

Supplementary Information

One-Dimensional Isomeric and Hierarchical TiO<sub>2</sub>  
Nanostructures: A Novel Air Stable Semiconducting Building  
Block

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## I. Experimental Details

### *Chemicals:*

Poly(vinyl pyrrolidone) (PVP,  $M_w=1,300,000$ ) was purchased from Aldrich. Tetrabutyl titanate ( $Ti(OBu)_4$ ), acetic acid, ethanol and hydrochloric acid were purchased as analytically pure reagents from Tianjin Tiantai Fine Chemicals Co. (China). All chemicals used as received without any further purification.

### *Synthesis of Anatase Nanofibers:*

In a typical procedure for electrospinning, 1.5 g of tetrabutyl titanate was mixed with 3 mL of acetic acid and 3 mL of ethanol in glovebox under vigorous stirring for 10 min. Subsequently, this solution was added to 7.5 mL of ethanol containing 0.45 g of poly(vinyl pyrrolidone) (PVP,  $M_w=1,300,000$ , Aldrich) under vigorous stirring for 30 min. Then, the mixture was loaded into a glass syringe and connected to high-voltage power supply. 12 kV was provided between the cathode (a flat aluminum foil) and anode (syringe) at a distance of 20 cm. The conversion of tetrabutyl titanate to anatase  $TiO_2$  and the complete removal of PVP in the as-spun nanofibers were achieved by calcining at 450 °C for 5 h in air. All the measurements were carried out on the calcined fibers.

### *Isomeric and Hierarchical $TiO_2$ Nanostructure Fabrication:*

A homogenous solution was prepared by mixing 15 mL deionized water with 15 mL HCl. Then 0.5 mL  $Ti(OBu)_4$  was injected into the solution in a 30 mL Teflon-lined autoclave. After vigorous stirring for 10 minutes, a suit amount  $TiO_2$  nanofibers was put into the autoclave. Then autoclave was sealed and heated to 150°C for 4 hours.

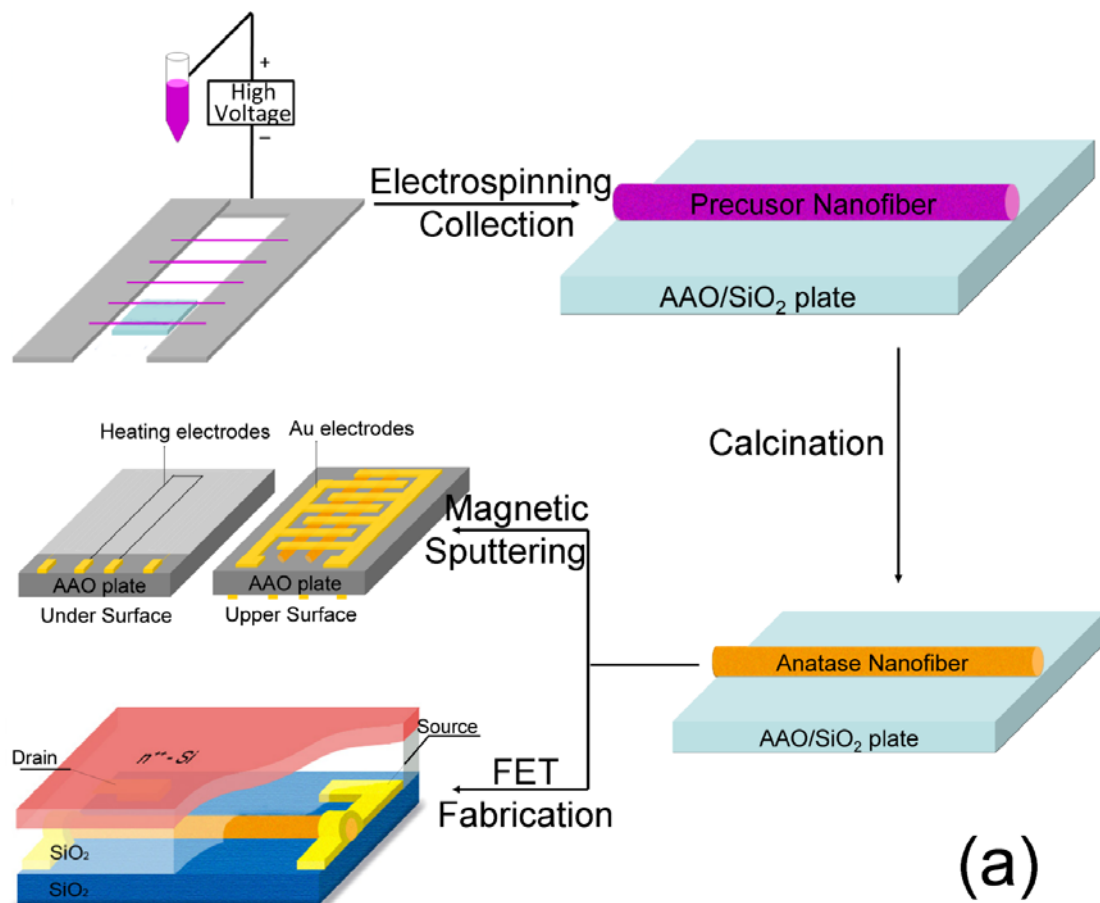
The as-obtained product is washed with deionized water and ethanol to remove any ionic residual then dried in oven at 60°C for 4 hours for further characterization.

***Characterization:***

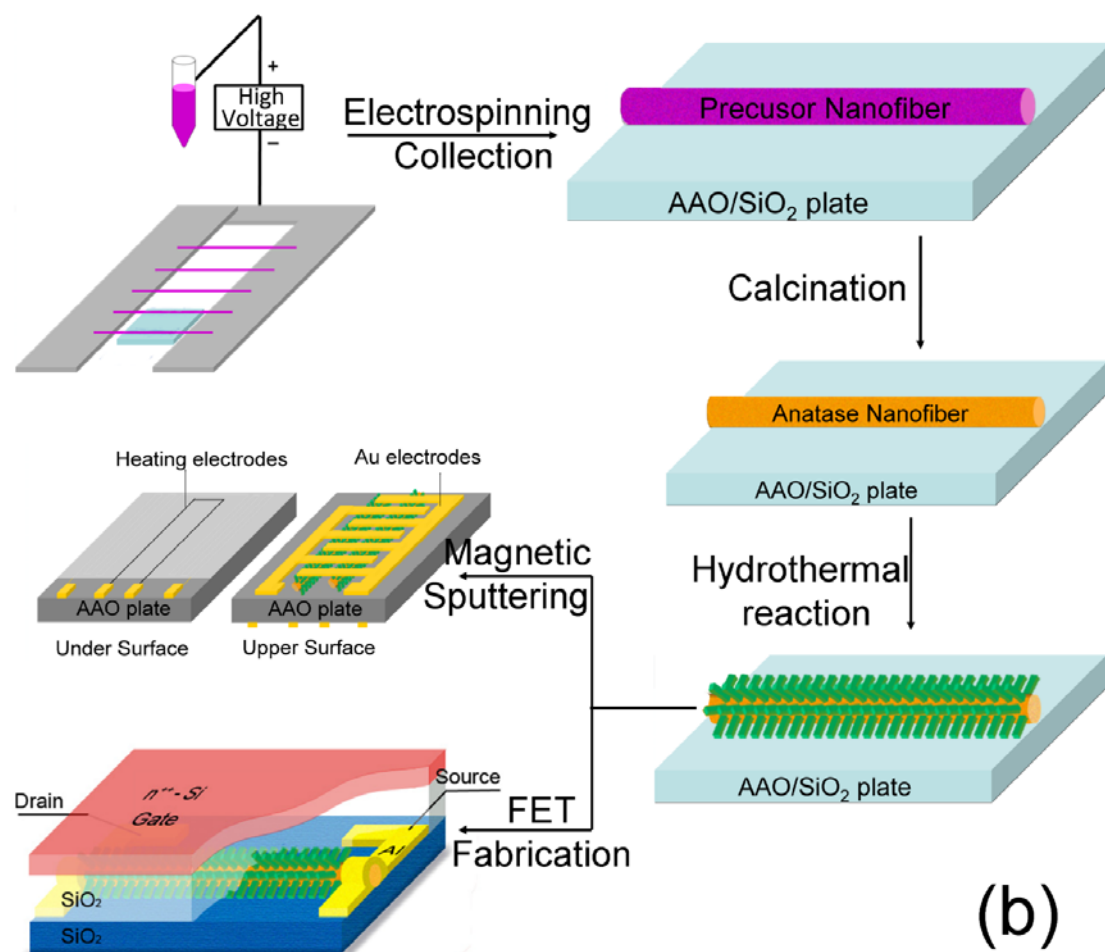
Scanning electron microscopy (SEM) images were recorded on a Shimadzu SSX-550 instrument. The X-ray powder diffraction (XRD) data were collected on a Scintag XDS 2000 diffractometer with a Cu K $\alpha$  radiation.

***Chemical Resistor Fabrication:***

The schematic diagrams of procedure are illustrated in **Scheme S1**. To obtain an assembled 1D IHTNs into a chemical resistor, a modified fiber collector was used during the electrospinning process. Two copper filaments placed in a side-by-side parallel arrangement with a void gap of 2 cm were used as collectors, which can align the nanofibers uniaxially over long length scales during the electrospinning process. The nanofibers were then directly transferred to a blank AAO plate (7 mm  $\times$  5 mm, 0.5 mm thick) after spinning 5 s. The calcination and hydrothermal process were followed. Then three pairs of Au interdigital electrodes (electrodes width and distance: 0.15 mm) were deposited on the top of the plate via the magnetic sputtering method. The device with TiO<sub>2</sub> nanofibers was also fabricated by the same procedure without hydrothermal method.



(a)



**Figure S1.** Synthesis route for the chemical resistors and FET based on separate sample. (a) Synthesis route for the chemical resistors and FET based on anatase nanofibers. (b) Synthesis route for the chemical resistors and FET based on 1D isomeric and hierarchical TiO<sub>2</sub> nanostructure.

The characteristic curves of humidity sensitivity were measured on a ZL5 intelligent LCR testmeter (Made in Shanghai, China) at room temperature. The voltage applied in our studies was AC 1 V. The controlled humidity environments were achieved using supersaturating aqueous solutions of different salts of LiCl, MgCl<sub>2</sub>, Mg(NO<sub>3</sub>)<sub>2</sub>, NaCl, KCl and KNO<sub>3</sub> in a closed glass vessel at room temperature, which yielded

11%, 33%, 54%, 75%, 85% and 95% RH, respectively. This method was established by Wang [1, 2]. We also choose ethanol to test the sensing property by the CGS-1 intelligent test system (Beijing Elite Tech Co. Ltd., China) [3]. The optimized operate temperature was fixed at 320 °C by the heating electrodes deposited on the backside of the AAO plate.

### ***Top-Gate Isomeric and Hierarchical TiO<sub>2</sub> FET Fabrication:***

To clearly see the whole process, all the procedures have been illustrated in **Scheme S1**. The same modified electrospinning process as demonstrated before was used to obtain aligned nanofibers. The nanofibers were then directly transferred to a SiO<sub>2</sub> wafer after spinning 5 s. After the calcination and hydrothermal process, aluminum electrodes were then deposited on the isomeric and hierarchical TiO<sub>2</sub> by thermal evaporation using a mask to form 100 μm of the channels. Then a little of polyvinylpyrrolidone aqueous solution was dipping onto the sides of SiO<sub>2</sub> substrates as binder for attaching top-gate electrode. Finally, a highly n<sup>++</sup>-doped Si wafer coated with a 1.6 μm thick SiO<sub>2</sub> dielectric was used as the top-gate electrode. Gaps between this mechanically contacted top-gate electrode automatically filled with dry air (5% RH - 20% RH), which serves together with the SiO<sub>2</sub> as the gate dielectric. The device with TiO<sub>2</sub> nanofibers was also fabricated by the same procedure without hydrothermal method. The current-voltage (I-V) characteristics of the OFETs were measured in a clean and metallicly shielded box at room temperature in air (5% RH - 20% RH), and recorded using a Keithley 4200 SCS.

## **II. Data analysis**

### ***Method to Calculate Weight Fraction of Rutile:***

Here, from the XRD patterns, the anatase (101) peak at  $2\theta = 25.3$  and the rutile (110) peak at  $2\theta = 27.4$  were chosen to calculate the weight fractions of rutile  $\text{TiO}_2$  in the heterostructured materials using the formula [4]:

$$x = \left( 1 + 0.8 \frac{I_A}{I_R} \right)^{-1}$$

Where  $x$  is the weight fraction of rutile in the sample, and  $I_A$  and  $I_R$  are the X-ray intensities of the anatase and rutile peaks, respectively.

#### ***Comparison with Other 1D Nanostructures to Chemical Gases and Humidity:***

The results obtained by various workers on 1D nanostructure gas and humidity sensors are summarized in Table S1 and S2. It can be clearly observed that they are easily influenced by ambient gases and relative humidity (RH%), causing the serious air instability of they-based devices. And by comparing with our experimental results, it can be easily concluded that constructing 1D isomeric semiconducting nanorods on 1D semiconducting nanostructure to form 1D isomeric and hierarchical semiconducting nanostructure can not only stabilize 1D semiconducting nanostructures in air but also maintain their electrical properties.

Table S1. 1D semiconducting nanostructures in gas sensing applications.

1D nanostructure resistive sensor	Gas	Gas conc. (ppm)	Sensitivity	Operating temp. (°C)	Ref.
$\text{SnO}_2$ nanowire	$\text{H}_2$	500	3	RT	[5]
$\text{SnO}_2$ nanoribbon	$\text{NO}_2$	100	7	RT	[6]
$\text{SnO}_2$ nanotube	Ethanol	7.8%	20	400	[7]
ZnO nanowire	CO	400	3200	275	[8]
ZnO nanowire	Ethanol	100	45	270	[9]
$\text{In}_2\text{O}_3$ nanowire	Ethanol	100	27	370	[10]
$\alpha\text{-Fe}_2\text{O}_3$ nanotube	Ethanol	10	7	RT	[11]
$\text{CeO}_2$ nanowire	CO	200	2	RT	[12]
$\text{WO}_{2.72}$ nanowire	$\text{H}_2$	1000	22	RT	[13]

Table S2. 1D semiconducting nanostructures in humidity sensing applications.

1D nanostructure humidity sensor	Humidity range	Response time (s)	Recovery time (s)	Sensitivity	Reference
WO <sub>3</sub> nanowire	25-85%			4.5 mV/% RH at 60 °C	[14]
Al <sub>2</sub> O <sub>3</sub> nanowire	11.3-97.3%	30	50	1.3% pF/%RH at 40Hz	[15]
CeO <sub>2</sub> nanowire	15.2-97%	3	3	85 at 97%RH	[16]
TiO <sub>2</sub> nanowire	12-97%	< 2min	<2 min	0.35MΩ/%RH at 25 °C	[17]
TiO <sub>2</sub> nanotubes	11-95%	100	190		[18]
TiO <sub>2</sub> nanofibers	40-90%	1	4	20 MΩ/%RH at 100 Hz	[19]
Li <sup>+</sup> -doped TiO <sub>2</sub> nanofibers	11-95%	2	5	240Ω/%RH at 100 Hz	[20]
Mg <sup>2+</sup> /Na <sup>+</sup> -doped TiO <sub>2</sub> nanofibers	11-95%	2	1	0.47MΩ/%RH at 100 Hz	[21]

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