Preparation and NH$_3$ Gas-Sensing Properties of Double-Shelled Hollow ZnTiO$_3$ Microrods

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Abstract: A novel double-shelled hollow (DSH) structure of ZnTiO$_3$ microrods was prepared by self-templating route with the assistance of poly(diallyldimethylammonium chloride) (PDDA) in an ethylene glycol (EG) solution, which was followed by calcining. Moreover, the NH$_3$ gas-sensing properties of the DSH ZnTiO$_3$ microrods were studied at room temperature. The morphology and composition of DSH ZnTiO$_3$ microrods films were analyzed using scanning electron microscopy (SEM), transmission electron microscopy (TEM) and X-ray diffractometry (XRD). The formation process of double-shelled hollow microrods was discussed in detail. The comparative gas-sensing results revealed that the DSH ZnTiO$_3$ microrods had a higher response to NH$_3$ gas at room temperature than those of the TiO$_2$ solid microrods and DSH ZnTiO$_3$ microrods did in the dark. More importantly, the DSH ZnTiO$_3$ microrods exhibited a strong response to low concentrations of NH$_3$ gas at room temperature.

Keywords: Double-shelled hollow; ZnTiO$_3$ microrods; NH$_3$ gas sensor; room-temperature

1. Introduction

ZnO and TiO$_2$ films have been extensively studied for use in sensing, but traditional ZnO and TiO$_2$ gas sensors, which are based on ZnO and TiO$_2$ films, can typically only be used at temperatures from 300 to 500 °C [1,2]. Additionally, selectivity is also an important property of metal oxide-based sensors. Several designs of sensors’ construction were proposed for achieving the selectivity of these sensors, such as directly doping small amounts of noble metals (Au, Pd, and Pt), a suitable filter containing the noble metal catalysts method, and nano-carbon-based composite materials film [3–6]. ZnO and TiO$_2$ are well known inorganic photocatalysts, so that ultra-violet (UV) irradiation has been used to reduce the operating temperature of these sensors [7–10]. ZnO–TiO$_2$ binary oxide systems have a better photocatalytic performance than single systems [11]. The ZnO-TiO$_2$ binary oxide system had three compounds: they are ZnTiO$_3$ (cubic, hexagonal), Zn$_2$TiO$_4$ (cubic, tetragonal) and Zn$_2$Ti$_3$O$_8$ (cubic) [12–18]. ZnTiO$_3$ has attracted particular interest because of its potential for use in the photocatalysis of the degradation of organic pollutants, and in adsorption and microwave devices [18–20]. Numerous reports have revealed that ZnTiO$_3$ has favorable photocatalytic properties in visible light [21–24], favoring its use for gas sensors at room temperature [25]. Yadav et al. [25] fabricated a ZnTiO$_3$ nanopowders film using a physicochemical method for sensing liquefied petroleum gas (LPG) at room temperature. Ippolito et al. [26] fabricated an acetone gas sensor that was made of ZnTiO$_3$ nanoarrays using a hydrothermal method. The limit of detection (LOD) of this sensor under light and at 350 °C was 10 ppb.

One-dimensional (1D) nanostructured materials such as tubes, wires, belts, and rods have great potential for use in gas sensors, not only because of their excellent optical, electrical, and mechanical properties, but also because of their efficiency and activity sites, which are caused by their high porosity and large surface area [18,27]. Hollow micro/nanostructures have also attracted enormous interest because of their many hollow cavities, which make the surface area of hollow structures...
significantly greater than that of their solid counterparts [28]. In recent decades, many methods have been used to prepare ZnTiO$_3$ nanopowders, such as the conventional solid-state reaction, the molten salt method, the sol-gel method, the chemical bath deposition and the hydrothermal method [13–16,29–31]. The physicochemical properties of ZnTiO$_3$ nanopowders depend on their morphology, the size of the crystallites, and the crystallographic structure. Recently, Chi et al. [18] fabricated pristine solid ZnTiO$_3$ microrods, and You et al. [32] fabricated a reduced graphene oxide decorated solid ZnTiO$_3$ microrod composite using the polyvinylpyrrolidone (PVP)-assisted sol-gel method for use in the photo-degradation of rhodamine B. However, no attempt has been made to prepare a double-shelled hollow (DSH) structure of ZnTiO$_3$ microrods and to study their NH$_3$ gas-sensing properties at room temperature.

Ammonia (NH$_3$) is known to be highly hazardous to the environment and the human body because of its high toxicity. Accordingly, the fabrication of NH$_3$ gas sensors that can be used at room temperature, with a high response and a low production cost, has attracted much attention. In this work, a novel room-temperature NH$_3$ gas sensor with a high sensitivity, based on novel DSH ZnTiO$_3$ microrods, was fabricated. DSH ZnTiO$_3$ microrods were prepared using a self-templating approach, by heating sol-gel derived Zn-Ti glycolates with poly(diallyldimethylammonium chloride) (PDDA) in an ethylene glycol (EG) solution and then calcining. This method is very simple, has a low production, and does not involve heterogeneous coating, so it can be easily scaled up for the fabrication of sensors. A plausible process for the fabrication of DSH structures is proposed. X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), selected-area electron diffraction (SAED), and energy dispersive X-ray (EDX) analysis were used to characterize the composition and morphologies of the DSH ZnTiO$_3$ microrods. The NH$_3$-sensing properties of DSH ZnTiO$_3$ microrods at room temperature, including the sensing response, sensing linearity, selectivity, response/recovery times, repeatability, stability, and sensing mechanism, were also studied.

2. Experimental Methods

2.1. Materials

The following chemicals were used as received without further purification: titanium (IV)-ethylhexanoate (Ti[(OOCCH(CH$_2$)$_4$(CH$_3$)$_2$])$_4$ (TE, Alfa Aesar), zinc acetate dehydrate (Zn(OAc)$_2$·2H$_2$O; Sigma-Aldrich, St. Louis, MO USA), ethylene glycol (EG, J. T. Baker), poly(diallyldimethylammonium chloride) (PDDA, molecular weight (Mw) = 200,000–350,000, Aldrich).

2.2. Fabrication of Gas Sensors Based on DSH ZnTiO$_3$ Microrods and Measurement of Their Sensing Properties

1.25 g TE, 0.25 g Zn(OAc)$_2$·2H$_2$O and 0.3 mL PDDA were added to a 10 g EG solution, which was then stirred at 190 °C for 1.5 h. An as-prepared precursor solution (PDDA-Zn-Ti-glycolates rods precursor) was drop-coated on an alumina substrate with interdigitated electrodes (IDE). The system was then calcined at 500 °C for 4 h at a heating rate of 5 °C min$^{-1}$ for decomposing the matrix polymer and organic groups, and for oxidizing and crystallizing the Zn-Ti-glycolates. Figure 1a shows a picture of the structure of the as-prepared NH$_3$ gas sensors. The preparation and characterizations of the TiO$_2$ solid microrods were completed according to our previous report [33].

The electrical and NH$_3$ gas-sensing characteristics of the DSH ZnTiO$_3$ microrods were measured using a bench system, as shown in Figure 1b. The volume of the bench system is 18 L. A Direct current (DC) mode was used to measure the resistance of the as-prepared sensors. A power supply (GW, PST-3202) applied a fixed 5 V to the sensor circuit. A DAQ device (NI, USB-6218) was used to measure the resistance of the sensor in various concentrations of NH$_3$ gas. A standard 1000 ppm NH$_3$ gas in N$_2$ gas (Shen Yi Gas Co., Taiwan) was used to prepare the required various NH$_3$ gas concentrations. The desired various gas concentrations were prepared by diluting the known volume of standard NH$_3$ gas with dry air, and were calibrated by a standard gas sensor system (Dräger, MiniWarn). A fan was used to disperse the testing gases inside the bench system and was purged with air. All
Experiments were measured at room temperature (about 23.0 ± 1.5 °C) and the relative humidity at 45% RH. The response (S) of the sensors was calculated according to Equation (1):

$$S(\%) = \frac{(R_{\text{air}} - R_{\text{gas}})}{R_{\text{air}}} \times 100\%.$$  

$R_{\text{air}}$ and $R_{\text{gas}}$ are the electrical resistances of the sensor in the air and testing gas at the exposure time of 300 s, respectively.

2.3. Characterization of DSH ZnTiO$_3$ Microrods

The composition and morphologies of the DSH ZnTiO$_3$ microrods film coated on an alumina substrate were investigated using X-ray diffraction (XRD) using Cu K$_\alpha$ radiation (Shimadzu, Lab XRD-6000), scanning electron microscope (SEM, JEOL JSM-5310), transmission electron microscopy (TEM, JEM-1400; JEOL, Tokyo, Japan), selected-area electron diffraction (SAED) and energy dispersive X-ray (EDX) analysis.

3. Results and Discussion

3.1. Characteristics of DSH ZnTiO$_3$ Microrod Film

3.1.1. XRD Characterization of DSH ZnTiO$_3$ Microrods

Figure 2a,b presents the XRD spectra of the DSH ZnTiO$_3$ microrods that were calcined at 500 °C for 4 h and without calcining, respectively. The reflections at (220), (311), (400), (511) and (440) agree closely with the cubic crystal phase of ZnTiO$_3$. No peak that corresponded to the TiO$_2$, ZnO or zinc titanates, all of which are associated with other stoichiometries, was observed. These results are consistent with the literature [18,32]. The XRD results further verified that the formation and crystallinity of the as-prepared ZnTiO$_3$ at temperatures as low as 500 °C were attributable mainly to the short diffusion paths of metal ions during the heat treatment of the PDDA-Zn-Ti-glycolates rods as the precursor in the polyol processing [14]. Additionally, the diffraction peaks of the DSH ZnTiO$_3$ microrods without calcining were unobvious and broad, indicating a poor crystalline structure (Figure 2b).
Figure 2. The XRD patterns of the DSH ZnTiO₃ microrods that were fabricated via the self-templating approach, followed (a) by calcining and (b) without calcining.

3.1.2. SEM and TEM Analyses of Morphology of DSH ZnTiO₃ Microrod Film

Figure 3 presents the SEM images of the partially DSH ZnTiO₃ microrod film that was prepared by the self-templating approach, which was followed by calcining. Figure 3a reveals the presence of clearly regular microrods, which had aggregated into bundles. The high-magnification SEM image of the DSH ZnTiO₃ microrods (Figure 3b) shows that the microrods were linked together in an interconnected porous network structure. The length and diameter of the DSH ZnTiO₃ microrods were about 3~6 µm and 0.25~0.45 µm, respectively. The microrod structure had round and narrow tips and open ends (indicated by arrows). Figure 4 presents the TEM images of the DSH ZnTiO₃ microrods that were synthesized by PDDA-assisted self-templating. The low-magnification TEM image of a single DSH ZnTiO₃ microrod (Figure 4a) shows a partially hollow structure at its end. The higher-magnification TEM image of the selected area in Figure 4a indicates that the ZnTiO₃ microrods had a double-shelled structure (indicated by arrows) (Figure 4b). The shell was thin, and the internal diameter of the hollow rod was about 0.23 µm. The high-resolution TEM (HRTEM) image of the DSH ZnTiO₃ microrods indicates that the lattice spacing of the adjacent lattice planes was about 0.27 nm, consistent with the (220) crystal plane of cubic ZnTiO₃ (Figure 4c). The SAED pattern (inset in Figure 4c) confirms that the microrods comprised cubic ZnTiO₃ consistent with the relevant XRD results. To further investigate the composition of the DSH ZnTiO₃ microrods, EDX elemental mapping and an elemental analysis (Figure 4e) were conducted. The EDX elemental mapping (Figure 4d) suggested the presence of Zn, Ti, and O only in the DSH ZnTiO₃ microrods. The EDX elemental analysis (Figure 4e) revealed an atomic ratio of Zn to Ti of close to 1:1, revealing a close match with the stoichiometric composition.
Figure 3. The SEM images of the DSH ZnTiO₃ microrods that were fabricated via the self-templating approach, followed by calcining: (a) low magnification and (b) high magnification.
**Figure 4.** The TEM images of the DSH ZnTiO$_3$ microrod: (a) low-magnification TEM, (b) high-magnification TEM, (c) HRTEM (the inset is the corresponding SAED pattern), (d) EDX elemental maps and (e) EDX spectrum.

Figure 5 presents a plausible synthesis of the DSH ZnTiO$_3$ microrods. First, chain-like sol-gel-derived Zn-Ti-glycolates were formed by heating in an EG solution. EG is well known to serve as a complexing agent in the formation of Zn-glycolate and Ti-glycolate from Zn$^{2+}$ and Ti$^{4+}$ ions (path (1)) [34], respectively. The Zn-glycolate was then intercalated with Ti-glycolate, forming chain-like Zn-Ti-glycolates, similar to those described elsewhere [34–36]. Then (path (2)), during the sol-gel process, PDDA was adsorbed on the surface of these chain-like Zn-Ti-glycolates by electrostatic attraction at a high temperature, forming hollow PDDA-Zn-Ti-glycolates rods as a precursor. In the cooperative assembly process, PDDA exhibited the dual action of protecting and etching. PDDA molecules were wrapped outside the chain-like Zn-Ti-glycolates in the initial stage of heating, protecting them in a stable shell. Since the PDDA (with quaternary amines) was coated on the surfaces of chain-like Zn-Ti-glycolates, the increase in the amount of counterions (OH$^{-}$) nearby increased the local alkalinity and facilitated etching accordingly. Hollow PDDA-Zn-Ti-glycolates rods were thus formed as a precursor [28,37]. Additionally, if many of the surface Zn-Ti-glycolates rods became covered by PDDA, the penetration of etching species into the interior of the Zn-Ti-glycolates rods was prevented, and no hollow structure was formed. Finally (path (3)), the hollow PDDA-Zn-Ti-glycolates rods as the precursor underwent a post-calcination treatment at a high heating rate (5 °C min$^{-1}$). The outmost PDDA-Zn-Ti-glycolates layer with a limited thickness was concentrated; the outermost ZnTiO$_3$ shell was degraded and oxidized; and the inner PDDA-Zn-Ti-glycolates layer was contracted. Thereafter, the outermost ZnTiO$_3$ shell separated from the shrinking internal PDDA-Zn-Ti-glycolates layer. Subsequently, the inner ZnTiO$_3$ shell formed in the same way until the organic groups in the precursor PDDA-Zn-Ti-glycolates burned out [38]. As a result, DSH ZnTiO$_3$ microrods were formed.

\[ 	ext{H}_2\text{O} + \text{Ti}[(\text{OOCCH}_2\text{CH}_3)_n\text{CH}_2\text{COO}]_4 \xrightarrow{190^\circ C} \text{H}_2\text{O} + \text{Ti} + \text{Zn} \]

(1)

\[ \text{H}_2\text{O} + \text{Ti} + \text{Zn} + \text{PDDA} \xrightarrow{190^\circ C} \text{H}_2\text{O} + \text{Ti} + \text{Zn} + \text{PDDA} \]

(2)

**Figure 5.** Schematic illustration of the fabrication of DSH ZnTiO$_3$ microrods by the self-templating approach.
3.2. NH3 Gas-Sensing Properties of DSH ZnTiO3 Microrod Film

Figure 6 presents the responses (S) of the TiO2 solid microrods, ZnTiO3 powders, DSH ZnTiO3 microrods, and DSH ZnTiO3 microrods in the dark, to 100 ppm of NH3 gas at room temperature. The response (S) values for the TiO2 solid microrods, ZnTiO3 powders, DSH ZnTiO3 microrods, and DSH ZnTiO3 microrods in the dark were 16.17, 17.75, 45.32, and 21.07, respectively. The DSH ZnTiO3 microrods exhibited a stronger response (S) than those of the TiO2 solid microrods and ZnTiO3 powders, and the DSH ZnTiO3 microrods in the dark. This result may be attributable to the fact that the DSH ZnTiO3 microrods exhibited a higher surface area, larger pores, and a greater total pore volume than the TiO2 solid microrods and ZnTiO3 powders did. Moreover, the fact that ZnTiO3 exhibited a higher response in the visible light than in the dark may be attributable to the fact that the DSH ZnTiO3 microrods had a good photocatalytic activity in the visible light [39,40]. Figure 7a presents the dynamic responses (S) of the DSH ZnTiO3 microrods to various concentrations of NH3. They exhibited a response (S) of 5.1%, even to a low NH3 testing concentration of 1 ppm. The limit of detection (LOD) was estimated at the lower calibration point of 1 ppm by considering a S/N of 3. The LOD was 0.45 ppm. Figure 7b presents the linear dependence of the response (S) of the DSH ZnTiO3 microrods on the concentration of NH3 gas. The sensitivity (S) is obtained from the slope of the linear sensing curve. The linear sensing properties in the ranges of 1 to 20 ppm and 20 to 200 ppm of NH3 gas differed. The sensitivity at 5 to 150 ppm of NH3 gas was larger than that at 150 to 300 ppm, and a rapid decrease in the slope was observed from 20 to 200 ppm of the NH3 gas. This result was related to the synergistic effect of the surface area and the photocatalytic activity of the DSH ZnTiO3 microrods. As the concentration of NH3 increased to 20–200 ppm, the number of active sites for adsorption decreased, causing a rapid decline in the slope. Figure 8 plots the real-time resistance of the DSH ZnTiO3 microrods to 5 ppm of NH3 over time. The response time (ResT90) and recovery (RecT90) times are calculated as the time taken for the resistance of the sensor to change by 90% of its maximum change after the exposing time of the NH3 gas at 300 s. The response (ResT90) and recovery (RecT90) times of the DSH ZnTiO3 microrods were 93 and 363 s, respectively. Figure 9 plots the response and recovery times as a function of the NH3 gas concentration. The recovery time increased with an increasing NH3 gas concentration. The rather long recovery time was attributable to the hollow interior cavities of the DSH ZnTiO3 microrods. The sensor also exhibited a good reversibility. Figure 10 plots the effect of the ambient humidity on the response (S) of the DSH ZnTiO3 microrods. The response (S) of the DSH ZnTiO3 microrods decreased with an increase in the ambient humidity, with measurements at testing concentrations of NH3 of 5 ppm. This result was reasonable because the physisorbed water occupied the active sites of the DSH ZnTiO3 microrods. Figure 11 plots the results concerning the interfering effects of CO, H2, NO2, NO, and SO2 gases on the DSH ZnTiO3 microrods. These interfering gases may be regarded as having unobvious interference effects with NH3 at 100 ppm. However, NO2 and NO gases detectably interfered with NH3 at less than 5 ppm. Figure 12 plots the long-term stability of the DSH ZnTiO3 microrods. The mean response (S) of the DSH ZnTiO3 microrods to 50 ppm and 5 ppm NH3 gas for 68 days were 49.11 and 17.34, respectively. The response drift for 68 days was calculated as the relative standard deviation (RSD). The RSD for the DSH ZnTiO3 microrods to 50 ppm and 5 ppm NH3 gas were 6.5% and 8.3%, respectively. The relative standard deviation (RSD) of the response (S) of the DSH ZnTiO3 microrods to 50 ppm NH3 gas was 6.0%, indicating its favorable repeatability. The NH3 gas-sensing properties of the presented NH3 sensor was compared with those of sensors in the literature, as shown in Table 1 [41–46]. The DSH ZnTiO3 microrods had the lowest detection limit for sensing NH3 gas at room temperature.
Figure 6. The response (S) of intrinsic TiO₂ microrods, ZnTiO₃ powders, DSH ZnTiO₃ microrods, and DSH ZnTiO₃ microrods in the dark, in 100 ppm NH₃ gas at room temperature.

Figure 7. (a) The response (S) of the DSH ZnTiO₃ microrods to various concentration of NH₃ gas at room temperature, and (b) the linear dependence of the response (S) of the DSH ZnTiO₃ microrods on the concentration of NH₃ gas at room temperature. The sensitivity (ΔS/ΔC) is determined from the slope of the linear curve.

Figure 8. The response and recovery of the DSH ZnTiO₃ microrods to 5 ppm NH₃ at room temperature.
Figure 9. The response and recover times vs. the NH₃ gas concentration. (■) response time and (▲) recovery time.

Figure 10. The effect of the ambient humidity on the response (S) of the DSH ZnTiO₃ microrods.

Figure 11. The response (S) of the DSH ZnTiO₃ microrods to various gases.
Figure 12. The long-term stability of a NH₃ gas sensor based on DSH ZnTiO₃ microrods (dotted line as the average response (S) value). (■) 50 ppm and (▲) 5 ppm NH₃ gas.
Table 1. Comparison of the performance of the NH₃ gas sensor developed herein with the literature.

| Sensing Material                    | Operating Temperature (°C) | Detection Limit (ppm) | Response/Recovery Time (s) | References |
|-------------------------------------|----------------------------|-----------------------|---------------------------|------------|
| TiO₂                                | 25                        | 5                     | 34/90                     | [41]       |
| TiO₂ microspheres/RGO               | 25                        | 5                     | −/−                       | [42]       |
| TiO₂/RGO                            | 25                        | −                     | 55/−                      | [43]       |
| ZnO/NiO                             | 25                        | 15                    | 20/90                     | [44]       |
| ZnO/Pd                              | 200                       | 30                    | 198/334                   | [45]       |
| Pd NPs/TiO₂ MRs/RGO                 | 25                        | 2.4                   | 420/3000                  | [46]       |
| DSH ZnTiO₃ microrods                | 25                        | 1                     | 93/363                    | This work  |
3.3. Electrical Properties and NH₃ Gas-Sensing Mechanism of DSH ZnTiO₃ Microrod Film

Figure 13 plots the real-time resistance of the DSH ZnTiO₃ microrod film as a function of time for various concentrations of NH₃. The resistance of the DSH ZnTiO₃ microrod film herein was reduced by exposure to NH₃ gas (electron-donating). Accordingly, the prepared DSH ZnTiO₃ microrod film had the electrical property of an n-type semiconductor. Therefore, the changes in resistance of the DSH ZnTiO₃ microrod film by exposure to NH₃ gas have been suggested from the reports of Hieu et al. [47], Gupta et al. [48], and Shi et al. [49], as illustrated in Equations (2)–(4) [47–49]:

\[ \text{O}_2(g) + e^- \rightarrow \text{O}_2(ads), \quad (2) \]

\[ \text{NH}_3(g) \rightarrow \text{NH}_3(ads), \quad (3) \]

\[ 4 \text{NH}_3(ads) + 3 \text{O}_2(ads) \rightarrow 2 \text{N}_2 + 6 \text{H}_2\text{O} + 6 e^- \]. \quad (4)

First, the atmospheric oxygen adsorbed electrons from the conduction band of the surface of the DSH ZnTiO₃ microrod film, forming O₂(ads)(Equation (2)). Then, the adsorption of electron-donating NH₃ gas molecules interacts with pre-adsorbed oxygen ions (O₂(ads)⁻) and releases electron carriers into the n-type DSH ZnTiO₃ microrod film, causing its electrical resistance to decrease, while increasing the concentration of NH₃ gas (Equations (3) and (4)). From all of the above, two main effects are proposed to explain why the DSH ZnTiO₃ microrod film had the strongest response (S). First, the DSH ZnTiO₃ microrods had hollow cavities, and their consequently large surface area favored NH₃ gas adsorption. Second, the fact that the response of the DSH ZnTiO₃ microrod film in light was stronger than in the dark is directly related to its photocatalytic activity. In the presence of sunlight, electrons were photo-excited from the valence band to the conduction band of the DSH ZnTiO₃ microrods, and these photo-generated electrons at the surface of the DSH ZnTiO₃ microrods were then transferred to the adsorbed oxygen, increasing the adsorbed oxygen ions, favoring the chemisorption of NH₃, and thereby improving the response of the DSH ZnTiO₃ microrods [28, 29, 33, 34].

![Figure 13. The real-time resistance of DSH ZnTiO₃ microrods as a function of time (s) toward different NH₃ concentrations from 1 to 200 ppm.](image)

4. Conclusions

Novel DSH structures of ZnTiO₃ microrods were fabricated via a PDDA-assisted self-templating approach in an EG solution and were then calcined. The synergistic surface-protecting and core-etching of chain-like Zn-Ti-glycolates by PDDA explains the formation of double-shelled hollow structures of the ZnTiO₃ microrods. The ZnTiO₃ microrods exhibited a strong response to low concentrations of NH₃ gas at room temperature, including a good sensitivity (5.1%) at 1 ppm NH₃, a
good linearity ($Y = 1.5575 X + 7.5526; R^2 = 0.9068$) at 1–20 ppm NH$_3$, a fast response time (93 s), a good repeatability, a good reversibility, a high selectivity, and a good long-term stability (at least 68 days).

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