



The effect of multiwalled carbon nanotube doping on the CO gas sensitivity of TiO₂ xerogel composite film

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ABSTRACT

A simple sol–gel method was applied for the synthesis of 0.01 wt% multiwalled carbon nanotubes (MWCNTs)-doped TiO₂ xerogel composite film. The film's CO gas sensing properties were then evaluated. Doped MWCNTs were coated with TiO₂ and distributed on a TiO₂ xerogel matrix. The TiO₂ xerogel showed an anatase structure after heat treatment at 450 °C under vacuum. The specific surface area of the composite material was larger than the pure TiO₂ xerogel material. The CO gas sensitivity of the MWCNTs(0.01 wt%)-doped TiO₂ xerogel composite film was found to be seven times higher than that of pure TiO₂ xerogel film and to have good stability. This higher gas-sensing property of the composite film was due to both an increase of specific surface area and the n–p junction structure of the TiO₂ xerogel coated on MWCNTs. The electrons generated from TiO₂ after adsorption of CO gas induces electron transfer from the TiO₂ to the MWCNTs. This induces a characteristic change in the MWCNTs from p-type to n-type, and the resistance of MWCNTs-doped TiO₂ xerogel composite sensor is therefore decreased.

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1. Introduction

Semiconductor gas sensors based on metal oxides are of considerable interest due to their high sensitivity to pollutant gases, low cost, and small size. Various nanostructured metal oxide materials such as SnO₂ [1], WO₃ [2], TiO₂ [3], In₂O₃ [4], and ZnO [5] have been reported to be good candidates for novel semiconductor thin film gas sensors. Among them, TiO₂ is a well-known functional material used in a variety of applications such as photocatalysts, solar cells, batteries, and pigments. An important feature of TiO₂-based gas sensors is that they can be operated at relatively high temperatures as their anatase structural form is chemically stable at elevated temperatures [6]. Various synthesis methods including a wet chemical solution process [7], sol–gel process [8], photolithographic process [9], glancing angle deposition [10], and anodized aluminum oxide templating [11] have been demonstrated as being feasible for the fabrication of nanostructured TiO₂ thin films. The current research aim for TiO₂-based gas sensors is to achieve high stability and high sensitivity with low power consumption.

Aerogels have drawn considerable interest in science and technology arenas because of their low bulk density (up to 95% of their volume is air), low thermal conductivity, and large surface area. Due to their unique porous structure, aerogels have

potential applications as highly efficient insulation materials [12], acoustic impedance coupled materials [13], drug carriers [14], catalysts [14,15], and catalyst carriers [16]. It has been proposed that enhancement of the specific surface area would lead to an increase in the sensitivity of gas sensors, thus a well-dispersed nanostructure might result in an improved sensor [17]. However, due to the high porosity of aerogels, their resistance is also high, thus limiting their use as gas sensors. On the other hand, xerogels have lower porosity than aerogels and may therefore be more useful as gas sensors. The gas sensitivity and response time of TiO₂ thin film gas sensors fabricated using xerogels varies as a function of porosity. Xerogels are synthesized using a sol–gel process, and special drying techniques must be applied to replace the pore liquid with air while maintaining a solid network structure. Supercritical drying is most commonly used for this purpose; however, recently developed methods allow for removal of the liquid at atmospheric pressure after chemical modification of the inner surface of the gels, leaving only a porous TiO₂ network filled with air [18].

Multiwalled carbon nanotubes (MWCNTs) exhibit unique electronic properties, a high aspect ratio, and excellent chemical and environmental stability, all of which makes them ideal candidates for use in nanodevices. Previous research has explored attaching metal or semiconductor nanoclusters onto MWCNTs in the development of new properties and applications [19–21]. In this study, we focus on synthesis using solvothermal drying and spin coating of MWCNTs-doped TiO₂ xerogel composite thin film for the purpose of developing a gas sensor. Investigating the influence of MWCNTs

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on the sensing properties of TiO₂ thin film fabricated using xerogels is critical in the development of nanostructured thin film gas sensors.

2. Experimental details

The synthesis of TiO₂ xerogel followed these key steps: (1) TiO₂ gel formation, (2) solvothermal drying of the gel, (3) annealing of TiO₂ xerogel at 450 °C under vacuum, (4) deposition of powders in film form by spin coating technique, and (5) drying of the film. For comparison, a MWCNTs(0.01 wt%)-doped TiO₂ xerogel sample was prepared under the same conditions with the addition of 0.01 wt% functionalized MWCNTs to TiO₂ sol. Sol-gel synthesis of TiO₂ gel was carried out using titanium isopropoxide (TIP; Sigma Aldrich) as a precursor, isopropanol as a solvent, and nitric acid as a catalyst. After gelation, the white gel was aged at 80 °C for 3 h. This gel was transferred to a Teflon liner, placed in a stainless steel autoclave, and acetone was added for the solvothermal drying process. The gel was heated in the autoclave at 50, 100, and 175 °C for 3, 3, and 12 h, respectively, to obtain TiO₂ xerogel. For comparison, MWCNTs-doped TiO₂ composites were prepared using the same experimental procedure with the addition of 0.01 wt% MWCNTs. MWCNTs prepared by chemical vapor deposition were purchased from Iljin Nanotech Co. Ltd. (Seoul, Korea). For functionalization, the MWCNTs were first suspended in a refluxing nitric/sulfuric acid mixture for 1 h to modify the MWCNTs surface, then rinsed and dried. For the synthesis of the films, as-prepared TiO₂ xerogel powders or MWCNTs-doped TiO₂ xerogel powders were mixed with ethanol, terpineol, and ethyl cellulose. To achieve proper dispersion of the powders, the mixture was sonicated for 30 min and spin-coated on the pre-treated silicon wafer substrates at 2000 rpm for 30 s. In order to guarantee satisfactory adhesion of the films to the substrates, the films were dried at 80 °C for 10 min on a hot plate.

The responses of the fabricated gas sensors to CO gas were measured at 300 °C by monitoring the change in the sensor resistance under gas flow ranging from dry air to 50 ppm CO balanced with dry air. The film resistance was measured under a DC bias voltage of 3 V using a source measurement unit (Keithley 2635a). The ratio $[(R_a - R_g)/R_a]$ was used to evaluate the sensitivity of the samples, where R_a and R_g are the resistances of the sensors exposed to pure air and 50 ppm CO balanced with air, respectively. The microstructures of the films were analyzed by means of scanning electron spectroscopy (SEM). X-ray diffraction (XRD) patterns of the samples were recorded on a Rigaku Ultima diffractometer. BET (Brunauer–Emmett–Teller) and BJH (Barrett–Joyner–Halenda) methods were used to determine the surface area. Chemical bonds were assessed by Fourier-transform infrared spectroscopy (FT-IR).

3. Results and discussion

Fig. 1 shows the FT-IR spectra of pure TiO₂ xerogel film and MWCNTs(0.01 wt%)-doped TiO₂ xerogel film. The MWCNTs/TiO₂ xerogel film spectra shows C–C groups at 1125 cm⁻¹, C–H groups at 1238 cm⁻¹, and H–C–H groups at 2852 and 2923 cm⁻¹ [22]. The C–H and H–C–H bonds resulted from functionalized reaction of MWCNTs, and the C–C bonds are from the MWCNTs themselves. This result demonstrates that functionalized MWCNTs are present in the TiO₂ xerogel.

Fig. 2 shows SEM images of the fracture surface of (a) calcined pure TiO₂ xerogel film and (b) TiO₂ xerogel film doped with 0.01 wt% functionalized MWCNTs. The pure TiO₂ xerogel films have particle sizes between 20 and 40 nm. However, the particle size of TiO₂ xerogel film hybridized with functionalized MWCNTs remained around 20 nm. Due to a usage of nitric/sulfuric acid

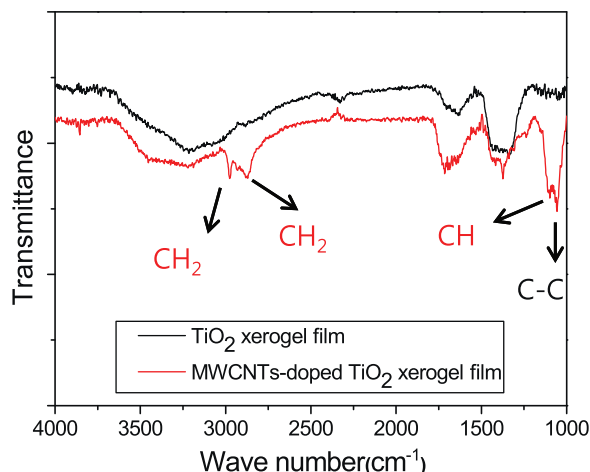


Fig. 1. FT-IR spectra of pure TiO₂ xerogel film and MWCNTs(0.01 wt%)-doped TiO₂ xerogel hybrid film.

mixture for the functionalization of MWCNTs, TiO₂ sol doped with functionalized MWCNTs showed relatively lower pH than pure TiO₂ sol without MWCNTs. In the sol-gel reaction, when the pH is less than 5, the condensation reaction is faster and smaller particle size is obtained [23]. As shown in Fig. 2(b), MWCNTs bundles were imbedded in the TiO₂ xerogel. The MWCNTs were well-dispersed and there was no obvious heavy agglomeration of MWCNTs in the TiO₂ xerogel matrix.

The N₂ adsorption-desorption isotherms of the samples obtained under different conditions are shown in Fig. 3. Fig. 3(a) shows the isotherm of the pure TiO₂ xerogel powder and Fig. 3(b) shows that of the MWCNTs(0.01 wt%)-doped TiO₂ xerogel hybrid powder. The MWCNTs-doped TiO₂ xerogel sample adsorbed a

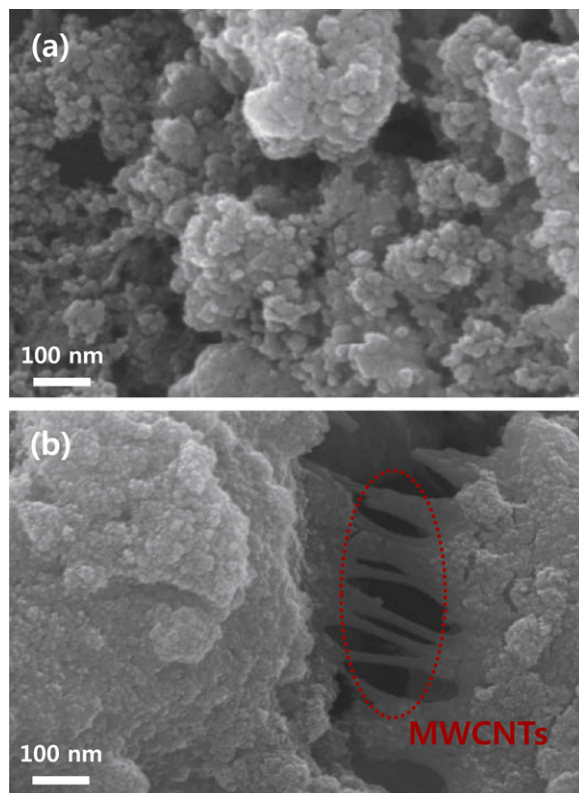


Fig. 2. SEM images of (a) pure TiO₂ xerogel film and (b) MWCNTs(0.01 wt%)-doped TiO₂ xerogel film.

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