Sensors and Actuators B 248 (2017) 324–331

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

journal homepage: www.elsevier.com/locate/snb

P-CuPcTS/n-SnO_2 organic-inorganic hybrid film for ppb-level NO_2 gas sensing at low operating temperature

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ARTICLE INFO

Article history:
Received 25 November 2016
Received in revised form 20 March 2017
Accepted 2 April 2017
Available online 3 April 2017

Keywords:
Gas sensor
Copper phthalocyanine
Organic-inorganic
ppb-Level NO_2
SnO_2 film

ABSTRACT

Design and fabrication of organic-inorganic hybrid sensing materials is a promising strategy to combine the advantages of good stability of inorganic species and high sensitivity, selectivity and low operating temperature of organic ones. In this work, CuPcTS(Copper (II) Phthalocyanine Tetrasulfonic Acid Tetrasodium Salt)/SnO_2 organic-inorganic hybrid film was prepared through a simple soak-assembling process. The p-type CuPcTS molecules were homogenously adsorbed on the surfaces of n-type SnO_2 film to form p-n heterojunctions. Due to the low adsorption energy of NO_2 on CuPcTS at low temperature, the CuPcTS/SnO_2 hybrid film exhibits significantly improved sensing performance towards ppb-level NO_2 with high sensitivity (R_g/R_a = 2400 up to 1 ppm NO_2), ultra-low theoretical detection limit (~40 ppb when signal-to-noise ratio is 3) and excellent selectivity. The ultrahigh sensitivity and selectivity upon ppb-level NO_2 indicate the promising capability of CuPcTS/SnO_2 hybrid film for environmental monitoring of NO_2 concentrations.

1. Introduction

Nitrogen dioxide (NO_2), as one of the main environmental pollutants, has drawn great attention considering its hazardous effects on human health at extremely low concentration [1–3]. Actually, 15 ppb of NO_2 induces cough, nasal and eyes irritations; for 30 ppb, exposed people can be affected by the hyperactivity of airway muscles; above 80 ppb, the incidence in respiratory infections and sore throats drastically increases [4,5]. Therefore, ppb-level NO_2 sensors are highly required for environmental monitoring.

Chemiresistive gas sensors, using metal oxide semiconductors (MOSs, e.g. SnO_2, WO_3, In_2O_3, ZnO, and so on) as sensing materials, have been demonstrated to be promising candidates for NO_2 detecting, because of their high sensitivity, long-term stability, simplicity in fabrication and low cost. Up to now, MOSs based various structures and composites have been widely investigated to accomplish the high response to ppm or sub-ppm-levels NO_2 by decreasing grain size, improving gas accessibility, modifying with sensitizers and forming p-n heterojunctions [6–12]. However, the response and selectivity to ppb-level NO_2 need to be further improved. Furthermore, the optimal working temperature of MOSs based gas sensors is usually superior to 200 °C owing to the high activation energy of reaction with gas molecules and the accelerated desorption of gas molecules. The high working temperature means high power consumption, which restricts the integration and the use of materials for device assembling.

Metal-phthalocyanines (MPcs), as a kind of p-type organic small molecule semiconductors with excellent thermal and chemical stability, have attracted great attentions as room temperature gas sensing materials due to the unique doping/dedoping sensing mechanism [13–16]. In the presence of oxidative/reductive gases, the gases are chemisorbed on MPc molecules, followed by the charge transfer occurring (doping). Consequently, the conductivity of MPc films increases in oxidative atmospheres or decreases in reductive atmospheres. On the contrary, when the oxidative/reductive gases are removed, the desorption of surface-adsorbed gaseous molecules occurs (dedoping), and the extrinsic charge carriers are annihilated, leading to conductivity recovery. Additionally, the gas sensing properties of MPcs can be manipulated by incorporating the specific central metal ions [17,18]. Copper phthalocyanine (CuPc), in particular, has been intensively studied to demonstrate the high sensitivity to NO_2 at low temperature because of the low adsorption energy (~0.06 eV) of NO_2 on CuPc moleculars [17,19,20]. However, the practical applications of

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http://dx.doi.org/10.1016/j.snb.2017.04.003
0925-4005/

CuPc based gas sensors are limited mainly by the relatively low conductivity, poor gas accessibility, irreversible recovery and poor long-time stability.

Design and fabrication of organic-inorganic hybrid composites for gas sensing is a promising strategy to overcome the disadvantages of organic and inorganic materials, which affords novel or enhanced functionalities through a synergic interaction between the two phases [21–23]. In the particular field of gas sensing materials, organic-inorganic hybrid materials, combining the advantages of good stability of inorganic species and high sensitivity/selectivity of organic ones, have been demonstrated to be highly suitable for sensing applications with enhanced stability, sensitivity and selectivity [24–28].

In this work, an CuPcTS(Copper (II) Phthalocyanine Tetrasulfonic Acid Tetrasodium Salt)/SnO_2 organic-inorganic hybrid film was prepared through a simple soak-assembling process. The p-type CuPcTS molecules were homogenously absorbed on the surfaces of n-type SnO_2 film to form p-n heterojunctions. The NO_2-sensing characteristics of the CuPcTS/SnO_2 hybrid film were systematically investigated at low working temperature of 50 °C. Combining the advantages of the high conductivity and good chemical stability of SnO_2 and the high sensitivity to NO_2 at low wording temperature of CuPcTS, the CuPcTS/SnO_2 hybrid film were demonstrated to exhibit a significantly improved sensing performance with ultrahigh sensitivity and selectivity to ppb-level NO_2.

2. Experimental section

2.1. Fabrication of CuPcTS/SnO_2 hybrid film

The CuPcTS/SnO_2 hybrid film was fabricated as follows (Fig. 1). Firstly, SnO_2 paste (20 ± 0.3 mg), composed of SnO_2 nanoparticle (particle size: 50–70 nm, purchased from Mackin Biochemical Co., Ltd), binder, polymer and organic solvents, was coated on interdigitated Au-alloy electrode by spin coating, the parameters were set as 5000 r/min for 60 s with an acceleration of 500 r/min^2. The obtained wet SnO_2 film was dried at 80 °C for 30 min, and then calcined at 600 °C for 2 h to remove the organic solvents and polymer. Thereafter, the solid SnO_2 film was soaked in 0.5 wt.% CuPcTS (Purchased from Alfa-Aesar (China) Chemical Co., Ltd) aqueous solution for 1 day, and then the excess CuPcTS aqueous solution was removed by spin coating. Finally, the CuPc/SnO_2 hybrid film was obtained by drying at 80 °C for 30 min and heat-annealing at 300 °C for 1 h.

2.2. Characterization

The CuPcTS/SnO_2 composite powder was scraped and collected from the CuPc/SnO_2 hybrid film for the characterization of scanning transmission electron microscopy (STEM), Fourier transform-infrared (FT-IR) spectroscopy, and ultraviolet-visible (UV–vis) spectroscopy. The scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS) were carried out directly by using CuPcTS/SnO_2 hybrid film. The microstructure and morphology of the hybrid film were analyzed by SEM and STEM. SEM was performed on a Hitachi TM-1000 microscope with an accelerating voltage of 10 kV. STEM was carried on a Tecnai G2F20 electron microscope with an accelerating voltage of 200 kV. The characterization of XPS, FT-IR and Uv–vis were used to demonstrate the existence of CuPcTS molecules in hybrid film. The FT-IR spectroscopy was recorded using KBr pellets on a BRUKER VECTOR22 Spectrometer. XPS was carried out by AXIS HIS 165 spectrometer (Kratos Analytical) with a monochromatized Al Kα X-ray source (1486.71 eV photons). The UV–vis spectroscopy was acquired by using Lambda 650 (Perkin Elmer) spectrometer.

2.3. Gas sensing characteristics

The gas sensing properties of CuPcTS/SnO_2 hybrid film and pristine SnO_2 film for comparison were operated using an intelligent gas sensing analysis system (CGS-4TPs, Beijing Elite Tech Co., Ltd., China) and a home-made gas control system, as shown in Fig. 2. The concentration of gases was accurately controlled using a computerized mass flow controller (MFC) gas control system by diluting the test gas (e.g. 10 ppm NO_2 in air, purchased from NIMTT Co., Ltd, China) with highly purified dry air. The volume of testing chamber is 1.8 L and the total constant flow rate was set at 1000 sccm. Before the measurement, the highly purified dry air was injected into the testing chamber to displace the ambient air until the humidity was under 10 RH%. The humidity was measured by a humidity sensor, which was integrated in the intelligent gas sensing analysis system (Fig. 2). UV irradiation (365 nm UV-LED) was employed to accelerate the recovery rate in recovery process.

The sensing response was defined as: $S = R_g/R_a$, where the R_a is the sensor resistance in the air, and R_g is the sensor resistance in the target gas.

3. Results and discussion

3.1. Microstructure and morphology characterization of the CuPcTS/SnO_2 hybrid film

The existence of CuPcTS molecules in the hybrid film was firstly demonstrated by the characterization of XPS and FT-IR. The XPS spectrum of CuPcTS/SnO_2 hybrid film is shown in Fig. 3a, from which the peaks of C, N, O and Sn can be observed. The peak of Cu is relatively weak, maybe due to the extremely low content. The high-resolution C 1s spectrum can be fit into two peaks at 284.6 and 286.0 eV, as shown in Fig. 3b. The main peak located at 284.6 eV corresponds to the aromatic carbon atoms in C—C and C—H bonds and the smaller peak located at 286.0 eV corresponds to the carbon atoms in C—N bonds [29]. From the high-resolution and curve fitted N 1s spectrum (Fig. 3c), two peaks at 398.9 eV and 400.9 eV can be attributed to the binding energy of the nitrogen atoms in C—N=C and C—N—Cu bonds, respectively [30]. Accordingly, we can confirm the existence of CuPcTS molecules in the hybrid film, which was further identified by the FT-IR characterization, as shown in Fig. 3d. The characteristic peaks of SnO_2 are located at 610 and 677 cm^{-1}, which are assigned to Sn—O and Sn—O—Sn stretching modes of surface bridging oxide formed by the condensation of adjacent hydroxyl groups [31]. The peak at 1638 cm^{-1} is corresponding to the bending vibration of adsorbed water molecules on the surfaces of SnO_2 nanoparticles. The spectrum of CuPcTS shows the primary characteristic peaks at 1271, 1471 and 1583 cm^{-1}, which are corresponding to the skeleton stretching [32].

The morphology and microstructure of the CuPcTS/SnO_2 hybrid film were investigated by SEM and STEM. The SEM image of the CuPcTS/SnO_2 hybrid film is shown in Fig. 4a. The CuPcTS/SnO_2 hybrid film displays porous structure, which has the similar morphology with the pristine SnO_2 film (Fig. 4b). The result indicates that the CuPcTS molecules are highly dispersed in SnO_2 film. The STEM image (Fig. 4c) and the corresponding elemental mapping of Sn (Fig. 4d), O (Fig. 4e), and N (Fig. 4f) reveal that the CuPcTS molecules are homogenously adsorbed on the surfaces of SnO_2 nanoparticles through an electrostatic self-assembly process. The successful synthesis of CuPcTS/SnO_2 hybrids was further confirmed by ultraviolet-visible (UV–vis) absorption spectra, as shown in Fig. S1. The absorption band at ~550–800 nm in the UV–vis spectrum (Fig. S1a and its inset) indicates that SnO_2 was modified successfully by CuPcTS molecules. The band corresponding to the absorbance of CuPcTS is very weak, possibly due to the strong background absorp-