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Gas sensors based on carbon nanoflake/tin oxide composites for ammonia detection

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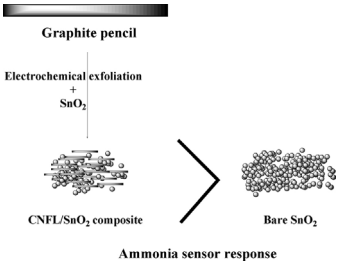
HIGHLIGHTS

- Effective sensing of toxic chemicals has revealed great awareness in material science and chemical sensor research.
- CNFL/SnO_2 composite material was developed to make use of ammonia gas sensor.
- CNFL/SnO_2 composite material showed better performances as a gas sensor compared to pristine SnO_2.

GRAPHICAL ABSTRACT



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ABSTRACT

Carbon nanoflake (CNFL) was obtained from graphite pencil by using the electrochemical method and the CNFL/SnO_2 composite material assessed its potential as an ammonia gas sensor. A thin film resistive gas sensor using the composite material was manufactured by the drop casting method, and the sensor was evaluated to test in various ammonia concentrations and operating temperatures. Physical and chemical characteristics of the composite material were assessed using SEM, TEM, SAED, EDS and Raman spectroscopy. The composite material having 10% of SnO_2 showed 3 times higher sensor response and better repeatability than the gas sensor using pristine SnO_2 nano-particle at the optimal temperature of 350 °C.

1. Introduction

Ammonia widely used in industry is an odorous toxic gas aroused from various sources. It also needs to be investigated from the medical and industrial points of view. Ammonia has a very strong, irritating smell, and its permissible maximum concentration is 50 ppm. It is dangerous to inhale ammonia at 2500–6500 ppm for more than 2 h. Thus, development of reliable and affordable gas sensors for ammonia detection is important and research is ongoing [1–3]. In addition, many researchers have recently focused on the development of novel materials; metal oxide, polymer, organic, and dyes [4–13]. Among them, SnO_2 is an n-type semiconductor which is widely used as a material of resistive type gas sensors. A gas sensor using SnO_2 can detect various toxic or flammable gases and can be manufactured into an inexpensive, tiny sensor for the detection of low concentrations. Since the discovery of the catalytic effect of SnO_2 in 1962, a number of studies have been conducted with the aim of improving the sensor's characteristics [14,15]. To improve sensitivity, various noble metals doped materials have been tested. However, the problem in complicated manufacturing process and irreversible characteristic remains. Furthermore, to overcome the limitation of irreversible

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response, trials have been undertaken, for example identifying the optimal heat treatment condition, or the application of a chemically stable material. Nevertheless, low response and reproducibility problems still exist [16–20].

Recently, to overcome these problems, studies have concentrated on modifying the characteristics of materials by manufacturing a composite-material using metal oxide or an organic materials with a various type of carbon based material such as carbon nanotube (CNT) and graphene. One study reported an improvement in the sensitivity and reproducibility of an ammonia gas sensor using the complex materials CNT and polyaniline (PANI), the other study showed an improvement in the sensitivity of ozone and ammonia sensors using SnO_2 decorated CNT. Preparation using the fore and latter mentioned sensors can improve the responsibilities, however, poor response time and an irreversible response were seen [21,22].

In this study, a CNFL/SnO_2 composite gas sensor was fabricated for the detection of ammonia. The reason that the CNFL/SnO_2 composite material was selected because the composite material had a large surface area and numerous electrical contact points which are advantageous characteristics of a good gas sensor. This composite gas sensor was compared with a gas sensor consisting of pristine SnO_2 nanoparticles and a CNFL. The experiment's result showed that the composite material based gas sensor had improvements in sensitivity, reproducibility and response time, which help it overcome the limitations of the conventional pristine material based ammonia gas sensors.

2. Experimental

2.1. Preparation of the carbon nanoflake (CNFL) and characterization

The carbon nanoflake was obtained by a modified electrochemical method, as previously described [23]. In brief, the graphite pencil (Fiber-Castell, Germany) was used as an electrode and source of CNFL for electrochemical exfoliation. The graphite pencil was immersed 2 cm as anode into the 2 M of H_2SO_4 solution and the coil type Pt wire was located side by side to the graphite pencil with a separation of 5 cm. The electrochemical exfoliation process was carried out by applying pulsed DC bias (30 min 1 V, 1 min −10 V) on the graphite pencil. All of these electrochemical exfoliation experiments were performed at room temperature. To prepare the CNFL suspension, the exfoliated CNFL were collected with a 10 nm porous filter and washed with DI water by vacuum filtration. After drying, they were dispersed in dimethyl formamide (DMF) solution by gentle water-bath sonication for 5 min. To remove unwanted large graphite particles produced in the exfoliation, the resultant dispersion was then centrifuged using a centrifuge (MEGA25, Hanil, Korea) for 60 min at 2500 rpm and supernatant was used. Furthermore sample morphology was studied using a high resolution tunneling electron microscopy (HR-TEM, Hitachi, Japan) and field emission scanning electron microscopy (FE-SEM, Hitachi S-4200, Japan) equipped with energy dispersive spectroscopy (EDS). The bonding structure of the sample was examined using a Raman Spectrometer (inVia Raman Microscope, Renishaw, UK) with an Ar laser at the excitation wavelength of 514 nm.

2.2. Sensor preparation and measurement

The gas sensor was manufactured by dropping CNFL/SnO_2 composite solution on the substrate where Pt electrode was pre-patterned on a sapphire. 1 mg of SnO_2 powder and 0.25 mL of DMF, ground in an agate mortar, were mixed to make the composite solution, and 10 μL of the composite solution was dropped using auto-pipette. The substrate was dried at the temperature of 70 °C for over 24 h in a vacuo condition and after that, heated at 600 °C for 12 h using a muffle furnace to eliminate organic binders in a graphite pencil. The manufactured sensors were stabilized for over 12 h under the conditions of 350 °C and 10^{-3} Torr to eliminate moisture and then, sensor response was tested.

The sensing measurement was conducted using a testing apparatus which comprises a gas mixing system, an electrical properties characterization system and a specialized vacuum probe station. The gas mixing system automatically dilutes pre-calibrated mass flow controller (5115E, Brooks, USA) with 10 ms incremental using real-time PXI-based controller (National Instruments, USA). Electrical properties characterization system is consisted with source measure unit (4200SCS, Keithley, USA), which has preamp which is pA level precise measurement is possible and a specialized vacuum probe station can collect electrical signal of a sensor using a manipulator. The temperature controller is supplied electricity using a P.I.D control based external power supply for precise operation of heating mantle (Omniprove VH, Woosin-cryovac, Korea). Sensor response of a sensor was defined by percent change of current when exposed to air and ammonia gas, $\{(I_a - I_g)/I_a\}$*100, where I_a and I_g are the currents in air and in the presence of ammonia, respectively.

3. Result and discussion

3.1. Structure and compositional characterization of materials

The morphology of CNFL was characterized by SEM. As shown in Fig. 1(a), the CNFL presents nearly flake-like shape with a length up to 7 μm and a width of 5 μm. Also, direct morphological observation of the as- prepared SnO_2 NPs attached to the surface of the CNFL was shown in Fig. 1(b). In Fig. 1(b) we can really see bunches of SnO_2 nanoparticles on the surface of the CNFL. The average size of SnO_2 NPs was 30–50 nm. In order to further confirm the

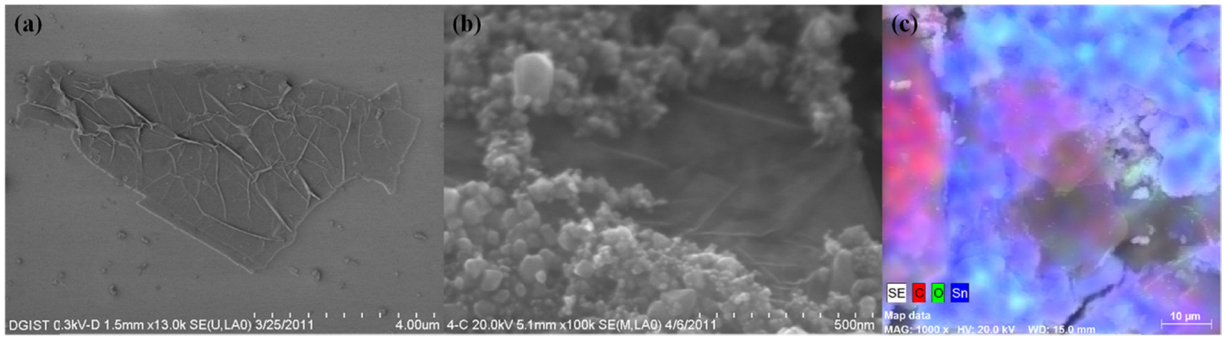

Fig. 1. SEM images show the morphology of the CNFL/SnO_2 on an alumina substrate. (a) Bare CNFL, (b) CNFL/SnO_2 composite and (c) EDS mapping image of CNFL/SnO_2 composite.