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# A strategy for supportless sensors: Fluorine doped $TiO_2$ nanosheets directly grown onto Ti foam enabling highly sensitive detection toward acetone



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#### ABSTRACT

Herein, a facile approach was adopted to synthesize  $TiO_2$  nanosheets directly onto Ti foam via hydrothermal method. On this basis, controlled fluorine doping in  $TiO_2$  nanosheets was achieved via impregnation. The obtained  $TiO_2/Ti$  foam and F- $TiO_2/Ti$  foam were structurally characterized using scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM) and X-ray diffraction analysis. Furthermore, they were developed as self-supported sensors for detecting acetone at room temperature (25 °C). It was found that the sensors had excellent acetone sensing properties, including high response, good selectivity, decent repeatability and long-term stability. The sensitivities of  $TiO_2/Ti$  foam and F- $TiO_2/Ti$  foam toward 100 ppm acetone were 4.58 and 5.95, respectively, and the detection linear range was 25–800 ppm. The F- $TiO_2/Ti$  foam exhibited higher sensitivity, faster response/recovery toward acetone as compared to the undoped counterpart. The results suggested that fluorine doping could be therefore considered as a favorable method for improving the sensitivity of prepared gas sensor. Furthermore, the in-situ growth of gas-sensing nanosheets onto the support can be a promising strategy for fabricating various supportless sensors.

#### 1. Introduction

Acetone is a hazardous and volatile chemical solvent that is used extensively in industry or laboratory. The release of acetone would cause certain damage to human brain, nerves, skin and endocrine system due to its volatility and chronic toxicity [1]. On the other hand, it is often regarded as a biomarker to reflect human health and diagnose diseases [2]. As early as 1857, acetone detection has been adopted for diagnosis of diabetes [3]. Currently, common and effective techniques for gas analysis include gas chromatography (GC) [4] and spectrophotometry [5]. Although these analytical techniques based on large-scale equipment are adequately accurate and sensitive, they suffer from high cost, poor portability and long assay time. Thus, designing cheap, easy-to-operate, prompt and small gas sensors are essential for the detection of acetone.

At present, chemiresistive gas sensors based on metal oxide semiconductor (MOS) like ZnO [6],  $In_2O_3$  [7],  $Fe_2O_3$  [8],  $WO_3$  [9] and  $TiO_2$ maintain a dominant presence for acetone detection due to its high sensitivity, fast response and recovery, ease of use and good portability. Among them, TiO<sub>2</sub> has been widely studied in the sensing field. Up to now, the majority of acetone sensors using TiO<sub>2</sub> focused on one-dimensional (1D) nanostructures, such as nanotubes, nanorods [10], nanofiber, nanobelts [11], etc. However, sensitivity and operation temperature of these sensors are far from satisfactory. For example, the sensor based on TiO<sub>2</sub> nanotubes only yielded a response of 3.35 ( $(R_a R_g$  / $R_g \times 100$ , where  $R_a$  and  $R_g$  are the electric resistance obtained in air and in target gas, respectively) toward 1000 ppm acetone at room temperature [12]. The response of sensor fabricated from TiO<sub>2</sub> nanofibers was less than 3 ( $R_a/R_g$ ) toward 50 ppm acetone at 240 °C [13]. Hence, pursuit of higher sensitivity and lower power consumption is urgently required. Generally, gas sensing performance highly depends on the exposed surface area for the reason that large area offers increased number of active sites and leads to superior sensitivity. Owing to excellent carrier mobility and large specific surface area, two-dimensional (2D) nanostructured gas sensors are expected as ideal sensing tools [14-17]. Recently, some successes have been achieved in

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this respect. Wang et al. prepared porous  $Co_3O_4$  nanosheets via a facile hydrothermal method and the sensor attained a response of 11.4 ( $R_g/R_a$ ) toward 100 ppm acetone at low working temperature [18]. Thus, exploring 2D nanostructured TiO<sub>2</sub> as sensing material can be expected to achieve sensors with great performance in detecting acetone.

In general, sensing materials are prefabricated and then coated onto ceramic tubes or interdigital electrodes (IDEs) to build sensor devices. However, it is often difficult to gain uniform and stable sensing films through the manual transfer operation. Also, this procedure usually suffers from low efficiency and large item-to-item variations. In order to solve the above mentioned problems, in-situ growth of sensing materials directly onto electrode surface is an ingenious approach. Till now, only a few literatures have reported such methodology for modification of 2D materials. Cao et al. have reported [19] a gas sensor prepared by direct growth of Al doped ZnO ultrathin nanosheets, whose response reached 90.2  $(R_a/R_g)$  toward 100 ppm ethanol. Yu et al. have demonstrated a sensor based on porous NiO nanowalls grown on ceramic tubes, which can detect H<sub>2</sub>S in the 1 ppm level at a low temperature [20]. Undoubtedly, in situ decoration affords sensor with good sensing properties, since this unique approach avoids agglomeration and peeling of materials. Besides, doping of gas sensing materials has long been considered as a feasible method to manipulate gas sensing properties. Many studies have proved that non-metal doping (such as C, N and F) of nanomaterials could increase gas sensing performance. For instance, carbon-doped TiO<sub>2</sub> exhibited excellent sensitivity for ethanol sensing [21]. Fluorine doping in SnO<sub>2</sub> changed surface property and improved gas sensing capability of SnO<sub>2</sub> [22].

In this work,  $TiO_2$  nanosheets with thickness of about 14 nm were directly grown on Ti foam, and fluorine was doped into the  $TiO_2$  ultrathin nanosheets. The  $TiO_2/Ti$  foam and  $F-TiO_2/Ti$  foam were developed as self-supported sensors, and their sensing properties to acetone were studied thoroughly. The freestanding sensors could work independently and are exempt from any supporting elements (like ceramic tube [23], IDEs [24] and plastic substrates [25]). In addition, sensitivity, response/recovery time and stability for the newly prepared sensors in determination of acetone vapor were investigated. Furthermore, we also discussed and interpreted the gas-sensing mechanism.

#### 2. Materials and methods

#### 2.1. Reagents and apparatus

Ti foam (purity  $\geq$  99.9%) was obtained from Longshengbao Electronic Material Co., Ltd. (Jiangsu, China), whose size is  $2 \text{ cm} \times 1 \text{ cm} \times 0.75 \text{ mm}$ . Acetone, methanol, ethanol, isopropanol and hydrofluoric acid (HF, 50 wt%) were acquired from Titan Scientific Co. Ltd. (Shanghai, China). Hydrochloric acid (HCl), NaOH, NaF and perchloric acid (HClO<sub>4</sub>) were supplied by Guangfu Tech. Co. Ltd. (Tianjin, China). MgCl<sub>2</sub>, Mg(NO<sub>3</sub>)<sub>2</sub>, CuCl<sub>2</sub>, NaBr, NaCl, and KCl were purchased from Shengao chemical reagent Co. Ltd. (Tianjin, China). H<sub>2</sub>S, CO<sub>2</sub> and NO<sub>2</sub> at 10000 ppm as well as pure air (synthetic air) were bought from Shanghai weichuang standard gas Co. Ltd. (Shanghai, China). The reagents and chemicals are of analytical grade. All solutions were formulated by double distilled water (DDW).

#### 2.2. Instruments and characterization

Gas-sensing properties of the fabricated sensors were investigated by using Fluke 8846A digital precision multimeter (Fluke Shanghai Co. Ltd., Shanghai, China). Dynamic gas distribution device was bought from Laifeng Technology Co. Ltd. (Chengdu, China). Mott Schottky measurement was conducted by a Electrochemical Workstation (CHI 660E, ChenHua Instruments Co.,Shanghai, China) with a standard threeelectrode system. The morphology of employed materials was investigated by scanning electron microscope (SEM) images using a Zeiss Supra 55 V P and transmission electron microscope (TEM) images using a FEI Tecnai G2 F20. The energy-dispersive spectrometer (EDS) was employed for elemental identification. The crystal lattice orientation of materials was characterized using a Rigaku Ultima IV X-ray diffractometer (XRD) with Cu K $\alpha$  radiation ( $\lambda = 1.5418$  Å). X-ray photoelectron spectroscopy (XPS) data were recorded on Thermo ESCALAB 250XI (Thermo Fisher Scientific., USA) to analyze solid surface and element valence of the material.

#### 2.3. Synthesis of TiO<sub>2</sub>/Ti foam and F-TiO<sub>2</sub>/Ti foam

The TiO<sub>2</sub> nanosheets were grown on Ti foam in three steps [26–28]. Firstly, Ti foam was degreased by ultrasonic treatment sequentially in acetone, methanol and isopropanol, each for 10 min to remove surface impurities. Then it was etched in 2.5 wt% HF for 660 s to wipe surface oxidation layer, washed ultrasonically with DDW for 10 s, and dried under 60 °C in a vacuum furnace. The dried Ti foam was placed in a 100 mL of stainless-steel Teflon-lined autoclave containing NaOH (1 M, 40 mL), maintained at 200 °C for 12 h. Subsequently, the modified Ti foam was placed into 0.6 M HCl solution for 1 h in order to exchange Na<sup>+</sup> with H<sup>+</sup>. After substitution, the product was rinsed by DDW and dried at room temperature. Finally, the Ti foam was annealed at 500 °C for 2 h with heating rate of 2 °C/min for obtaining TiO<sub>2</sub>/Ti foam. As for preparing F-TiO<sub>2</sub>/Ti foam composite, the TiO<sub>2</sub>/Ti foam was immersed in 10 mM NaF (pH = 3) solution for 12 h. The obtained product was rinsed by DDW and dried in a vacuum furnace at 50 °C for 2 h.

#### 2.4. Gas-sensing experiments

To investigate sensing performance of the self-supported sensors, the electrical resistance changes of TiO<sub>2</sub>/Ti foam and F-TiO<sub>2</sub>/Ti foam were measured by placing them into a chamber and connecting with a digital multimeter (Fluke 8846A), which was shown in Fig. 1 [29-31]. For the organic analyte, the vapor stream was obtained by flowing synthetic air through a reservoir containing target organic solvents, whose flow rate  $(f_1, \text{ sccm})$  was controlled by a mass flow controller (MFC<sub>1</sub>). Then the vapor flow was diluted with carrier gas (synthetic air) through MFC<sub>2</sub> with a rate ( $f_2$ , sccm). The total gas flow was fixed at 1000 sccm by MFC<sub>1</sub> and MFC<sub>2</sub>. Concentration of organic analyte was calculated by Eq. No. (1). As for  $H_2S$ ,  $CO_2$  and  $NO_2$ , they were injected at a rate of  $f_3$  (sccm), and subsequently diluted by synthetic air through another channel at a rate of  $f_4$  (sccm). Flow rate of the three inorganic gases and the synthetic air was controlled by MFC3 and MFC4, respectively, of which the total flow rate was kept constant at 1000 sccm and the concentration was calculated by Eq. No. (2):

$$C \quad (\text{ppm}) = \left(\frac{P_{\text{s}}}{P} \times \frac{f_1}{f_1 + f_2}\right) \times 10^6 \tag{1}$$

$$C \ (\text{ppm}) = \frac{C_{\text{gas}} \times f_3}{f_3 + f_4}$$
(2)

where *P* is the total pressure, and  $P_s$  is the saturated partial pressure (in mm of Hg) of target VOCs obtained by Eq. No. (3) [32]:

$$\operatorname{Log} P_{s} = A - \frac{B}{C+T}$$
(3)

where T is the temperature, A, B, and C are Antoine coefficients. The relative humidity levels (33%, 43%, 52%, 57%, 75%, and 84%) were attained by keeping the saturated solutions of MgCl<sub>2</sub>, Mg(NO<sub>3</sub>)<sub>2</sub>, CuCl<sub>2</sub>, NaBr, NaCl, and KCl in an airtight container. All the tests were performed at 25 °C with the humidity of about 20%. The sensor response (*S*) was defined as  $(\Delta R/R_a) \times 100$ , where  $\Delta R$  as  $(R_g - R_a)$ ,  $R_a$  and  $R_g$  represent the electric resistance obtained in the presence of air and target gas, respectively. The response or recovery time referred to the time at which 90% of the total resistance change was reached upon exposure to target gas or air.



Fig. 1. Schematic diagram of the sensing measurement system.



Fig. 2. (A) Schematic diagram of preparing TiO<sub>2</sub>/Ti foam and F-TiO<sub>2</sub>/Ti foam. SEM image of (B) Ti foam; (C) TiO<sub>2</sub>/Ti foam and (D) F-TiO<sub>2</sub>/Ti foam; (E, F) TEM image of TiO<sub>2</sub>/Ti foam; (G) XRD patterns of TiO<sub>2</sub>/Ti foam and F-TiO<sub>2</sub>/Ti foam.

#### 3. Results and discussions

## 3.1. Preparation and characterization of $TiO_2/Ti$ foam and F-TiO\_2/Ti foam

The synthesis process of TiO<sub>2</sub>/Ti foam and F-TiO<sub>2</sub>/Ti foam is shown in Fig. 2A schematically. TiO<sub>2</sub>/Ti foam was obtained by hydrothermal method using the treated Ti foam, where the ultrathin 2D TiO<sub>2</sub> nanosheets grew on the Ti foam firmly. Subsequent immersion of the resulting TiO<sub>2</sub>/Ti foam in NaF solution allowed for replacement of part of O atoms with F atoms. As shown in Fig. 2B and C, the microscopic morphology of the samples changed significantly from the planar structure of the original Ti foam to the 2D nanosheet architecture of TiO<sub>2</sub>/Ti foam. The thickness of TiO<sub>2</sub> nanosheets was approximately 14 nm. Fig. 2D shows that the surface of TiO<sub>2</sub>/Ti foam was unchanged through modification. The TEM image of TiO2/Ti foam is shown in Fig. 2E and F. The lattice fringes with an interplanar distance of about 0.35 nm can be associated with the (101) lattice planes of anatase TiO<sub>2</sub>. In addition, XRD patterns were adopted to demonstrate the phase transformation. As shown in Fig. 2G, some new peaks of TiO<sub>2</sub>/Ti foam were observed together with the characteristic peaks of titanium, which have a good match with the patterns of the anatase TiO<sub>2</sub> standard cards (JCPDS-21-1272). The diffraction peaks of TiO<sub>2</sub>/Ti foam were higher than those of the F-TiO2/Ti foam, which may be ascribed to the substitution of F atoms for O atoms.

EDS data display the composition of TiO2/Ti foam before and after fluorine doping. F element is absent in TiO2/Ti foam, while its content is significantly increased after doping (Fig. S1). Fig. 3 presents the XPS spectra of Ti 2p, O 1s and F 1s of TiO<sub>2</sub>/Ti and F-TiO<sub>2</sub>/Ti foams. As shown in Fig. 3A, peaks at 458.5 eV and 464.2 eV correspond to Ti 2p<sub>3/2</sub> and Ti  $2p_{1/2},$  while the positions of Ti  $2p_{3/2}$  peak and Ti  $2p_{1/2}$  peak shifted after fluorine doping. The binding energy of peaks Ti  $2p_{3/2}$  and Ti  $2p_{1/2}$  are 458.7 eV and 464.4 eV, respectively, resulting from some oxygen atoms replaced by fluorine atoms. Compared with oxygen, the greater electronegativity of fluorine will reduce the electron density of Ti atoms, and the corresponding Ti nucleus's ability to bind electrons outside the nucleus will be strengthened, resulting in increased binding energy. In Fig. 3B, the O 1s profile having one peak at the 529.6 eV is ascribed to typical Ti-O-Ti bonds (lattice oxygen), and two additional peaks at 530.2 eV and 531.2 eV are related to defects and chemisorbed oxygen. Furthermore, the O 1s band of F-TiO2/Ti foam could be divided into three peaks at 529.7, 530.2 and 531.2 eV (Fig. 3B). The peaks located at 530.2 eV and 531.2 eV can be attributed to Ti-Ovac and Ti-O-OH bonds. The two peaks were found to be higher in F-TiO<sub>2</sub>/Ti foam, which suggested that F-doping enhances adsorption of oxygen species and promotes the gas-sensing capacity. The F 1s spectrum in Fig. 3C was separated into two peaks at 684.2 eV and 685.4 eV, and the peak at 684.2 eV is associated with the surface-O-Ti-F species in F-TiO2/Ti foam, while the minor peak at 685.4 eV can be ascribed to a fraction of F atoms which have replaced two OH<sup>-</sup> groups coordinated to the same Ti

atoms

#### 3.2. Gas sensing performances of $TiO_2/Ti$ foam and F-TiO<sub>2</sub>/Ti foam

Based on our present work on self-supported gas sensor, we demonstrate that the acetone molecules react with the protons (H<sup>+</sup>) and hydronium ion (H<sub>3</sub>O<sup>+</sup>) adsorbed on TiO<sub>2</sub>/Ti foam and F-TiO<sub>2</sub>/Ti foam, which is shown schematically in Fig. 4. Gas sensing performances of the TiO<sub>2</sub>/Ti foam sensor and the F-TiO<sub>2</sub>/Ti foam sensor were investigated toward acetone at 25 °C. Before exposed to acetone, both the TiO2/Ti foam and the F-TiO<sub>2</sub>/Ti foam self-supported electrodes were allowed to stabilize their electrical resistance in pure air until the baseline became stable. Upon exposure to 400 ppm of acetone gas, the F-TiO<sub>2</sub>/Ti foam produced a large positive resistance variation, while the TiO<sub>2</sub>/Ti foam produced a relatively small positive response. Therefore, we can draw the conclusion that both sensors exhibit the p-type sensing response behavior. In addition, the gas response of F doped TiO<sub>2</sub>/Ti foam is higher compared to TiO<sub>2</sub>/Ti foam, which indicated that the doping F exerts a preferable effect on the sensing toward acetone. As depicted in Fig. S2, the gas response of F-TiO2/Ti foam increased with the concentration of NaF solution from 0 to 20 mM, and then dropped sharply, indicating that the optimum concentration is 10 mM. The response of F-TiO<sub>2</sub>/Ti foam was 11.91 at RT for 400 ppm acetone, which is higher than that of  $TiO_2/$ Ti foam ( $S = (R_g - R_a)/R_a \times 100$ ). This phenomenon can be ascribed to fluorine modification at TiO<sub>2</sub> surface, which creates active functional groups and more oxygen vacancies. The active functional groups and oxygen vacancies are beneficial for adsorption and dissociation of water molecules, increasing proton concentration and accelerating proton migration. Thus, the response intensity has been enhanced effectively. However, the responsive intensity decreases when the concentration of NaF exceeds 10 mM. The modification of excessive fluorine might hinder the adsorption of water molecules on the surface of TiO<sub>2</sub>. Therefore, the sensing response would decrease at over-high concentration of NaF. Response and recovery behaviors of TiO2/Ti foam and F-TiO<sub>2</sub>/Ti foam were investigated by exposing the sensors to different



Fig. 4. Schematic drawing of the suggested sensing mechanism for the  $TiO_2/Ti$  foam self-supported gas sensor.



Fig. 3. (A) Ti 2p; and (B) O 1s of the XPS spectra of TiO<sub>2</sub>/Ti foam and F-TiO<sub>2</sub>/Ti foam; (C) F 1 s XPS spectra of F-TiO<sub>2</sub>/Ti foam.

concentrations of acetone gases at 25 °C. The electrical resistance fluctuations of TiO<sub>2</sub>/Ti foam and F-TiO<sub>2</sub>/Ti foam were shown in Fig. 5A and B. Compared with TiO<sub>2</sub>/Ti foam, the lower initial resistance of F-TiO<sub>2</sub>/Ti foam demonstrated that the doping F can effectively enhance the conductivity of TiO<sub>2</sub>. Also, as shown in Fig. S3, both sensors exhibited good response ranging from 25 to 800 ppm, indicating a low detection limit of 25 ppm, and their corresponding responses are in the range of 2.92~12.46 for TiO<sub>2</sub>/Ti foam and 4.57~17.42 for F-TiO<sub>2</sub>/Ti foam. In Fig. 5C, the F-TiO<sub>2</sub>/Ti foam revealed a higher response than undoped foam. Besides, the sensors also presented good linear relationship between response intensity and concentration of acetone (C). The linear equations are Response intensity =  $0.0122 \times C + 3.1162$  ( $R^2 = 0.9840$ ) for the TiO<sub>2</sub>/Ti foam sensor, Response intensity =  $0.0164 \times C + 4.6670$  $(R^2 = 0.9906)$  for the F-TiO<sub>2</sub>/Ti foam sensor. The response-recovery time curves of F-TiO<sub>2</sub>/Ti foam and TiO<sub>2</sub>/Ti foam to 400 ppm acetone were displayed in Fig. S4. The calculated response and recovery times of F-TiO<sub>2</sub>/Ti foam were 162.0 s and 220.5 s, respectively, shorter than those of TiO<sub>2</sub>/Ti foam (190.8 s and 268.2 s). To investigate the repeatability of F-TiO<sub>2</sub>/Ti foam sensor, the sensor was periodically exposed to 400 ppm of acetone (Fig. 5D). Clearly, the response of sensor has no distinct shift during the five cycle tests, proving excellent repeatability. Fig. 5E displays the selectivity of TiO<sub>2</sub>/Ti foam and F-TiO<sub>2</sub>/Ti foam, whose gas response for 400 ppm acetone is much higher than that toward other gases such as methanol (CH<sub>3</sub>OH), ethanol (CH<sub>3</sub>CH<sub>2</sub>OH), H<sub>2</sub>S, CO<sub>2</sub> and NO<sub>2</sub>, indicating the good selectivity for acetone. Fig. 5F presents the responses of the sensors after 35 days of operation. Compared with the initial signals, the responses of the TiO<sub>2</sub>/Ti foam and F-TiO<sub>2</sub>/Ti foam exhibited no significant alteration at 400 ppm of acetone, demonstrating that the self-supported sensors have good stability.

The conduction type of semiconductor can be obtained by determining the sign of the slope of linear part about the Mott Schottky curve. As shown in Fig. 6A, the slope of the linear part of curve is positive, confirming the n-type semiconductivity of TiO<sub>2</sub> nanosheets grown on Ti foam [33–35]. Fig. 6B exhibits the influence of relative humidity (RH) on electrical resistance and gas response properties of sensor. With the increase of RH, the resistance decreased from  $2.99 \times 10^5$  to  $2.55 \times 10^5 \Omega$  and the gas response increased gradually, which indicates that humidity plays an important role in influencing the initial electric resistance and p-type response. In addition, the corresponding sensing responses of TiO<sub>2</sub>/Ti foam toward 400 ppm acetone at different operating temperatures were displayed in Fig. 6C. Distinctly, with temperature increasing from RT to 150 °C, the intensity of p-type response ( $\Delta R/R_a$ ) rose at the beginning, then went down, and the maximum value was attained at 50 °C. When the temperature was above 250 °C, the p-type response of TiO<sub>2</sub>/Ti foam converted into n-type response ( $\Delta R/R_g$ ). Accompanying the further increase of operating temperature, the magnitude of the n-type response increased first and then decreased, and the highest response was up to 132.73 at 350 °C.

#### 3.3. Gas sensing mechanism

According to the aforementioned discussion, a surface sensing mechanism related to water molecules can be put forward to explain the p-type response of TiO<sub>2</sub>/Ti foam at room temperature (Fig. 7). First, when TiO<sub>2</sub>/Ti foam was exposed to practical environment (low RH), chemisorption of water molecules on TiO<sub>2</sub> surface occurred, followed by the water molecules dissociating into H<sup>+</sup> ions and OH<sup>-</sup> ions [36]. Then, the H<sup>+</sup> ions were bonded with the lattice oxygen on the surface of TiO<sub>2</sub> nanosheets, accompanying by the release of electrons to the conduction band of TiO<sub>2</sub>. The dissociating and bonding process of water molecules can be described by Eq. No. (4) and Eq. No. (5) [37]:

$$H_2O \leftrightarrow H^+ + OH^- \tag{4}$$

$$H_2O_{(gas)} + Ti_{Ti} + O_0 = (Ti^+ - OH^-)_{Ti} + (OH) + e^-$$
 (5)

At the low humidity level, protons ( $H^+$  ions) migrate through the adjacent  $OH^-$  ions, which are the dominant charge carriers [38]. With the increase of RH, multilayers of water molecules were adsorbed on TiO<sub>2</sub> surface, promoting the formation of  $H^+$  ions as well as hydronium ion ( $H_3O^+$ ) further. Owing to release of electrons and conduction of protons, the resistance of the TiO<sub>2</sub> nanosheets in high humidity decreased compared with that in the low humidity [39]. As showed in



**Fig. 5.** Gas sensing activities of  $TiO_2/Ti$  foam and F- $TiO_2/Ti$  foam. (A, B) Sensing transients (electrical resistance changes) of  $TiO_2/Ti$  foam and F- $TiO_2/Ti$  foam to different concentrations of acetone at 25 °C; (C) Fitted curves of the sensor responses with acetone concentrations; (D) Repeated dynamic sensing responses of F- $TiO_2/Ti$  foam to 400 ppm acetone; (E) Selectivity and (F) long term stability of  $TiO_2/Ti$  foam and F- $TiO_2/Ti$  foam to 400 ppm acetone.



**Fig. 6.** (A) Mott Schottky plot of  $TiO_2/Ti$  foam; (B) Electrical resistance and responses of  $TiO_2/Ti$  foam toward 400 ppm acetone at 25 °C under various relative humidity (RH) from 20 to 90%; (C) The corresponding sensing responses of  $TiO_2/Ti$  foam-based sensor to 400 ppm acetone at various temperatures.



Fig. 7. Schematic illustration of gas sensing reaction of TiO<sub>2</sub>/Ti foam and F-TiO<sub>2</sub>/Ti foam in air and in acetone at room temperature.

Fig. 6B, a significant decrease in resistance of sensor had been demonstrated with increasing RH. Under the definite humidity, when water molecules sorption reached saturation, the resistance of materials would get to a stable value, which was regarded as the initial electric resistance. Subsequently, when the sensor was exposed to acetone, the H<sup>+</sup> ions and H<sub>3</sub>O<sup>+</sup> were bonded with acetone molecules, generating a big intermediate of (CH<sub>3</sub>)<sub>2</sub>COH<sup>+</sup>·(H<sub>2</sub>O)<sub>2</sub>. The formation of (CH<sub>3</sub>)<sub>2</sub>COH<sup>+</sup>·(H<sub>2</sub>O)<sub>2</sub> resulted in the increase of resistance of TiO<sub>2</sub> due to its lower ionic diffusion coefficient and larger ion radius. This chemisorption may interpret why the sensor exhibits p-type sensing response under low temperature conditions. Taken together, the protonation of acetone can be denoted by equations Eq. No.(6).

$$H_{3}O^{+} \cdot (H_{2}O)_{2} + CH_{3}COCH_{3} \leftrightarrow (CH_{3})_{2}COH^{+} \cdot (H_{2}O)_{2} + H_{2}O$$
(6)

Besides, more  $(CH_3)_2COH^+ \cdot (H_2O)_2$  was generated with the increase of RH, and therefore, the response magnitude was also increased, as confirmed in Fig. 6B. When the temperature above 150 °C, the water molecules hardly existed on the surface of TiO<sub>2</sub> nanosheets, displaying a lower p-type sensing response toward acetone. At operating temperatures higher than 250 °C, the water adsorption was replaced by oxygen adsorption, and the n-type sensing mechanism based on oxygen species was dominant [40].

Compared with other reported sensors (Table S1), the TiO<sub>2</sub>/Ti foam and F-TiO<sub>2</sub>/Ti foam self-supported sensors exhibit good performance in the aspects of sensitivity and operation temperature. It can be concluded that the increased response to acetone is mainly ascribed to the structural effect and chemical sensitization effect. First of all, due to the ultrathin nanosheets of TiO<sub>2</sub>/Ti foam, it possesses much larger specific surface area and greater electron mobility for reaction and adsorption. In addition, the presence of oxygen vacancies in TiO<sub>2</sub> nanosheets will undoubtedly improve the acetone sensing performance of TiO<sub>2</sub>/Ti foam and F-TiO<sub>2</sub>/Ti foam. In general, abundant oxygen defects suggest more water molecules can be induced to generate H<sup>+</sup> ions and OH<sup>-</sup> ions, ultimately enhancing the sensing properties. Secondly, as for F-TiO<sub>2</sub>/Ti foam sensor, the doping fluorine formed hydrogen bonding with water molecules due to its large electronegativity to promote the adsorption of water molecules. In addition, the doping of F in the TiO<sub>2</sub> can promote generation of oxygen vacancy on the surface of  $TiO_2$  [41,42], which can act as active sites and then induce the dissociation of adsorbed water molecules. Therefore, compared with  $TiO_2/Ti$  foam, the F- $TiO_2/Ti$  foam sensor exhibits better gas sensing performance.

#### 4. Conclusions

 $TiO_2$  nanosheets were in-situ grown on Ti foam through hydrothermal process. The as-prepared  $TiO_2/Ti$  foam exhibited pronounced acetone gas sensing properties at RT due to their large specific surface area, abundant oxygen vacancies, and high electron mobility. The direct growth of sensing materials onto the suitable support will provide a broad window for designing sensors with superior properties. Furthermore, fluorine doping in  $TiO_2$  lattice can effectively promote the sensing performances of  $TiO_2/Ti$  foam by creating active functional groups and more oxygen vacancies on  $TiO_2$  surface. Finally, the sensor features the strengths of low power consumption, easy fabrication, and admirable response, demonstrating that the developed sensors are very promising for detecting of acetone gas.

#### CRediT authorship contribution statement

Zeguo Feng: Conceptualization, Methodology, Investigation, Writing - original draft. Lu Zhang: Data curation, Formal analysis. Wen Chen: Software, Visualization. Zhengchun Peng: Supervision, Validation, Project administration. Yingchun Li: Supervision, Validation, Project administration.

#### **Declaration of Competing Interest**

The authors declare that they have no competing interests.

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#### Appendix A. Supplementary data

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