Research Article

Improvement of NO Gas Sensing Properties of Polyaniline/MWCNT Composite by Photocatalytic Effect of TiO₂

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The highly sensitive and rapid NO gas sensor was prepared with polyaniline/TiO₂/carbon nanotube composites. Aniline was polymerized on the surface of carbon nanotube (p-type semiconductor) with embedding TiO₂. The gas sensing property was measured by the changes of electrical resistance without or with UV irradiation to investigate the photodegradation of NO by TiO₂. The photo-degraded products such as HNO₂, NO₂, and HNO₃, which were adsorbed on the PANi-coated carbon nanotubes, resulted in the decreased electrical resistance in the p-type semiconductors of carbon nanotube and polyaniline. The advantages of TiO₂ photocatalyst in gas sensing were apparent in the improvement in both sensitivity and response rate.

1. Introduction

The demand of gas sensors has been increased extensively due to the increasing numbers of power plants, waste incinerators, and combustion engines. NO_x gases such as NO, N₂O and NO₂, which produce the nitric and nitrous acids, cause the acid rain and the photochemical smog. These NO_x gases are formed by combustion of fossil fuels at high temperature in the chemical processes. NO_x emissions generally consist of 90–95% NO with the remainder being N₂O, and NO₂ [1–4]. According to the American Conference of Governmental Industrial Hygienist (ACGIH), the threshold limit values (TLV) for NO is 25 ppm [5]. Therefore, the efficient gas sensing materials have been studied widely for the detection of very low gas concentration. Gas sensing materials can be classified mainly into two types, organic and inorganic materials. The metal oxides are used as gas sensing materials for long time due to their relatively low cost, high sensitivities, rapid response times, and simple sensing method. Nevertheless, there still exist some problems such as high working temperature of 150–350°C for SnO₂ and 673–723 K for ZnO causing the practical limits in actual applications [6, 7].

The conducting polymers, which work excellently at room temperature, have attracted much attention as new classes of sensing materials. Among the conducting polymers, polyaniline (PANi) is frequently used because of its ease of synthesis, unique electrical properties, environmental stability (in acidic condition), and intrinsic redox reaction [8]. Conductivity of polyaniline depends on its ability to transport charge carriers along the polymer backbone. However, the problems of conducting polymer as gas sensing materials are their inferiorities in processing ability, chemical stability, and mechanical strength [9]. The heterojunction between organic and inorganic materials has been studied in order to solve the problems in conducting polymers [10].

Carbon nanotubes (CNTs) have the extraordinary electrical and mechanical properties with one-dimensional structure [11]. The large surface area of CNTs is beneficial to the large gas absorptive capacity expecting the faster response and higher sensitivity even at lower operating temperatures [12, 13]. The composites of PANi/CNTs have also been investigated widely as gas sensing materials by many researchers [14–16]. However, these composites still need improvement in both sensitivity and response time to be applied in

highly efficient gas sensor. The main reason is the weak and slow interactions between sensing materials and target gas resulting in the lower sensitivity and slower response.

In this study, the modification of PANi/CNTs sensing materials was carried out with the photocatalyst TiO_2 in order to induce the stronger and faster chemical reactions between target gas and TiO_2 . Upon exposure to UV light, electron-hole pairs are generated in the conduction and valance bands of TiO_2 . Photo-generated holes are strong oxidants (~ 3.0 V) and can completely decompose most pollutants in air and water. NO is oxidized by TiO_2 to nitric acid (HNO_3) in air [17, 18]. The effect of TiO_2 additive on NO gas sensing properties of PANi/CNTs composites was studied in terms of photodegradation reaction, sensitivity, and response of gas sensors.

2. Materials and Methods

2.1. Preparation of PANi/MWCNT/ TiO_2 Composite. Aniline, ammonium persulfate (APS), and hydrochloride (HCl) were obtained from Aldrich. Aniline was distilled in vacuum before use. Multiwalled carbon nanotubes (MWCNTs) (95% purity, average diameter 130 ± 15 nm) were obtained from Aldrich. MWCNTs were used as the template for the in situ polymerization of aniline. The polymerization of aniline was carried out in the distilled water using HCl as oxidant of aniline and APS as initiator. 0.5 g of oxyfluorinated MWCNTs was dispersed in 30 mL water and ultrasonicated for 1 h as explained in our previous works [19, 20]. 0.5 mL of aniline monomer was dropped into the MWCNTs dispersion and stirred continuously for 10 min. 0.5 mL of HCl and 0.2 g of TiO_2 (anatase phase, average particle size < 25 nm, 99.7%, Aldrich) were then added in the aniline/MWCNT mixture. 0.5 g of APS dissolved in 10 mL distilled water was slowly added in the aniline/MWCNT/ TiO_2 mixture to initiate the polymerization. The polymerization was carried out for 6 h at 0°C with constant mechanical stirring. The synthesized PANi/MWCNT/ TiO_2 nanocomposites were filtered and rinsed several times with the distilled water, methanol, and acetone, respectively. The nanocomposite powders were dried under vacuum at 40°C for 24 h. Four different samples were prepared such as PANi, PANi/MWCNT, PANi/ TiO_2 , and PANi/MWCNT/ TiO_2 named as PA, PC, PT, and PCT, respectively.

2.2. Measurement of Gas Sensitivity. In order to evaluate the gas sensing properties of composites, the electrical resistance was measured using a programmable electrometer (Keithley 6514). The gas sensing device was prepared by using two Pt electrodes and a SiO_2 plate as shown in previous work [12, 21]. The electrical resistance was measured in a stainless steel chamber with a volume of 1500 cm^3 . The chamber was connected to gas cylinders (NO and wet air with a relative humidity of 50%), and the gas sensor sample was placed in a sealed vacuum chamber at a pressure of 1×10^{-6} mbar. Air was injected initially into the chamber in order to stabilize the electrical resistance of the sensor. The gaseous mixture containing 25 ppm NO in air was injected into the chamber

at a fixed rate of 500 sccm and the resultant change in the electrical resistance of gas sensor was measured at $22 \pm 1^\circ\text{C}$. The chamber was covered with a circulating water tube in order to maintain a constant temperature. The adsorbed gases on the gas sensor samples were removed by heating the specimens to 100°C at a pressure of 1×10^{-6} mbar for 5 min [12, 21]. Recovery testing was carried out three times.

2.3. Characterization of Samples. Field emission scanning electron microscope (FE-SEM, Hitachi, S-5500) was used to investigate the surface morphology of the prepared gas sensors. SEM images were taken without prior treatment in order to ensure the acquisition of accurate images. X-ray diffraction patterns of the samples were obtained on an XRD apparatus (D/MAX-2200 Ultima/PC, Rigaku, Japan) in order to investigate the phases and crystal structures of TiO_2 .

3. Results and Discussion

3.1. Surface Morphologies of Samples. FE-SEM images of the surface morphologies of samples are presented in Figure 1. PA sample showed the aggregated PANi phases of the uniform-sized spherical type. The average size of PANi spherical phases was measured as 193 ± 27 nm (average value measured five times) by the computer program installed in FE-SEM apparatus. The uniformly coated PANi on MWCNTs was observed for PC sample as shown in Figure 1(b). The average thickness of PANi coating layer was around 23 ± 8 nm considering the average diameter of MWCNTs (130 ± 15 nm). PANi was also coated on TiO_2 particles but was aggregated to some extent as shown in Figure 1(c). PCT sample showed the TiO_2 particles dispersed on the PANi-coated MWCNTs as shown in Figure 1(d).

3.2. XRD Analysis of Samples. XRD patterns of four prepared samples are presented in Figure 2. The original carbon peaks were observed at 002 position which is attributed to the well-oriented carbon structure for MWCNT [22, 23]. PA also showed the original peak of PANi clearly [24]. XRD pattern of TiO_2 showed the characteristics of anatase TiO_2 phase with a tetragonal structure which possessed the photocatalytic properties [25, 26]. All XRD peaks of PCT samples can be attributed to the diffraction of PANi, TiO_2 , and MWCNTs.

3.3. NO Gas Sensing Behavior by Resistive Response. The NO gas sensing behavior of the samples was determined by monitoring the electrical resistance and presented in Figures 3 and 4. The resultant sensitivities were expressed as $S(\%)$ according to the following equation [27, 28]:

$$S(\%) = \frac{(R - R_0)}{R_0} \times 100 = \frac{\Delta R}{R_0} \times 100, \quad (1)$$

where R_0 and R are the resistance measured in air and 25 ppm of NO, respectively. The NO gas sensing behavior in the absence of UV irradiation is shown in Figure 3. The electrical resistance decreased upon NO gas exposure for all the samples in accordance with the typical characteristics of a p-type semiconductor. The decrease in the electrical resistance

FIGURE 1: FE-SEM images of (a) PA, (b) PC, (c) PT, and (d) PCT samples.

FIGURE 2: XRD patterns of the prepared samples.

is attributed to the electron charge transfer between NO gas and the surface of PANi/MWCNT p-type semiconductors. The electrons are known to travel from p-type semiconductor to NO gas (oxidizing gas) resulting in the reduced electrical resistance [29–31]. The TiO_2 photocatalyst did not contribute to the NO gas sensing behavior directly because the metal oxide-based semiconductors were generally operated at high temperature [6, 7]. However, even the composite with n-type semiconductor TiO_2 showed some decrease in the electrical resistance. Among the various gas sensing materials, the highest sensitivity was observed for the PC sample which showed 13% change in the electrical resistance. This high

FIGURE 3: NO gas sensing behavior of various samples in the absence of UV irradiation.

sensitivity was attributed to the interaction of MWCNTs with PANi, leading to the expansion of compact PANi chains into more stretched conformations and resulting in the decrease of electric resistance. The improved gas sensing performance of PANi/CNT composite was also studied by the other group [32].

Totally different trends in the NO gas sensing behavior were observed under UV irradiation as shown in Figure 4. The addition of TiO_2 in the gas sensing material improved the sensitivity of NO gas sensor significantly. PCT sample showed the highest sensitivity indicating 23.5% change in

FIGURE 4: NO gas sensing behavior of various samples under UV irradiation.

the electrical resistance. This result was attributed to the decomposition of NO gas by the photocatalytic reaction of TiO_2 under UV irradiation [30, 33] as follows:

The electrons in TiO_2 are excited from the valence band to the conduction band under UV irradiation, generating the electron-hole pairs, which can recombine or initiate the redox reactions. Holes are trapped by water (H_2O) or hydroxyl groups (OH^-) that are adsorbed on the surface of material, producing the hydroxyl radicals ($\text{OH}^\bullet$). The electrons reduce the adsorbed oxygen, resulting in the formation of superoxide ions ($\text{O}_2^{\bullet-}$). Therefore, OH and O groups on the surface of TiO_2 play an important role in NO adsorption and oxidation [30].

Three different states are observed during the photocatalytic oxidation of NO [34, 35]. The primary oxidation product is HNO_2 in the initial state. In the transient state, HNO_2 is oxidized to NO_2 , which is subsequently oxidized to HNO_3 . As a result, the products of NO decomposition are HNO_2 , NO_2 , and HNO_3 . The photocatalytic decomposition products are adsorbed effectively on the PANi-coated MWCNTs because of the high gas adsorption capacity by high specific surface areas and pore volume of MWCNTs [12, 13] and the hydrophilicity of PANi polymer [36]. Although MWCNT

FIGURE 5: Reproducibility of NO gas sensing behavior of PCT sample under UV irradiation.

provide the high porosity for gas adsorption, its hydrophobicity results in the poor adsorption of hydrophilic gases such as HNO_2 , NO_2 , and HNO_3 . Therefore, the composite with PANi is beneficial for the adsorption of hydrophilic gases resulting in the decreased electrical resistance and the increased sensitivity of gas sensor. The photocatalytic activity of TiO_2 is maximized due to the effective suppression of the electron-hole pairs combination by conductive MWCNT and PANi. The large and rapid changes in electrical resistance upon NO gas adsorption under UV irradiation are attributed to the combination effects of improved conductivity of PANi/MWCNT composite and effective adsorption of photocatalytic decomposition products on MWCNTs.

The decomposition products, which were adsorbed on the sensing materials, were indirectly investigated by monitoring the variation in pH of the desorbing solution. The desorbed acidic HNO_3 may reduce the pH of desorbing solution. The adsorbed products were dissolved in water (20 mL) by putting PCT sample (0.2 g) under agitation at room temperature for 4 h. The pH of PCT suspension changed from 7.2 to 4.8 after desorbing the adsorbed products on PCT sample, indicating that the acidic molecules were adsorbed on the porous MWCNTs.

3.4. Recovery Properties of Gas Sensor. Figure 5 presents the reproducibility of the PCT gas sensor which showed the highest gas sensitivity. Perfect reproducibility was observed for the PCT sample due to the excellent gas desorption properties during the recovery process, which was performed at lower temperature of 100°C . The adsorption of NO gas on the PCT sample with relatively weak interaction was beneficial to the excellent recovery property of gas sensor.

4. Conclusions

The high-performance NO gas sensor was prepared by PANi/MWCNT/ TiO_2 composite using in situ polymerization method. The gas sensing behavior was evaluated by

measuring the changes in electrical resistance upon NO gas adsorption without or with UV irradiation to investigate the photodegradation effects of NO gas by TiO₂. The electrical resistance was decreased by p-type semiconductors of MWCNT and polyaniline. The TiO₂ photocatalyst improved both sensitivity and response of the PANi/MWCNT/TiO₂ gas sensor greatly. The improvement in gas sensing behavior was attributed to the effective photocatalytic decomposition of NO gas into HNO₂, NO₂, and HNO₃ acidic gases by TiO₂ and the effective adsorption on the hydrophilic sites of PANi-coated MWCNTs resulting in the decreased electrical resistance. PANi/MWCNT/TiO₂ gas sensor showed excellent reproducibility in gas sensing behavior during the recovery process at lower temperature of 100°C.

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