergistic effect between MPc-3 and MWCNTs, e.g. the stronger adsorption interaction of MPc-3 with NH_3, the high electrical conductivity of MWCNTs, and the fast charge transfer between MPc-3 and MWCNTs. The systematic study developed here provides a valid way to fabricate high-efficient NH_3 sensors.

1. Introduction

With increasing concerns of air pollution on human health and safety and progress of nanotechnology, the development of high sensitive, low cost, low power and portable gas sensors has become a significant research topic [1–3]. Ammonia (NH_3), as a toxic gas, is commonly produced from the waste product of livestock or from industry and automobile emissions [4]. Furthermore, the ammonia gas, which was widely used in various fields, including the production of fertilizers, plastics, synthetic fibers, dyes and pharmaceuticals, etc., is harmful to human health [5]. The lower limit of human ammonia perception by smell is tabulated to be around 50 ppm [6]. The limits for exposure to NH_3 as set by the National Institute for Occupational Safety and Health (NIOSH) are TWA 25 ppm or ST 35 ppm [7]. In order to satisfy the demands of effectively detecting toxic NH_3 gas, it is important to develop NH_3 sensors based on new materials with advanced gas sensing performance. To date the most effecting NH_3 sensing materials are metal nanoparticles, semiconductor metal oxides and polymers et al. [8–10]. However, the high operation temperature, slow response and recovery, and high cost would limit their further application. Therefore, it still brings a grand challenge to synthesize advanced room temperature sensing materials for widespread NH_3 sensor applications.

Carbon nanotubes (CNT) have unique one-dimensional carbon nanostructure, electronic properties and low cost, low operation temperature, which is a unique and attractive sensing material for gas sensor [11–14]. Recently, a variety of CNT/metal nanoparticles, metal oxides and polymers composites have also been applied as sensing materials to improve the performance of CNT-based gas sensors [15–21]. Phthalocyanines (Pcs) are organic macrocyclic compounds having interesting structure, physical properties, excellent thermal and chemical stability. More importantly, changes in conductivity property upon reactive gas make Pcs an attractive class of gas sensing materials [22–26], however,

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the very low electrical conductivity of Pcs structure makes it difficult to develop only Pcs-based chemiresistive sensors. CNTs have huge surface area, abundant microchannel porous structure, low resistivity and electron transfer rate. However, due to the strong Van der Waals attraction, CNTs tend to restack or aggregate both in solution and in the solid state, forming bundled structures that significantly reduce the active surface area, greatly reduce the gas sensing properties. Pcs have flat and planar structure that facilitates π-π interaction and binds to the CNTs' surface almost without altering the CNTs' electronic properties. Therefore, the Pcs/CNTs hybrids can be prepared by surface modification of CNTs with Pcs [27–32], which could overcome the conductivity issue of Pcs and the dispersibility issue of CNTs. In the Pcs/CNTs, the high electrical mobility of CNTs improves the sensor conductance, whereas the binds ability of Pcs toward different gas improves the sensing performance of the hybrid sensor when used as a sensing layer. In our previous work, MPc/single wall carbon nanotubes and multi-walled carbon nanotubes hybrids have been synthesized and hybrids sensors exhibit good NH_3 gas sensing response at room temperature, compared with pure CNTs [33,34]. Moreover, MWCNTs sensors exhibit better recovery performance than SWCNT sensors, due to the fact that it is more difficult for NH_3 molecules to move deeper into the internal of MWCNT. The gas molecules only locate at the external sites around the MWCNT. However, they are not good enough for commercial application, due to the lower response of the gas sensors, and no systemic studies have been reported on the effect of different central metal of MPcs on NH_3-sensing properties of MPcs/CNTs hybrids. Thereby, it is very essential to attach a serial of sensing MPcs on MWCNTs with special structure for demand fields.

On the basis of the above-mentioned, in this work we report the facile preparation of a new series of tetra-α-isopentyloxy metal phthalocyanine/multi-walled carbon nanotubes (MPc-3/MWCNTs, here M = Cu, Ni and Pd) hybrids by using a solution self-assembly method based on π–π stacking interactions. MPc-3, containing four isopentyloxy groups at the peripheral positions, were synthesized and used so as to achieve a desired dispersibility for MPc-3/MWCNTs hybrids. A systematic study was done to evaluate the NH_3–sensing performance of the hybrids operating in chemiresistive mode over a wide range of concentrations at room temperature. A schematic of the NH_3–sensing sensor composed of MPc-3/MWCNTs hybrids is shown in Scheme. 1. As expected, the as-prepared, well-dispersed MPc-3/MWCNTs hybrids show an enhanced sensitivity, response and recovery time in comparison to other NH_3-sensing materials. Furthermore, the developed sensors of the hybrids also have excellent reproducibility and selectivity. The results demonstrate that the MPc-3/MWCNTs hybrids can serve as an excellent sensing platform and has great potential applications in sensor development. Significantly, the central metals are directly correlated with the NH_3-sensing performance. Density functional theory (DFT) calculations were further carried out to reveal the interactions between NH_3 and MPc-3 with different center metals. It is believed that a fundamental understanding obtained by this work is of particular importance for fabricating MPcs/MWCNTs hybrids and for manufacturing chemical sensors.

2. Experimental

2.1. Reagents

Multi-walled carbon nanotubes (CNTs, purity >95%, 5–15 mm in length, 10–20 nm in diameter) purchased from Shenzhen Nanotech Port Co., Ltd. were purified to remove impurities by the established methods [35,36]. 3-Nitrophthalonitrile (99% purity), phydroxybenzoic acid (99% purity) and DBU (98% purity) were purchased from Sigma-Aldrich C. LLC. Ultrapure water (resistivity 18.2 MΩ cm) was obtained from a Milli-Q Water System (Millipore Corp., Bedford, MA, USA) and was used in the whole experimental process. Acidified multi-walled carbon nanotubes (MWCNTs) were prepared by a well-established method in our previous study [33,34]. Tetra-α-isopentyloxymetallophthalocyanine (MPc-3) were synthesized by the common template reaction of 3-(isopentyloxy)phthalonitrile with anhydrous metal(II) chloride in the presence of 1,8-diazabicyclo [5,4,0]undec-7-ene (DBU) (see the ESI† for experimental details). Ultrapure water was obtained by using a Millipore Milli-Q system (Millipore Corp. Bedford, MA, USA). All other reagents in this work were of analytical grade and used without further purification.

2.2. Preparation of MPc-3/MWCNTs hybrids

Three MPc-3/MWCNTs hybrids, via CuPc-3/MWCNTs, NiPc-3/MWCNTs and PbPc-3/MWCNTs, were prepared by the same general method: MWCNTs (10 mg) was sonicated in N,N-dimethylformamide (DMF) solution (20 mL) at room temperature for 1 h, and then MPc-3 (20 mg) was added under vigorous stirring. The ensuring mixture was stirred under nitrogen at room temperature for 48 h. The resultant solution was filtered through a 0.22 μm PTFE membrane filter. The filter cakes were washed thoroughly with ethanol, acetone, dichloromethane and tetrahydrofuran for several times, successively, until the filtrate became colorless, and then dried in a vaccum oven for 2 h at 80 °C, obtaining the desired black MPc-3/MWCNTs hybrids powders.

2.3. Sensors assembling and sensing measurement

A complete description of the gold interdigitated electrodes (IDEs) and the gas sensor testing device was already reported in our previous study. [33,34]

To prepare gas sensors composed of MPc-3/MWCNTs hybrids, the as-prepared MPc-3/MWCNT hybrids were dispersed in DMF to obtain a uniform suspension of 0.5 mg mL^{-1} by ultrasonication for 2 h, and then 3 μL of the homogeneous dispersion was drop cast onto the gold electrodes using a microsyringe until a resistance range (1–2 kΩ) was achieved. Low concentration dispersion was used to avoid overlapping MPc-3/MWCNTs hybrids. To remove the solvent of the sensor and improve the electrical contact between the hybrids and the gold electrodes, the sensor devices were annealed in a vacuum oven for 2 h at 80 °C before sensing tests. For comparison, gas sensor of free MWCNTs was also fabricated by the similar procedures.

A typical sensing test cycle consisted of three sequential steps. The sensors were dried in a vaccum oven for 1 h at 80 °C before measuring. First, a dry air flow was introduced into the sensing test chamber to record a baseline. Then, an appropriate amount of the dry NH_3 sample gas was injected to register sensor signals. Finally, the sensor was recovered in a dry air flow. In order to study the effect of relative humidity on the NH_3 response properties, dry air and air with controlling different humidity were used as both a carrier and a dilution gas, respectively, and all measurements were performed at 28 °C ± 0.5 °C. The change in resistance of the sensors was measured with a CUST•G2 gas sensing test system (Advaced sensor technology laboratory of Jilin university, China) applying DC output voltage of 5 V by a AC to DC regulator and recording the change in resistance passing through the sensor at a 1 s interval by a computer. In this study, Response is defined by the relative resistance change, as follows:

$$\text{Response}(\%) = \frac{\Delta R}{R_a} \times 100\% = \frac{R_g - R_a}{R_a} \times 100\% \quad (1)$$