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1 **A fast response and recovery H₂S gas sensor based on free-standing**
2 **TiO₂ nanotube array films prepared by one-step anodization method**

3

4 **Xin Tong^a, Wenhao Shen^{a*}, Xiaoquan Chen^a, Jean-Pierre Corriou^b**

5 ^aState Key Laboratory of Pulp and Paper Engineering, South China University of Technology

6 Guangzhou, 510640, P.R. China

7 ^bLaboratoire Réactions et Génie des Procédés, UMR 7274-CNRS, Lorraine University, ENSIC, 1,

8 rue Grandville BP 20451, 54001 NANCY Cedex, FRANCE

9

10 *Corresponding author.

11 Tel.: +86 20 87111634

12 E-mail address: ppwhshen@scut.edu.cn (Wenhao Shen)

13

14 **Abstract**

15 Free-standing TiNT array film was successfully synthesized by a one-step
16 anodization method. The characteristic techniques including scanning electron
17 microscopy (SEM), transmission electron microscopy (TEM) and X-ray diffraction
18 (XRD) were adopted to characterize the morphology and chemical composition of the
19 TiNT array film. Subsequently, gas sensor based on the TiNT array film was
20 fabricated and its sensing performance toward H₂S was investigated. The results
21 showed that the optimum operating temperature to detect H₂S gas was 300°C, the
22 detection range to H₂S gas was 1-50 ppm with the response value of 4.5-26.2, and a

23 good linearity of sensing characteristics could be observed. Meanwhile, the response
24 and recovery time of the sensor to 50 ppm H₂S gas were as low as 22 s and 6 s,
25 respectively. In addition, mechanisms of the development of the free-standing TiNT
26 array film and the sensor towards H₂S were discussed. In conclusion, its outstanding
27 sensing properties and readily fabrication of the TiNT array film sensor presented the
28 potential industrial applications.

29

30 Keywords: TiO₂ nanotube array film; Free-standing; Anodization; H₂S; Gas sensor

31

32 **1. Introduction**

33 Hydrogen sulfide (H₂S) is one of the main pollutants produced in various
34 industrial processes. It is colorless, highly toxic, extremely flammable and corrosive
35 in nature [1,2]. Humans exposed to H₂S at low concentrations suffer eye irritation,
36 olfactory fatigue, and damage to the lungs and nervous system. The inhalation of 320
37 ppm H₂S may collapse the heartbeat leading to sudden death [3,4]. Thus, from a
38 safety point of view, the monitoring of H₂S is crucial in many industrial areas.

39 Recently, there have been many reports on the H₂S sensors based on metal oxide
40 semiconductors, such as: Fe₂O₃ [5], CuO [6], ZnO [7], WO₃ [8] etc. In the past
41 decades, due to its interesting physical and chemical properties, titanium dioxide
42 (TiO₂) has been considered to be one of the important multifunctional materials with
43 photocatalytic, photoelectrochemical and gas sensor applications. In particular, being
44 similar to other metal oxide semiconductors, TiO₂ also has shown responses to several

45 kinds of gases [9-11]. Although the detection results have been reported so far, the
46 research on the H₂S sensors with TiO₂ is relatively new and their gas-sensing
47 performance needs to be improved [12,13]. Thus, developing new sensing material
48 with high response, good selectivity and quick response is extremely important for
49 real-time monitoring of H₂S.

50 Recently the improved surface reactivity of TiO₂ systems has been reported,
51 where the nanowires, nanorods and nanotubes have been used [14-16]. One of the
52 main features of these nanostructures is the large specific surface area that makes
53 them attractive for use as the sensitive films for gas sensors, which can improve the
54 gas sensitive performance effectively. Although the TiO₂ nanotube (TiNT) arrays have
55 been successfully synthesized with the electrochemical anodization method, most
56 sensitive performance were just obtained on the generated nanotube array without
57 assembling, which hinders the practical application of TiNT [16-18].

58 Several methods for the preparation of the independent TiO₂ nanotube arrays
59 have been reported, which are classified into physical methods and chemical methods.
60 The physical methods mainly included solvent evaporation film separation [19] and
61 ultrasonic oscillation [20], whose main drawback was that it was difficult to obtain the
62 large complete independent TiO₂ thin film, and the morphology of the titanium tube
63 was prone to be destroyed. The chemical methods mainly included the secondary
64 anodic oxidation [21] and the dissolution method in chemical solution [22]. In other
65 words, the secondary treatments were obligatory during the preparation process of the
66 TiNT array membrane and the thick film restricted their feasibility for gas sensing

67 applications.

68 In this work, in Section 3.1, the process of obtaining a complete free-standing
69 TiNT array membrane by the anodic oxidation method followed by annealing without
70 any secondary treatments is presented. In Section 3.2, the morphology of the TiNT
71 membrane obtained with this cost-effective and time-saving method is studied. In
72 Section 3.3, obtained free-standing array film of TiNT to fabricate a gas sensor is
73 explained and its gas sensing performances to H₂S are carefully investigated. In
74 Section 3.4, the gas sensing mechanisms of the developed free-standing TiNT array
75 film are also analyzed in the paper.

76

77 **2. Materials and methods**

78 **2.1 Synthesis of TiO₂ nanotube array**

79 Prior to the anodization experiments, the titanium foils (99.7% purity, 0.01 mm
80 thickness) were ultrasonically cleaned for 10 min in acetone, alcohol and deionized
81 water in sequence, finally dried in air. The anodization was conducted in a
82 two-electrode electrochemical cell with a platinum foil as cathode and the titanium
83 foil as anode at a constant potential. All the anodization experiments were carried out
84 at room temperature with stirring.

85 The anodizing was carried out at 30 V for 2 h using a direct-current stabilizer
86 (TASI-1305, Suzhou TASI electronic CO., LTD.). The growth of the nanotube arrays
87 was obtained using a glycol solution with 0.55 wt% ammonium fluoride and 20 wt%
88 deionized water. After that, the anodized titanium foil was rinsed with deionized water,

89 and dried in air. The samples were heated up to 100°C, 200°C, 300°C, 400°C for 10 min
90 orderly, at the rate of 10°C/min, and then annealed at 450°C for 2 h in the air.

91

92 **2.2 Characterization of the nanotube array film**

93 The morphologies of the free-standing TiNT array film samples were
94 characterized by the scanning electron microscopy (SEM) and the energy-dispersive
95 X-ray spectroscopy (EDS) (Merlin, Zeiss, Germany).

96 The X-ray diffraction (XRD) patterns were recorded at the room temperature
97 with Cu K α radiation of 0.15418 nm in an X-ray diffractometer (D8 ADVANCE,
98 Bruker, Germany), using a generator voltage of 40 kV and current of 40 mA. The data
99 were collected for scattering angles (2θ) ranging from 10° to 85° with a step of 0.02°
100 for 2 s per point. The transition electron microscope (TEM) was performed with the
101 transmission electron microscopy (JEM-2100F, Japan).

102

103 **2.3 Sensor fabrication**

104 For fabrication of the gas sensor, the alumina plate (1.0×1.5 mm) with the gold
105 electrodes and heating layer processed by the method of screen painting printing [23,
106 24] was used as the substrate. In order to remove the stain, the substrates were
107 immersed in acetone, ethanol and deionized water, successively, for 10 min.

108 A mixture of 10 mL of titanium tetraisopropoxide solution in ethanol with
109 terpinenol in volume ratio of 6: 3: 2 was painted onto the side of the substrate for
110 facilitation the later adhesion for the free-standing TiNT array membrane. Then, the

111 sensor attached with the nanotube layer was heated at 350°C for 30 min. After heating
112 treatment, the adhesive was transformed into the TiO₂ interlayer, which let the
113 connection between the substrate and TiNT array film became more compact.
114 Because of the little amount of TiO₂, the contribution of the TiO₂ interlayer to the
115 sensing performance can be considered negligible.

116 The schematic diagram of the sensor structure is shown in Fig. 1 for the sensing
117 measurements. To improve its stability and repeatability, the gas sensor was welded
118 on the pedestal, followed by aging at 450°C for 72 h in air.

119

120 **2.4 Gas sensing measurements**

121 The measurement of the gas sensing performances of the sensor were conducted
122 by a WS-30A Gas Sensing Measurement System (Weisen Electronic Technology Co.,
123 Ltd., China). Fig. 2 displays a schematic diagram the whole measuring process. The
124 final concentration of the H₂S inside the test chamber was controlled by mass flow
125 controllers (MFC) connected to calibrated bottles of N₂ and H₂S. The relative
126 humidity (RH) was about 50% in the whole testing process.

127 As shown in the measuring electric circuit (Fig. 2), in the sensing test process, an
128 appropriate bias voltage ($V_t=5$ V) is applied. The working temperature of the sensors
129 could be controlled from room temperature to 500°C by the heating voltage V_h . R_s is a
130 resistor of the sensor and R_l is a load resistor connected in series with the gas sensor.

131 The gas response was defined as the ratio of the stationary electrical resistance of
132 the sensor in the air R_a to the resistance in the test gas R_g , that is, $\text{Response}=R_a/R_g$.

133 The response and recovery times of the films were calculated from the response
134 curves automatically. The response and recovery times were defined as the time
135 required for a change of the response value to reach 90% of the equilibrium value and
136 falls to 10% of its maximum sensitivity after injecting and removing the detected gas,
137 respectively.

138

139 **3. Results and discussions**

140 **3.1 Development of the free-standing TiNT array film**

141 The formation of the free-standing TiNT array film by electrochemical
142 anodization is a complex process, its growth mechanism can be represented by Fig. 3.

143 The overall process of oxide formation was divided into four steps [25-27]:

144 (1) Formation of the TiO₂ via oxidation

145 At the beginning of this stage, the concentration of Ti⁴⁺ was raised by the
146 electrochemical etching of the Ti, then the amorphous TiO₂ film was formed through
147 the reaction between Ti⁴⁺ and adsorbed O²⁻ on the surface of the electrode.

148 (2) Formation of the pores

149 After the formation of the initial TiO₂ layer, fluorine ions could attack the oxide
150 leading to the formation of the pores through the produced water-soluble [TiF₆]²⁻
151 species. With the extension of the oxidation time, the ordered pores were formed on
152 the surface of the TiO₂ layer. Under the effect of electrochemical etching, the depth of
153 the pores would be increased gradually.

154 (3) Formation of the TiO₂ nanotube array

155 The electric field intensity on the concave surface of the pores is lower than
156 outside the pores, hence the corrosion rate of titanium dioxide on these sites is the
157 fastest [28]. With the migration of the charge density to the bottom of the nanotubes,
158 the oxidation film was dissolved along the axial direction of the tubes, gradually
159 forming the tubular structure film layer. However, as shown in Fig. 4 (a), as time goes
160 on, the dissolving speed decreases, so that the thickness of the nanotubes wall
161 gradually increased from top (13 nm) to bottom (36 nm).

162 Moreover, the metallic region between the tube holes also undergoes a similar
163 transition leading to the formation of the array of relatively independent nanotubes
164 (Fig. 4).

165 (4) Formation of the free-standing TiNT array film

166 The tube length is governed by competition between anodic oxide formation and
167 its chemical dissolution. While oxygen and fluorine ions around the titanium are
168 gradually consumed, both the fluorine ion etching rate and the TiO_2 forming rate
169 begin to decrease until reaching an equilibrium. As shown in Fig. 5, when the reaction
170 lasts 4 hours, the Ti substrate had been completely oxidated to TiNT array. However,
171 as presented in Fig. 4 (b-c), after 4 h, the pore mouths have been eroded. When the
172 reaction duration is increased to 6 h, the tube holes are more dissolved and begin to
173 collapse.

174 With the progress of oxidation time, the length of the TiNT increases leading to
175 an increased strain strength between the TiNT array film and Ti substrate. When the
176 reaction time attains 2 hours, the compressive stress reaches the critical debonding

177 stress. Moreover, annealing modifies the interface between them. Hence, the nanotube
178 array film can be desquamated off naturally after heating treatment [29].

179 In order to ensure the integrity of nanotube mouth and membrane, the oxidation
180 time was taken as 2 hours in the subsequent experiments.

181

182 **3.2 Structural and morphological characteristics**

183 Vertically oriented, high aspect ratio TiNT arrays grown by anodic oxidation of
184 Ti foil were flaked off naturally after the annealing treatment. The transparent TiNT
185 peeled off the Ti foil is shown in Fig. 6 (a). Fig. 6 (b-d) present the SEM images with
186 side, top and bottom views of the free-standing TiNT array film. The average inner
187 diameter of the nanotube was around 110 nm with a wall thickness of 13 nm and the
188 tube length was 3.8 μm . The hollow structure and the wall of the TiNT can be seen
189 clearly in Fig. 7. The enlarged TEM image shows a fringe pattern, where the resolved
190 spacing between the two parallel neighboring fringes is 0.35 nm, corresponding to the
191 interplanar distance of the {101} lattice planes in anatase TiO_2 (Fig. 4b) [30,31].

192 To better understand the crystalline form and the surface element distribution, the
193 XRD and EDS were performed. Fig. 8 shows the X-ray diffraction (XRD) patterns of
194 the TiNT array calcined at 450°C for 2 h. It can be seen that the phase present was
195 anatase (JCPDF No. 21-1272). The diffraction peaks at $2\theta = 25.1^\circ, 37.4^\circ, 47.8^\circ, 53.8^\circ,$
196 54.9° and 62.8° are identified to be the (101), (004), (200), (105), (211) and (204)
197 crystal faces, respectively [12,32]. These crystalline peaks indicate that the crystal
198 structure of TiNT film is the anatase phase. Moreover, Fig. 9 reveals the

199 stoichiometric TiO₂ composition of the film measured by the energy dispersive
200 spectroscopy method. Hence, the titanium nanotubes are mainly composed with the
201 titanium and oxygen element, which proved that the compound was titania.

202

203 **3.3 Gas sensing properties**

204 From the results mentioned above, we had obtained the free-standing TiNT array
205 film prepared by one-step electrochemical anodization followed by thermal annealing.

206

207 **3.3.1 Optimum operating temperature for gas sensing**

208 In order to evaluate the optimum operating temperature, the sensor was exposed
209 to 50 ppm H₂S at temperatures ranging from room temperature to 400°C. The response
210 of the sensor to H₂S with respect to its operating temperature is presented in Fig. 10.

211 Over this temperature range, the response of the sensor increased with the
212 temperature up to 300°C and then started to decrease. At temperatures below 300°C, an
213 increase in the operating temperature promoted H₂S chemisorption and the reaction
214 between the adsorbed H₂S molecules and the adsorbed oxygen species, leading to an
215 enhanced response to H₂S gas. When the operating temperature was 300°C, the
216 response value was 26.2. In contrast, at temperatures higher than 300°C, the response
217 to H₂S was reduced due to desorption of H₂S, which decreased the amount of H₂S
218 adsorbed on the sensor surface [5,33]. Therefore, the optimal operating temperature
219 was 300°C for the TiO₂ sensor.

220

221 **3.3.2 Response and recovery time**

222 The response and recovery time are two important parameters for a gas sensor in
223 practical application [34]. Fig. 11 is an image of the real-time gas sensing transient to
224 50 ppm H₂S at 300°C drawn to show the moments of gas input and gas stop. The
225 response value increased rapidly when the TiNT sensor was exposed to H₂S gas and
226 returned to the initial value when the H₂S gas supply was stopped and air was
227 introduced. The response and recovery times of the sensor are measured from Fig. 11
228 and presented in Fig. 12.

229 From Fig. 12, it can be seen that the sensing films have short response-recovery
230 times, suggesting that the sensors respond quickly to both the injection and removal of
231 the H₂S gas in air. Moreover, the response and recovery times do not dependent on the
232 concentration of H₂S at 1-50 ppm. However, the response times of the sensor exposed
233 to H₂S at 10-50 ppm are longer than at 1-10 ppm. The phenomenon reveals that the
234 response time increases with the increasing concentration of H₂S. When exposed to
235 50 ppm H₂S at 300°C, the response time and recovery time of the sensor were 22 s and
236 6 s, respectively.

237

238 **3.3.3 Effects of gas concentration**

239 The sensitive performance of the sensor was further investigated by exposing the
240 sensors to different concentrations of H₂S gas at the operating temperature of 300°C.
241 The curves of gas response versus time for 1-10 ppm of H₂S gas sensed by the TiNT
242 array film at 300°C are shown in Fig. 13 (a), where the response amplitude of the

243 sensor increases with H₂S concentration. Fig. 13 (b) shows that the sensitivity for the
244 TiO₂ sensor is improved with increasing H₂S concentration in the range of 1-50 ppm.
245 The sensor responses toward 1 and 10 ppm are found about 4.5 to 12.4, respectively.
246 It could be clearly seen that the response increases linearly with the concentrations in
247 this range, indicating a good linearity of sensing characteristics. Moreover, when the
248 concentration of H₂S exceeds about 10 ppm, the sensitivity still increases but at a
249 lower rate.

250

251 **3.3.4 Selectivity studies**

252 The gas sensing selectivity of the TiNT array film was further tested at 300°C by
253 exposing the sensors to 50 ppm potentially interfering gases including methanol,
254 formaldehyde, benzene, toluene, xylene and n-dodecane vapors, and the results are
255 depicted in Fig. 14. Clearly, the sensor based on the TiNT is the most sensitive to H₂S,
256 whereas it presents a low response to the other interfering gases at the same
257 temperature, implying that the sensor exhibits a better selectivity to H₂S than to other
258 gases.

259

260 **3.3.5 Stability and repeatability**

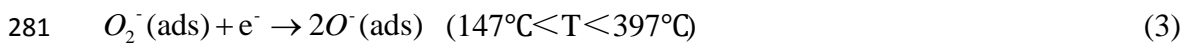
261 Thermal stability and repeatability of the sensor had been investigated by
262 repeating experiments for 50 ppm H₂S at 300°C. Fig. 15 displays the measured values
263 for the sensor response versus the storing time. As displayed in the figure, the
264 response results of the sensor possess a variation of $\pm 1.4\%$ from the initial result (26.2)

265 in one month. The free-standing TiNT array film demonstrated a good stability and
266 reproducibility with regard to 50 ppm H₂S gas at 300°C, which indicated a stable
267 morphology and good crystallinity of the fabricated sensing layer.

268

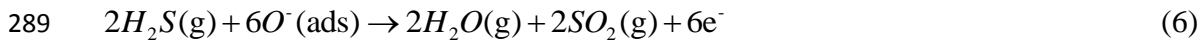
269 **3.4 Gas sensing mechanism**

270 It is well known that the sensing mechanism of TiO₂-based gas sensors belongs
271 to the surface-controlled type, which is based on the change in conductance of the
272 semiconductor [35,36]. When the sensor is exposed to air, electrons in the surface
273 region of the TiO₂ nanotube walls are consumed by the oxygen molecules that are
274 adsorbed on the TiO₂ surface. Then a depletion region is created on the wall of the
275 TiNT, leading to an increase in the electric resistance of the TiNT array film [37].
276 Another point to be noted is that the type of adsorbed oxygen species depends on the
277 working temperature of sensor. The changing process of oxygen molecules on the
278 nanotube surface is illustrated in Eqs. (1-4) [38,39]:



283 When the sensor was exposed to H₂S gas, which was a reducing gas, these
284 chemisorbed oxygen species played a crucial role in enhancing the H₂S gas sensitivity
285 as explained by the schematic diagram in Fig. 16. The H₂S reacted with these oxygen
286 species and got dissociated after releasing trapped electrons to the TiNT via the

287 speculated reactions given in Eqs. (5-6) [4,12]:



290 This led to an increase in the carrier concentration on the TiO₂ nanotube walls
291 and a decrease in the surface depletion layer width. Hence, there is an increase in the
292 response value as shown in Fig. 11.

293 Table 1 summarizes the results of gas response to H₂S using various forms of
294 TiO₂. The response and recovery time with most of the H₂S sensors prepared by TiO₂
295 materials were long, or a modification method was necessary to improve its gas
296 sensitive performances. However, in this work, the response value, response and
297 recovery times of the purified TiNT array film sensor toward H₂S gas were
298 comparable to those of the most other TiO₂ nanomaterials.

299 The following physical and chemical effects might contribute partly to the
300 enhanced H₂S sensing properties of the TiNT array film sensor: (1) electrons are
301 conducted through the wall of TiNT because of its particular structure, which reduces
302 the recombination of electrons and holes; (2) the TiNT that presents a large surface
303 area due to their tube array structure results in a better sensitivity.

304

305 **4. Conclusion and perspectives**

306 The free-standing TiNT array film was successfully synthesized by a one-step
307 anodization method. Then the film was fabricated and tested for H₂S gas sensing at
308 low concentrations.

309 The H₂S sensing properties including operating temperature, reversibility,
310 relationship between sensitivity and H₂S concentration, selectivity and stability were
311 studied. The results showed that the optimum operating temperature to detect H₂S gas
312 was 300°C, the detection range to H₂S gas was 1-50 ppm with the response value of
313 4.5-26.2, and a good linearity of sensing characteristics could be observed. It is
314 generally accepted that metal oxide gas sensors possess relatively longer response and
315 recovery times. However, the response and recovery time of the sensor to 50 ppm H₂S
316 gas were as low as 22 s and 6 s, respectively. Moreover, the growth mechanism and
317 gas sensing mechanism of the TiNT array film were studied.

318 It can be seen that the response values, response and recovery times of the sensor
319 were outstanding throughout the tests, which demonstrated that the fabricated TiNT
320 array film sensor presented the potential industrial applications. Moreover, this
321 electrochemical anodization method based on the Ti foil is relatively simple and,
322 hence, induces lower costs and makes it be attractive for developing gas sensors
323 devices.

324

325

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332

333

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Table 1. Comparison of the sensor responses to H₂S with different forms of TiO₂.

No.	Morphology	Crystal Structure	Response (R=R _a /R _g)	Concentration (ppm)	Temperature (°C)	Response time (s)	Recovery time (s)	Reference
1	Ag-doped TiO ₂ nanofiber	Anatase & rutile	8.5	100	350	-	-	Ma et al., 2016
2	TiO ₂ nanoparticle-decorated Fe ₂ O ₃ nanorods	anatase	7.4	200	300	150	157	Kheel et al., 2016
3	TiO ₂ -Al ₂ O ₃	rutile	38.7	1000	650	390	480	Arafat et al., 2017
4	CuO doped TiO ₂ nanoparticle	anatase	1.77	50	Room temperature	14	22	Chaudhari and Mishra, 2016
5	TiO ₂ nanoplates	anatase	4.8	10	300	10	-	Guo et al., 2016
6	TiO ₂ nanowires	rutile	11	80	140	-	-	Munz et al., 2013
7	TiO ₂ pellet	rutile	275	10	100	150	2500	Jagdale et al., 2015
8	Free-standing TiNT array film	anatase	26	50	300	22	6	Our work

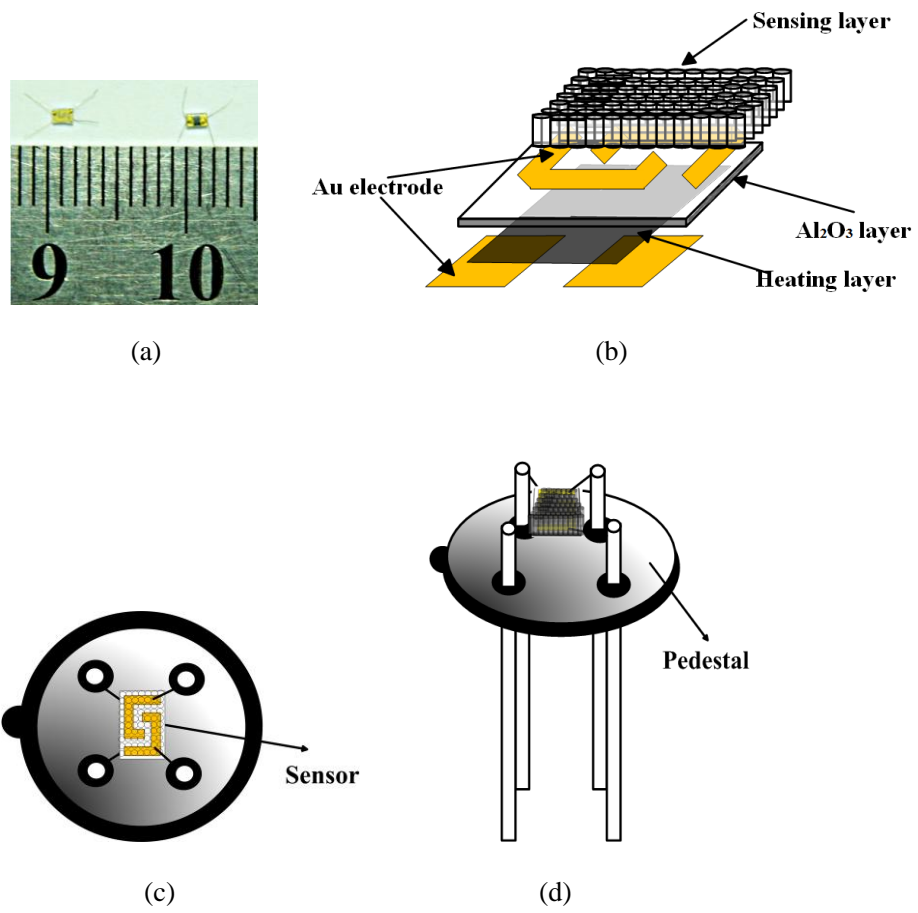


Figure 1. (a) Photographs of the blank sensor. (b) A schematic illustration of the sensor coated with the sensing material. (c) Top view and (d) side view of the fabricated sensor.

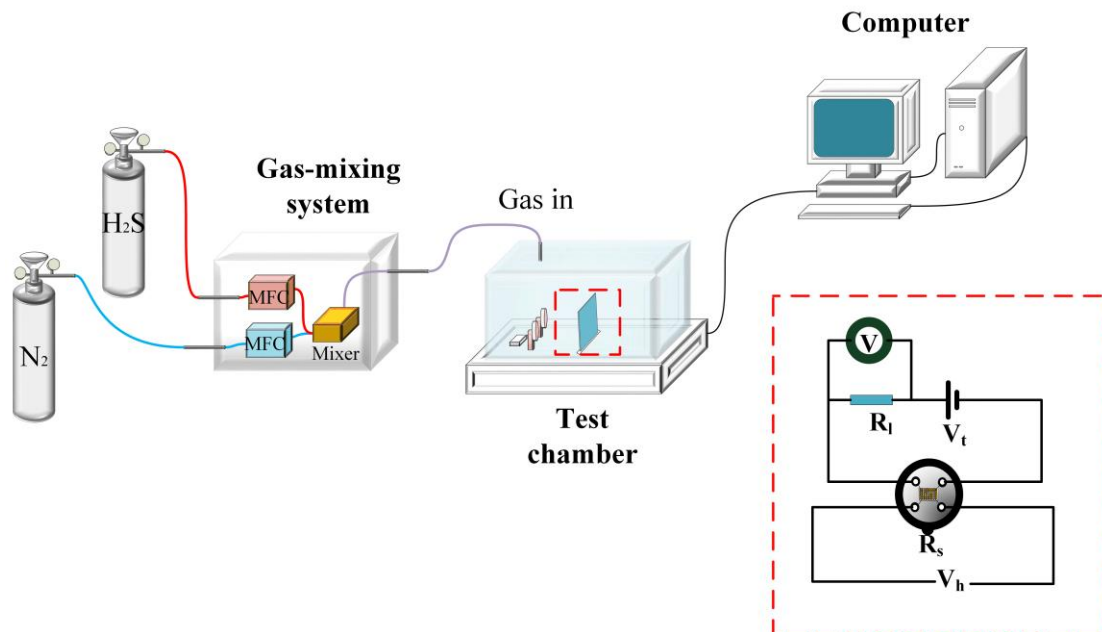


Figure 2. Experimental setup and measuring electric circuit for gas sensing performance.

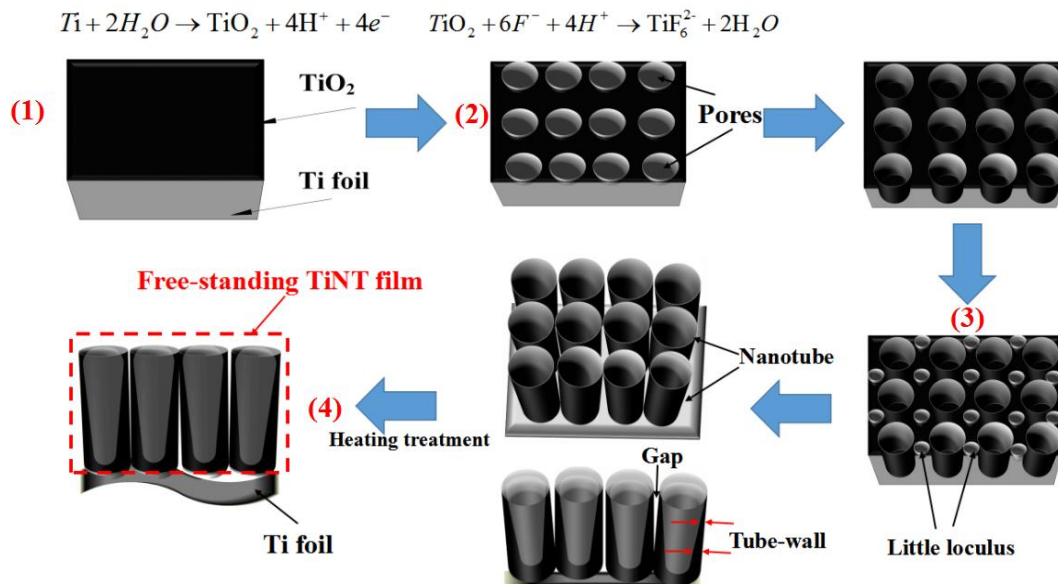
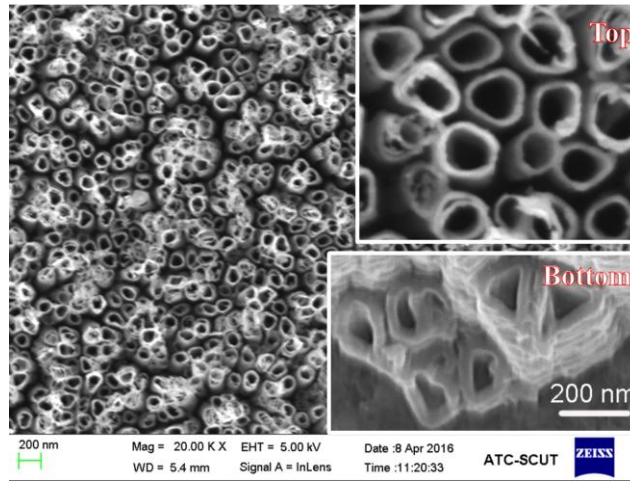
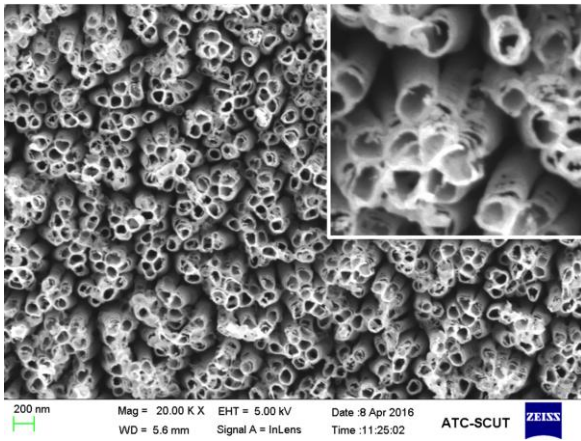


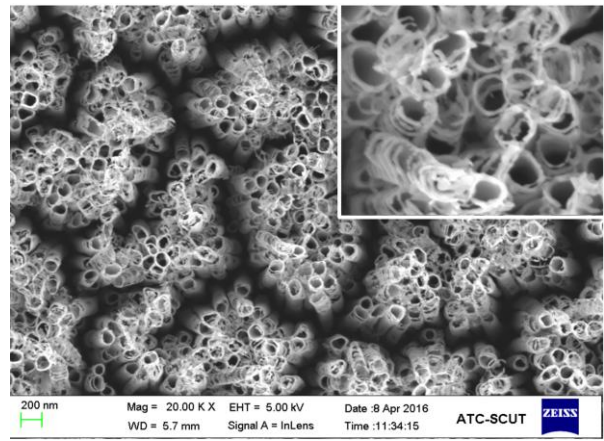
Figure 3. Schematic diagram of the growth mechanism of free-standing TiNT array film.



(a) 2h



(b) 4h



(c) 6h

Figure 4. Top-view SEM images of TiNT array film at different oxidation time.

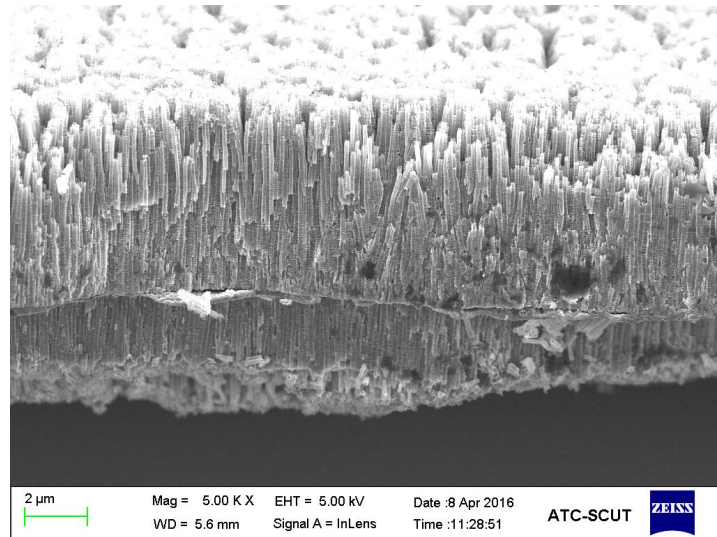


Figure 5. Side-view SEM image of the TiNT array at oxidation time of 4h.

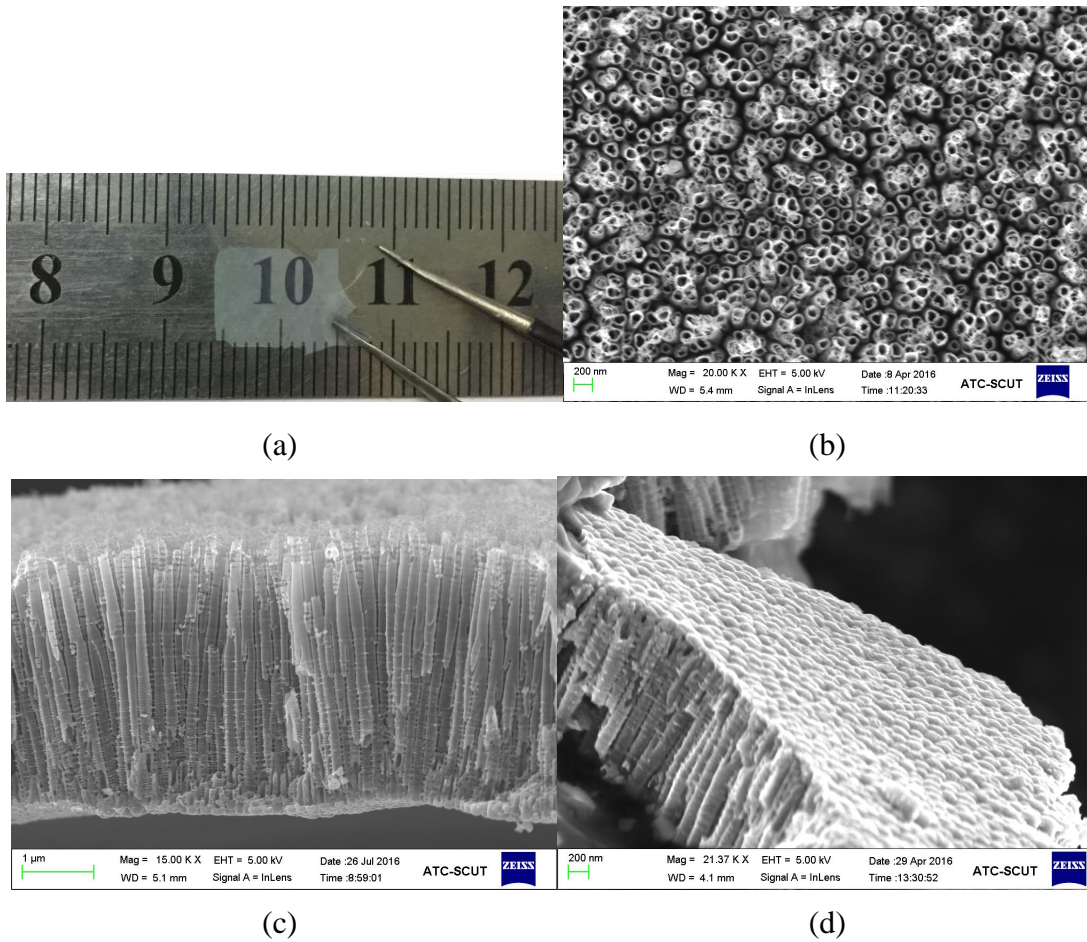


Figure 6. (a) Photographic image of the detached TiNT-array film, (b) Top-view SEM, (c) Side-view SEM, (d) Bottom-view SEM image of the TiNT array with the oxidation time of 2h..

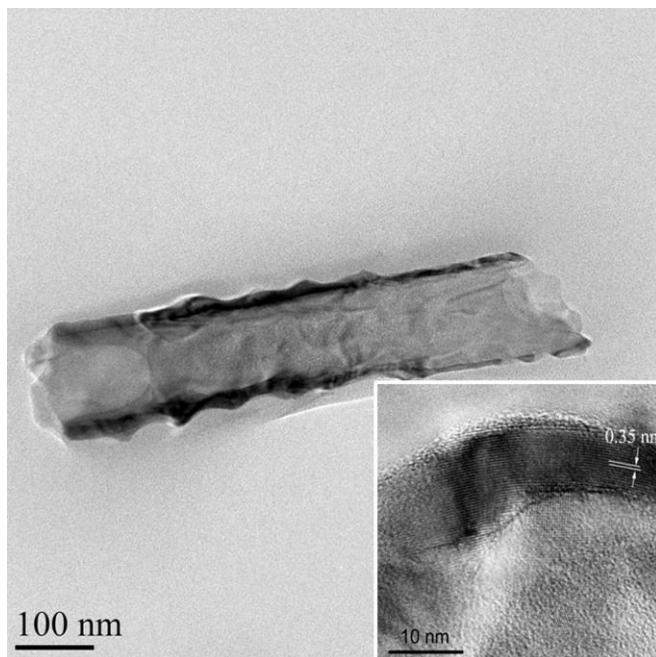


Figure 7. Wide-field TEM and HRTEM images of a single TiNT.

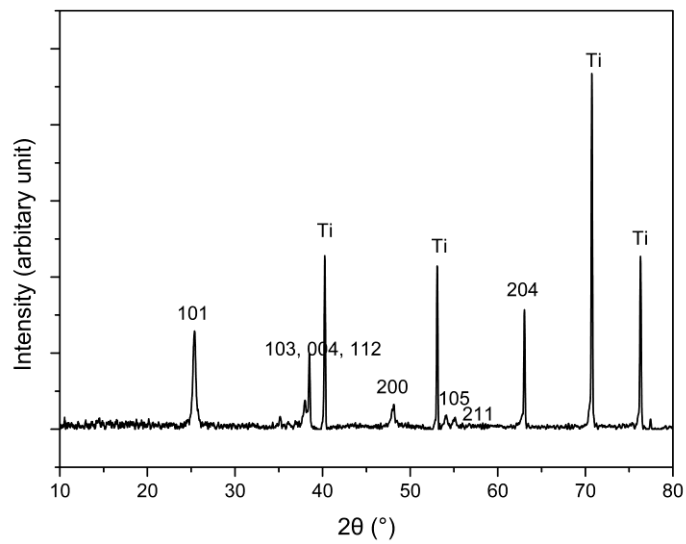


Figure 8. XRD peaks of the TiNT.

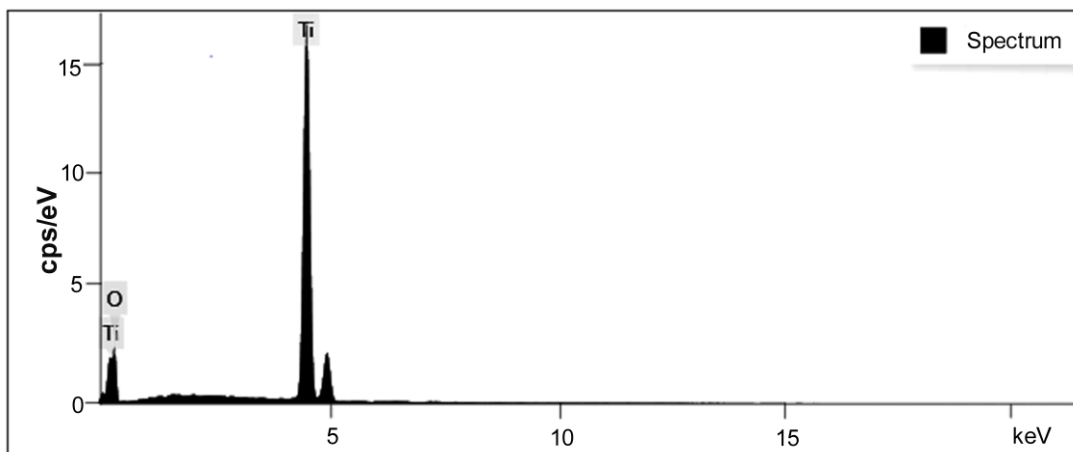


Figure 9. Energy dispersive spectroscopy spectrum of the TiNT arrays.

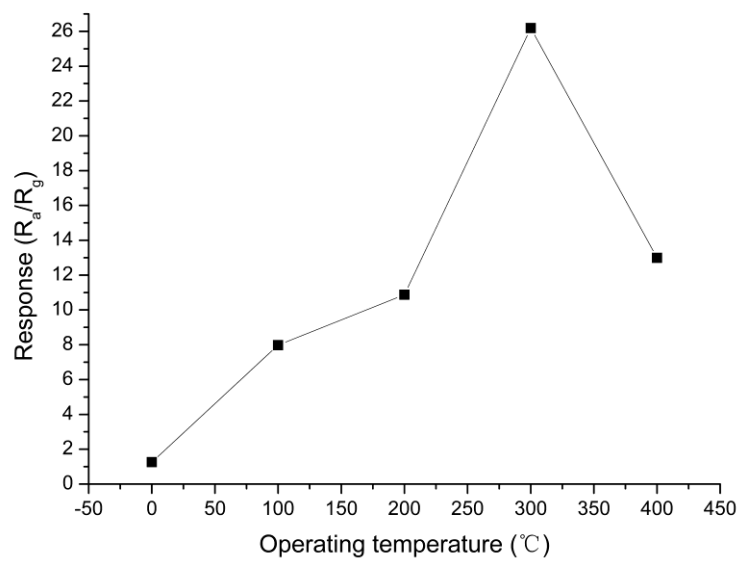


Figure 10. Response values of the free-standing TiNT array film to 50 ppm H_2S at various operating temperatures.

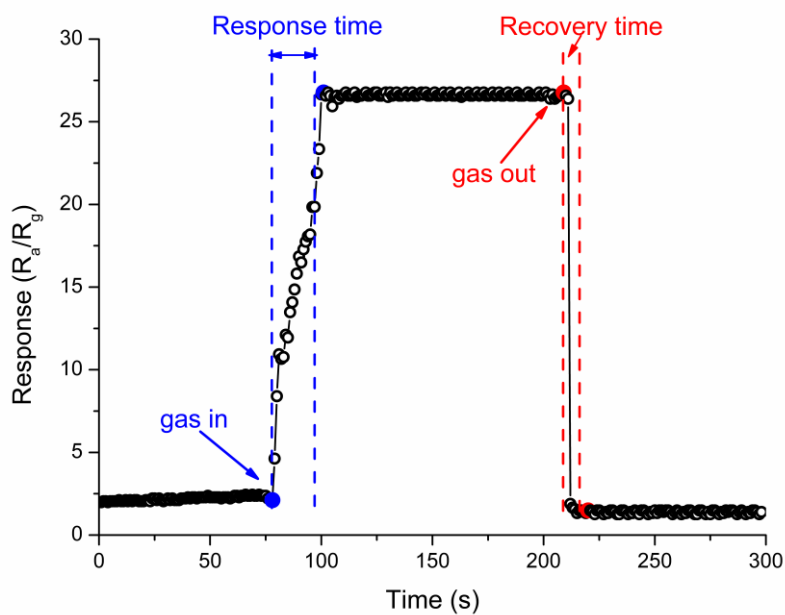


Figure 11. The real-time response curve to 50 ppm H₂S of the sensor at 300°C.

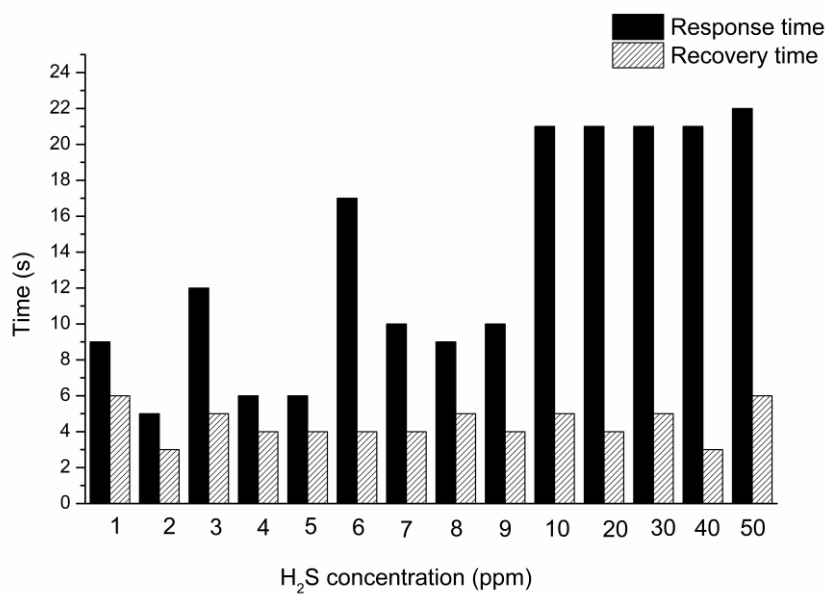


Figure 12. Summary of response time and recovery time of the sensor exposed to H₂S at different concentrations at 300°C.

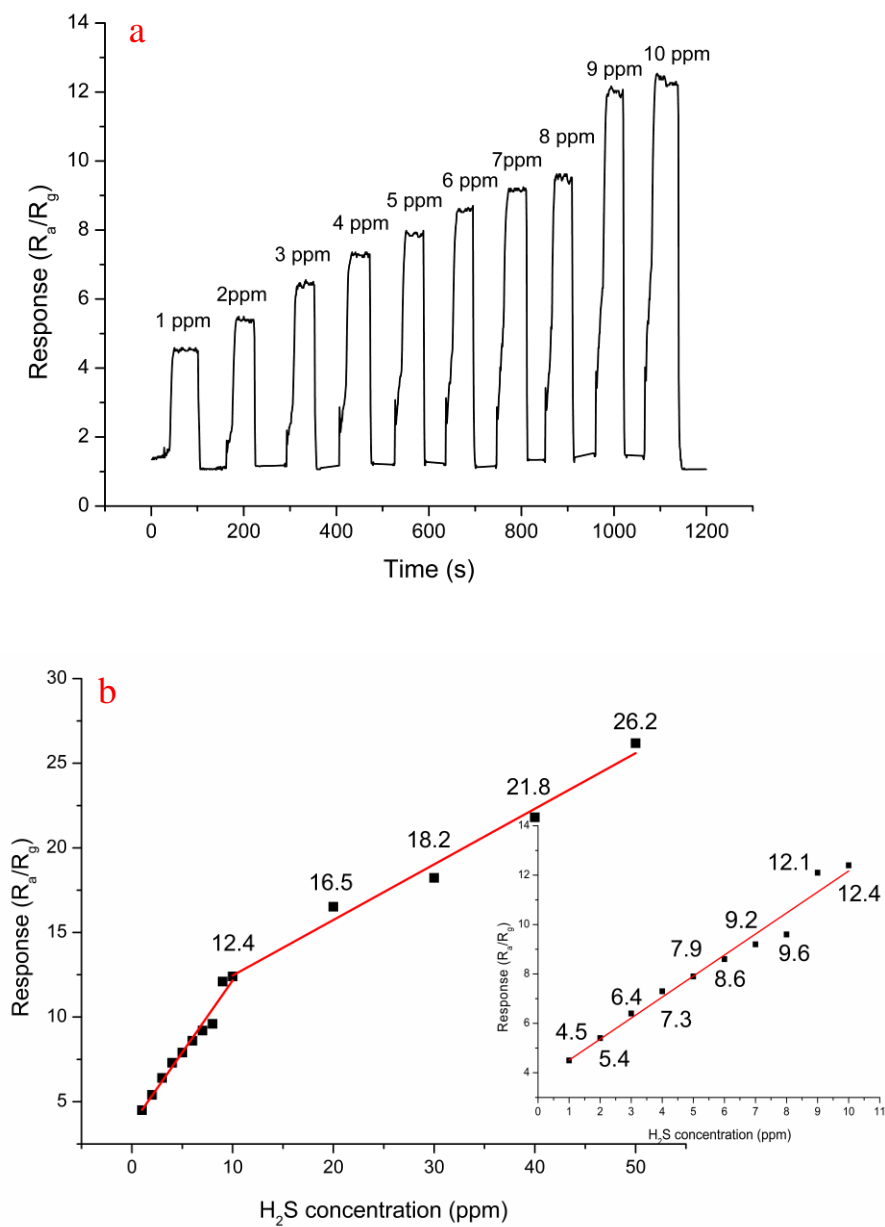


Figure 13. (a) Real-time response curve of the TiNT array film sensor to H₂S with increased concentration at a working temperature of 300°C; (b) Relationship between the sensitivity and H₂S concentration.

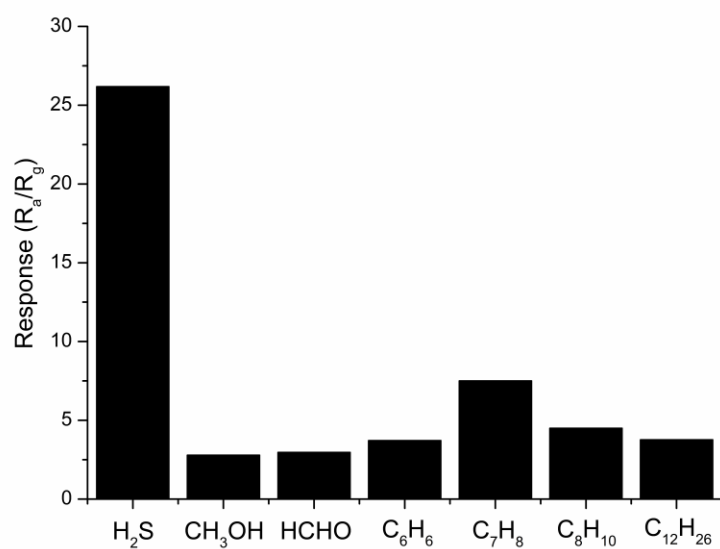


Figure 14. Comparison of sensor response obtained for different gases of 50 ppm.

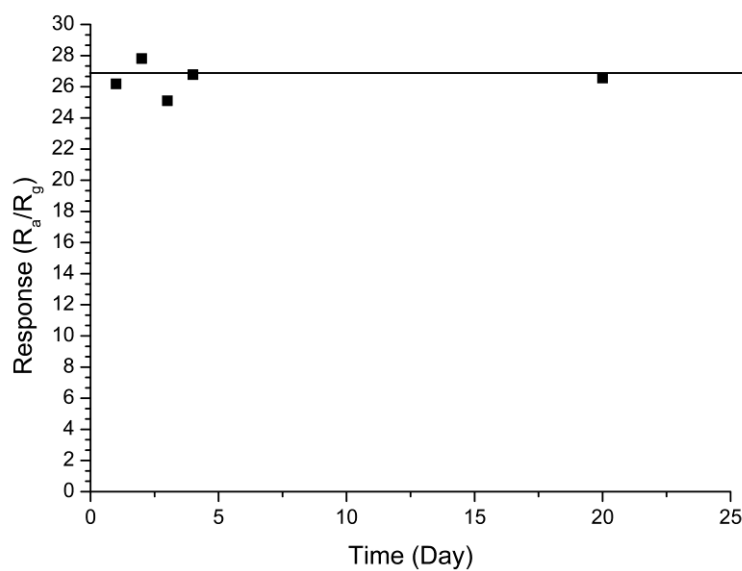


Figure 15. Variation of the sensor response to 50 ppm H_2S at 300 °C for different duration times.

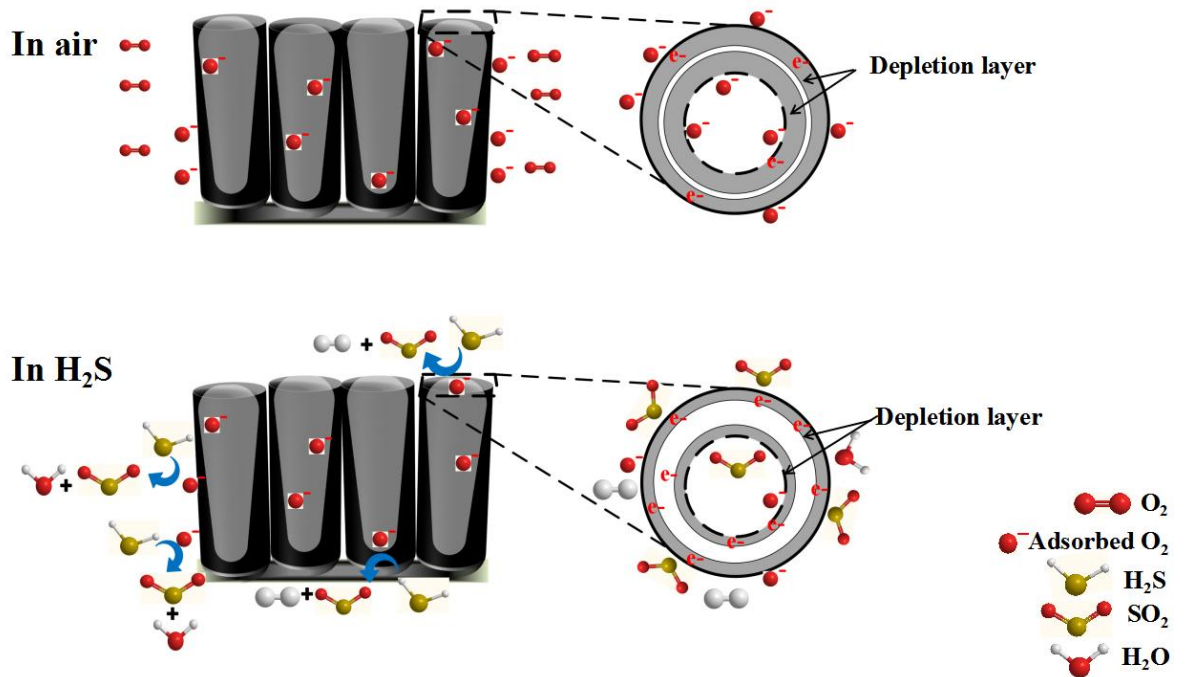


Figure 16. Band diagrams and schematic images of the surface reactions under different atmospheres: (a) exposed in the air (b) in the presence of H_2S gas.