SO$_2$-sensing properties of NiO nanowalls synthesized by the reaction of Ni foil in NH$_4$OH solution

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Abstract
Nickel oxide (NiO) is a p-type metal-oxide semiconductor with wide-ranging applications. Recent studies have focused on the gas-sensing properties of this semiconductor. This study introduces an easy process for growing NiO nanowalls on a glass substrate using Ni foil and aqueous NH$_4$OH. The morphology and structure of the NiO nanowalls are investigated and confirmed by field-emission scanning electron microscopy and x-ray diffraction (XRD) analyses. The gas-sensing properties of the prepared nanowalls are tested using a dynamic gas-testing system wherein the target gases are H$_2$S, NO$_2$, NH$_3$ and SO$_2$. Gas-sensing data show that the synthesized NiO nanowalls are highly responsive toward SO$_2$. Additionally, a sensing device prepared based on the NiO nanowalls is found to be stable during measurements, exhibiting a linear variation with changes in SO$_2$ concentration.

Keywords: NiO, nanowalls, gas sensors, surface reactions

Classification numbers: 4.00, 4.14, 5.00, 6.00, 6.08

1. Introduction
Nickel oxide (NiO) is a $p$-type semiconductor with a wide bandgap energy of 3.6–4.0 eV. NiO is a stable $p$-type metal oxide with high carrier transport performance [1, 2] and thus has wide-ranging applications, such as in lithium-ion batteries [3], supercapacitors [4], biosensors [5], and catalysts for water splitting [6]. Moreover, many groups claim that NiO nanomaterials exhibit excellent sensing properties toward formaldehyde, H$_2$S, ethanol, NH$_3$, H$_2$, and NO$_2$ [1, 2, 7–9]. However, studies on the SO$_2$-sensing behavior of NiO nanostructures are few.

NiO nanomaterials with wall-plate-like morphologies are predominantly synthesized [10–13] among others (e.g. nanorods, nanowires, nanoflowers, and nanotubes) [14–17]. Several groups introduce different approaches for the synthesis of NiO nanowalls on Ni metal surfaces. Zhan et al synthesized 3D NiO nanowalls on a Ni foam through a hydrothermal method [10]. Tang et al [13] used electrochemical corrosion approach to prepare NiO nanowalls grown on a Ni foam. Ni et al introduced an easy electrochemical corrosion method to fabricate NiO nanowalls [18]. NiO nanowalls can also be prepared by plasma-assisted oxidation [19]. Recently, our group introduced an easy, low-cost method of synthesizing Ni(OH)$_2$/NiO nanowalls through the surface reaction of Ni foil in aqueous NH$_4$OH [20]. Nonetheless, the gas-sensing properties of the NiO nanowalls fabricated by these methods remain lacking. The advantage of NiO nanowalls over other morphologies like nanowire, nanoparticles or nanosheets is to provide better film porosity which can enhance the adsorption and desorption processes of the target gases over the film surface.

In this study, Ni(OH)$_2$ nanowalls were fabricated through the chemical reaction of Ni foil with aqueous NH$_4$OH. The NiO nanowalls were obtained by dehydrating the Ni(OH)$_2$ nanowalls at 500°C using a hotplate. The SO$_2$, NO$_2$, NH$_3$
The sensing properties of the as-prepared NiO nanowalls were investigated and compared at a working temperature of 50 °C – 300 °C.

2. Experimental details

We used a facile method in our previous study to synthesize the NiO nanowalls using a Ni foil [20]. Figure 1 illustrates our synthesis process. Commercial pure Ni foil (thickness = 0.1 mm; purity = 99.99%; Aldrich) was cut into a 2 cm × 2 cm plate (figure 1(a)). The plate was immersed in acetic acid for 10 min and then ultrasonically cleaned in a bath sonicator with acetone, ethanol, and distilled water for 5 min. After drying under a flow of N2, the plate was folded at the corners to form table-like plate and was added to 25 ml of NH4OH solution in a 100 ml Duran laboratory bottle (figure 1(b)). Meanwhile, a cleaned glass (2 cm × 2 cm) was positioned under the plate. The Duran bottle was kept at 70 °C for 48 h in an oven. After treatment, the glass substrate was covered by a green film (figure 1(c)), dried in an oven at 70 °C for 12 h, and annealed at 500 °C for 1 h using a hotplate. As a result, the green film became a dark brown film (figure 1(d)). A simple parallel Au electrode was patterned on the film by thermal evaporation (figure 1(e)).

The morphologies of samples were characterized by field-emission scanning electron microscopy (FESEM; JEOL JSM-7610F). The structures of the samples were identified using x-ray diffraction (XRD; XPERT-PRO) with Cu Kα radiation of λ = 1.5418 Å. The NiO nanomaterial was extracted from the annealed sample and was dispersed on a molybdenum grid for transmission electron microscopy (TEM; Philips Telnai G2F20 S-TWIN) observations. The gas-sensing properties of the as-synthesized materials were measured using a dynamic gas-testing system. During measurement, the chamber was pumped and was maintained at a vacuum pressure of 10 Torr. The carrier gas was dry air and the total flux rate was 200 sccm. The operating temperature was from 50 °C to 300 °C (300 °C is the maximum value of our gas-testing system). Gas response was defined as $S = \frac{R_g - R_a}{R_a} \times 100\%$, where $R_g$ and $R_a$ represent sensor resistance in the target gas and air, respectively. Sensor response ($\tau_{Response}$) and recovery time ($\tau_{Recovery}$) are determined by the time for sensor resistance to reach 90% of its steady-state value from $R_a$ to $R_g$ and $R_g$ to $R_a$, respectively.

3. Results and discussion

Figure 2 shows the XRD patterns of the films before and after annealing at 500 °C for 1 h.

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### Table 1. Comparison of NiO nanowall-based SO2 sensor and other reported SO2 sensors.

| Material                     | Operating temperature (°C) | SO2 concentration (ppm) | Gas response | Response time (s) | Recovery time (s) | LOD  | Ref.       |
|------------------------------|----------------------------|-------------------------|--------------|-------------------|-------------------|------|------------|
| BiFeO3 nanoparticles         | 300                        | 5                       | 2.03         | 20                | 50                | 5 ppm| [25]       |
| Graphene oxide + SnO2 nanocomposites | 60                         | 10                      | 1.25         | ~10%              | ~150              | ~150 | 10 ppm    | [26]       |
| Ru/Al2O3/ZnO nanocomposites  | 350                        | 5                       | ~10%         | 60                | 360               | 5 ppm| [27]       |
| TiO2 nanotubes               | 200                        | 10                      | ~15%         | ~100              | ~100              | 10 ppm| [28]       |
| SnO2 thin film               | 180                        | 500                     | 55           | 80                | 70                | 50 ppm| [29]       |
| WO3 nanoparticles            | 260                        | 5                       | ~1.18        | ~180              | ~600              | 5 ppm | [30]       |
| SnO2 nano-dodecahedrons      | 183                        | 5                       | 1.5          | ~10               | ~15               | 200 ppb| [31]       |
| NiO nanowalls                | 300                        | 5                       | 4%           | 40                | 57                | 1 ppm | This work |

Figure 1. Experimental process model. (a) Ni foil, (b) Ni foil and glass substrate treated in NH4OH, (c) glass substrate after treatment, (d) glass substrate after annealing at 500 °C for 1 h, and (e) Au electrode patterned on the annealed substrate.

Figure 2. XRD patterns of the treated glass substrate (a) before and (b) after annealing at 500 °C for 1 h.
(001), (110), (111), and (301) planes of 3Ni(OH)\_2·2H\_2O [JCPDS file no. 00-022-0444, hexagonal structure, space group P–31 m (162)] (figure 2(a)). Minor peaks at 2\(\theta\) values of 19.4\(^{\circ}\), 32.5\(^{\circ}\) and 70.9\(^{\circ}\) correspond to (001), (100), and (103) planes of Ni(OH)\_2 [JCPDS file no. 00-014-0117, hexagonal structure, space group P–31 m (164)]. No other impurities form in the film. Figure 2(b) shows the XRD pattern of the annealed film, indicating that Ni(OH)\_2 was transformed to NiO. The peaks located at 36.8\(^{\circ}\), 42.8\(^{\circ}\) and 62.1\(^{\circ}\) well agree with (101), (012), and (110) planes of NiO [JCPDS file no. 98-016-6115, hexagonal structure, space group R–3 m (166)]. In this pattern, the second phase of Ni\(_3\)O\(_2\)(OH)\(_4\) [JCPDS file no. 00-006-0144, hexagonal structure] is also detected by the existence of (100), (006), and (105) planes at the diffraction peaks of 34\(^{\circ}\), 37.1\(^{\circ}\) and 46.2\(^{\circ}\), respectively. The board peaks observed in both patterns suggest that the film is composed of small crystallites. The crystallite size of NiO calculated through the Scherrer equation \[21\] with the 2\(\theta\) of 62.1\(^{\circ}\) is 2.2 nm.

The surface morphologies of the film before and after annealing at 500 °C for 1 h were similar (figures 3(a) and (c)). The films comprise curvy nanowalls with an average thickness of 15 nm. Cross-sectional FESEM images indicated that the thickness of both films is ~1450 nm (figures 3(b) and (d)). The sample before annealing (figure 3(b)) comprises a film layer (~314 nm) and a nanowall layer (~1122 nm). The sample after annealing is dense with a nanowall thickness of approximately 561 nm (figure 3(d)).

The synthesis of NiO nanowalls, in which Ni can react with NH\(_4\)OH to form Ni(OH)\(_2\), which was dispersed in the solution, was proposed in our previous study \[20\]. The nanowalls are probably formed by an oriented assembly of Ni(OH)\(_2\)\(^{2-}\) units onto the Ni(OH)\(_2\) nanoseeds. The transformation from Ni(OH)\(_2\) to NiO without morphology change at 500 °C is well documented \[20, 22, 23\].

Figures 4(a) and (b) show the TEM and HR-TEM images of the extracted NiO nanowalls, respectively. The nanowalls were composed of many small crystallites (figure 4(b)). The dimensions of all crystallites are analyzed in a histogram graph (figure 4(c)). The average diameter of the crystallites is 2.2 nm, which is similar to the calculated value using the XRD pattern equation above.

Figure 5 shows the gas responses of the as-prepared NiO nanowalls toward H\(_2\)S, NO\(_2\), SO\(_2\) and NH\(_3\). The device is highly sensitive to SO\(_2\). The SO\(_2\) response of the device gradually increases from 6.3% at 100 °C to 8.7% at 250 °C and saturates to 8.8% at 300 °C. The optimal operating temperature of the NiO nanowalls was 200 °C to H\(_2\)S and NO\(_2\) and 100 °C to NH\(_3\). Figure A1 (appendix) shows the transient curves of the device at different operating temperatures. The positive response of the device to reduced gases (H\(_2\)S, NO\(_2\) and SO\(_2\)) and to oxidizing gas (NO\(_2\)) suggests that the NiO nanowalls exhibit a p–type semiconductor sensing characteristic. The gas-sensing mechanisms of NiO to both types of gases are well documented \[7, 24\]. Table 1 shows a comparison of NiO nanowall-based SO\(_2\) sensor with other materials. The sensing performance, ‘gas response’ and ‘response/recovery
of the synthesized NiO nanowalls are not better than those of reported nanomaterials. However, the sensing performance of a gas sensor strongly depends on many factors, such as electrodes (material, gap, size, shape, and position), testing system set-up (gas inlet position and flux rate), and test chamber (chamber volume, medium with/without oxygen, and humidity). Thus, the limit of detection (LOD) to SO$_2$ should be considered for comparison. For this specification, the NiO nanowalls can detect down to 1 ppm SO$_2$ gas, which is better than many of the reported SO$_2$ sensors.

The SO$_2$—sensing behavior of the NiO nanowalls is related to the reaction of the adsorbed oxygen adatoms O$^-$ on the NiO surface with the SO$_2$ molecules, which can be described as equation (1):

$$\text{SO}_2(g) + O^- (ads) \rightarrow \text{SO}_3 - h^+. \quad (1)$$

After the reaction, the reduced number of holes in the accumulation zone results in increased sensor resistance. The sample exhibits higher response toward SO$_2$ than toward H$_2$S although both gases possessed sulfide in the molecules. This behavior can be attributed to the reaction of SO$_2$ with NiO as mentioned by Tyagi et al [31]. NiO can react with SO$_2$ gas to produce NiS:

$$\text{SO}_3(g) + O^- (ads) \rightarrow \text{SO}_2 + \text{O}_2(g) - h^+. \quad (2)$$

The produced SO$_3$ gas molecules react with the remaining oxygen adatoms on the NiO surface:

$$\text{SO}_3(g) + O^- (ads) \rightarrow \text{SO}_2 + \text{O}_2(g) - h^+. \quad (3)$$

Under the presence of oxygen, NiS can be transformed to NiO:

$$\text{NiS} + \frac{3}{2} \text{O}_2 \rightarrow \text{NiO} + \text{SO}_2. \quad (4)$$

The released SO$_2$ in equations (3) and (4) further reacts with oxygen adatoms following equation (1), thereby decreasing the number of holes in the accumulation. Thus, the NiO nanowalls are more sensitive to SO$_2$ than to H$_2$S.

Studies on the gas-sensing behavior of Ni$_3$O$_2$(OH)$_4$ are rare. However, Ni$_3$O$_2$(OH)$_4$ remained in the sample
after annealing. This phase is possibly remained at the bottom of the sample because of the thick/dense film. Ni$_3$O$_2$(OH)$_4$ can be easily transformed to NiO by giving off water molecules above 200 °C [32]. The decomposition of Ni$_3$O$_2$(OH)$_4$ may be prohibited at the bottom of the film because the film was thick and dense. Thus, the Ni$_3$O$_2$(OH)$_4$ layer may not influence the sensor performance during the test.

Device stability is confirmed by the transient curves after exposure to 5 pulses of 20 ppm SO$_2$ (figure 6(a)). Sensor resistances under ‘gas on’ and ‘gas off’ are retained. At 300 °C operating temperature, the response and recovery times of the device to 20 ppm SO$_2$ are 40 and 57 s, respectively (figure 6(b)). Figure 7 reveals the influence of SO$_2$ concentration on sensor resistance and sensor response. The minimum SO$_2$ concentration that the device can detect is 1 ppm (figure 7(a)) with a response of just above 2.5%. The relationship of the increase in sensor response with SO$_2$ concentration is linear (figure 7(b)). The linear correlation coefficient $R^2$ is 99%, indicating the high potential of the as-synthesized nanomaterial as a SO$_2$ sensor.

4. Conclusions

Curvy NiO nanowalls were grown on a glass substrate through the reaction of Ni foil in aqueous NH$_4$OH. The nanowalls are found to be uniform with an average thickness of 15 nm. The nanowalls are extremely sensitive to SO$_2$ compared with H$_2$S, NO$_2$, and NH$_3$. The highest response of the device to SO$_2$ is 8.8% at 300 °C, and this value is approximately two, six, and two times higher than the responses of the device to H$_2$S, NH$_3$, and NO$_2$, respectively. The as-prepared NiO nanowalls exhibit good stability (in terms of sensor resistance), reasonable response/recovery time (below 1 min), and linear variation of resistance with SO$_2$ concentration. The LOD of the NiO nanowalls to SO$_2$ is 1 ppm. Thus, the NiO nanowalls synthesized through our simple method are a high-potential SO$_2$ sensor.

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**Appendix**

**Figure A1.** Response versus recovery curves of the NiO nanowalls toward H$_2$S, NO$_2$, SO$_2$ and NH$_3$ at the operating temperature of 50°C (a), 100°C (b), 150°C (c), 200°C (d), 250°C (e), and 300°C (f).

**References**

1. Steinebach H, Kannan S, Rieth L and Solzbacher F 2010 H$_2$ gas sensor performance of NiO at high temperatures in gas mixtures Sensors Actuators B 151 162–8
2. Wang J, Yang P, Wei X and Zhou Z 2015 Preparation of NiO two-dimensional grainy films and their high-performance gas sensors for ammonia detection Nanoscale Res. Lett. 10 119
3. Yan X, Tong X, Wang J, Gong C, Zhang M and Liang L 2013 Hydrothermal-synthesized NiO nanowall array for lithium ion batteries J. Alloys Compd. 556 56–61
4. Zhao B, Wang T, Jiang L, Zhang K, Yuen M M F, Xu J-B, Fu X-Z, Sun R and Wong C-P 2016 NiO mesoporous nanowalls grown on RGO coated nickel foam as high performance electrodes for supercapacitors and biosensors Electrochim. Acta 192 205–15
5. Tyagi M, Tomar M and Gupta V 2013 NiO nanoparticle-based urea biosensor Biosens. Bioelectron. 41 110–5
6. Babar P T, Lokhande A C, Guang M G, Pawar B S, Pawar S M and Kim J H 2018 Thermally oxidized porous NiO as an efficient oxygen evolution reaction (OER) electrocatalyst for electrochemical water splitting application J. Ind. Eng. Chem. 60 493–7
7. Yu T, Cheng X, Zhang X, Sui L, Xu Y, Gao S, Zhao H and Huo L 2015 Highly sensitive H$_2$S detection sensors at low temperature based on hierarchically structured NiO porous nanowall arrays J. Mater. Chem. A 3 11991–9
8. Zeng W, Miao B, Lin L and Xie J 2012 Facile synthesis of NiO nanowires and their gas sensing performance Trans. Nonferr. Met. Soc. China 22 s100–4
9. Hotovy I, Rehacek V, Siciliano P, Capone S and Spiess L 2002 Sensing characteristics of NiO thin films as NO$_2$ gas sensor Thin Solid Films 418 9–15
10. Zhan S, Zhou Z, Liu M, Jiao Y and Wang H 2018 3D NiO nanowalls grown on Ni foam for highly efficient electro-oxidation of urea Catal. Today (in press)
11. Mao W, He H, Sun P, Ye Z and Huang J 2018 Three-dimensional porous nickel frameworks anchored with cross-linked Ni(OH)$_2$ nanosheets as a highly sensitive nonenzymatic glucose sensor ACS Appl. Mater. Interfaces 10 15088–95
12. Biswas P, Baek S-D, Kim J-W, Cho S R, Kwon D-K, Lee S J and Myoung J-M 2017 Enhanced photoluminescence in electrodeposited NiO nanowalls mediated by plasmonic Au nanoparticle Mater. Chem. Phys. 201 63–8
13. Tang J, Ni S, Chen Q, Han W, Yang X and Zhang L 2017 The electrochemical performance of NiO nanowalls/Ni anode in half-cell and full-cell sodium ion batteries Mater. Lett. 195 127–30
14. Zhang T, Wu M-Y, Yan D-Y, Mao J, Liu H, Hu W-B, Du X-W, Ling T and Qiao S-Z 2018 Engineering oxygen vacancy on NiO nanorod arrays for alkaline hydrogen evolution Nano Energy 43 103–9
15. Hoa N D, Van Tong P, Hung C M, Van Duy N and Van Hieu N 2018 Urea mediated synthesis of Ni(OH)$_2$ nanowires and their conversion into NiO nanostructure for hydrogen gas-sensing application Int. J. Hydrog. Energy 43 9446–53
16. Zhu L, Li Y and Zeng W 2018 Hydrothermal synthesis of hierarchical flower-like ZnO nanostructure and its enhanced ethanol gas-sensing properties Appl. Surf. Sci. 427 281–7
17. Tian Y, Li Z, Dou S, Zhang X, Zhang J, Zhang L, Wang L, Zhao X and Li Y 2018 Facile preparation of aligned NiO nanotube arrays for electrochromic application Surf. Coat. Technol. 337 63–7
18. Ni S, Lv X, Ma J, Yang X and Zhang L 2014 A novel electrochemical reconstruction in nickel oxide nanowalls on Ni foam and the fine electrochemical performance as anode for lithium ion batteries J. Power Sources 270 564–8
[19] Varghese B, Reddy M V, Yanwu Z, Lit C S, Hoong T C, Subba Rao G V, Chowdari B V R, Wee A T S, Lim C T and Sow C-H 2008 Fabrication of NiO nanowall electrodes for high performance lithium ion battery Chem. Mater. 20 3360–7

[20] Hien V X, Vuong D D, Chien N D and Heo Y-W 2018 Shape-controlled synthesis of Ni(OH)₂/NiO nanowalls by surface reaction of Ni foil in aqueous NH₄OH Mater. Chem. Phys. 217 74–81

[21] Klug H P and Alexander L E 1962 X-Ray Diffraction Procedures: For Polycrystalline and Amorphous Materials vol 4 (New York: Wiley)

[22] El-Kemary M, Nagy N and El-Mehasseb I 2013 Nickel oxide nanoparticles: synthesis and spectral studies of interactions with glucose Mater. Sci. Semicond. Process. 16 1747–52

[23] Spinner N and Mustain W E 2011 Effect of nickel oxide synthesis conditions on its physical properties and electrocatalytic oxidation of methanol Electrochim. Acta 56 5656–66

[24] Li G, Wang X, Liu L, Liu R, Shen F, Cui Z, Chen W and Zhang T 2015 Controllable synthesis of 3D Ni(OH)₂ and NiO nanowalls on various substrates for high-performance nanosensors Small 11 731–9

[25] Das S, Rana S, Mursalin S M, Rana P and Sen A 2015 Sonochemically prepared nanosized BiFeO₃ as novel SO₂ sensor Sensors Actuators B 218 122–7

[26] Tyagi P, Sharma A, Tomar M and Gupta V 2017 A comparative study of RGO-SnO₂ and MWCNT-SnO₂ nanocomposites based SO₂ gas sensors Sensors Actuators B 248 980–6

[27] Liu Y, Xu X, Chen Y, Zhang Y, Gao X, Xu P, Li X, Fang J and Wen W 2018 An integrated micro-chip with Ru/Al₂O₃/O₂/ZnO as sensing material for SO₂ detection Sensors Actuators B 262 26–34

[28] Zhang X, Zhang J, Jia Y, Xiao P and Tang J 2012 TiO₂ nanotube array sensor for detecting the SF₆ decomposition product SO₂ Sensors 12 3302–13

[29] Tyagi P, Sharma A, Tomar M and Gupta V 2016 Metal oxide catalyst assisted SnO₂ thin film based SO₂ gas sensor Sensors Actuators B 224 282–9

[30] Boudiba A, Zhang C, Bittencourt C, Umek P, Olivier M-G, Snyders R and Debliquy M 2012 SO₂ Gas sensors based on WO₃ nanostructures with different morphologies Proc. Eng. 47 1033–6

[31] Ma X, Qin Q, Zhang N, Chen C, Liu X, Chen Y, Li C and Ruan S 2017 Synthesis of SnO₂ nano-dodecahedrons with high-energy facets and their sensing properties to SO₂ at low temperature J. Alloys Compd. 723 595–601

[32] Bukovec P, Bukovec N, Orel B and Wissiak K S 1993 Thermal analysis of nickel oxide films J. Therm. Anal. 40 1193–6