

## Supporting Information

### Synthesis of TiO<sub>2</sub> decorated Co<sub>3</sub>O<sub>4</sub> acicular nanowire arrays and its application as an ethanol sensor

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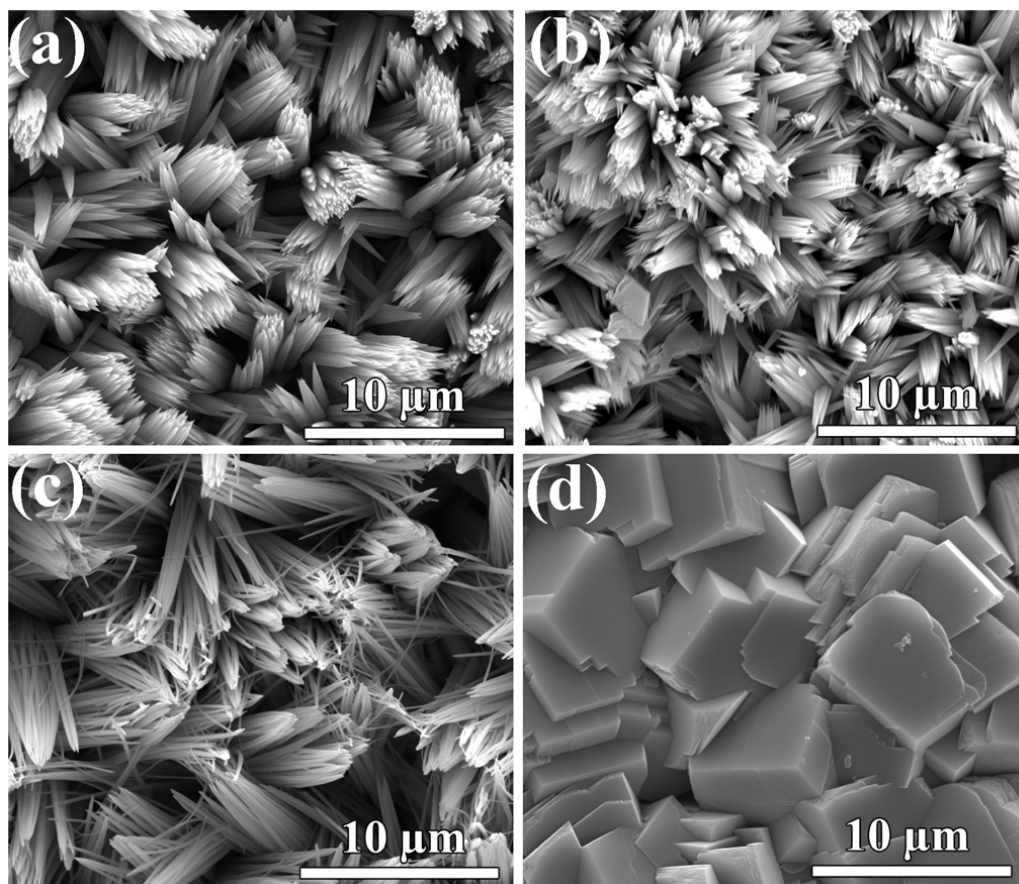
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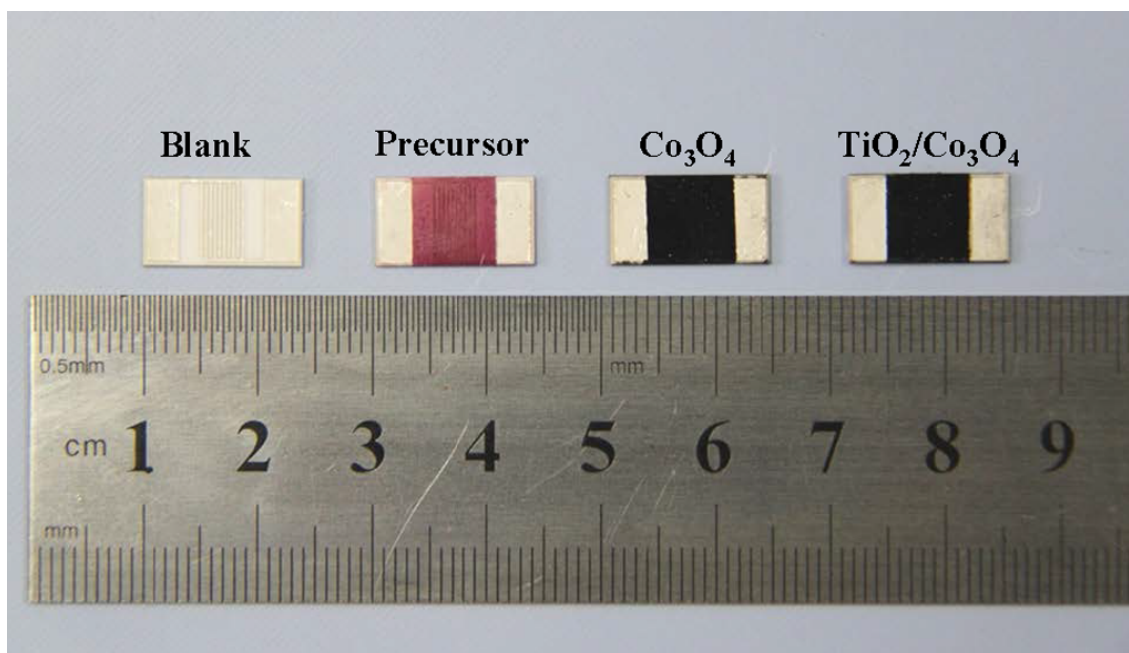
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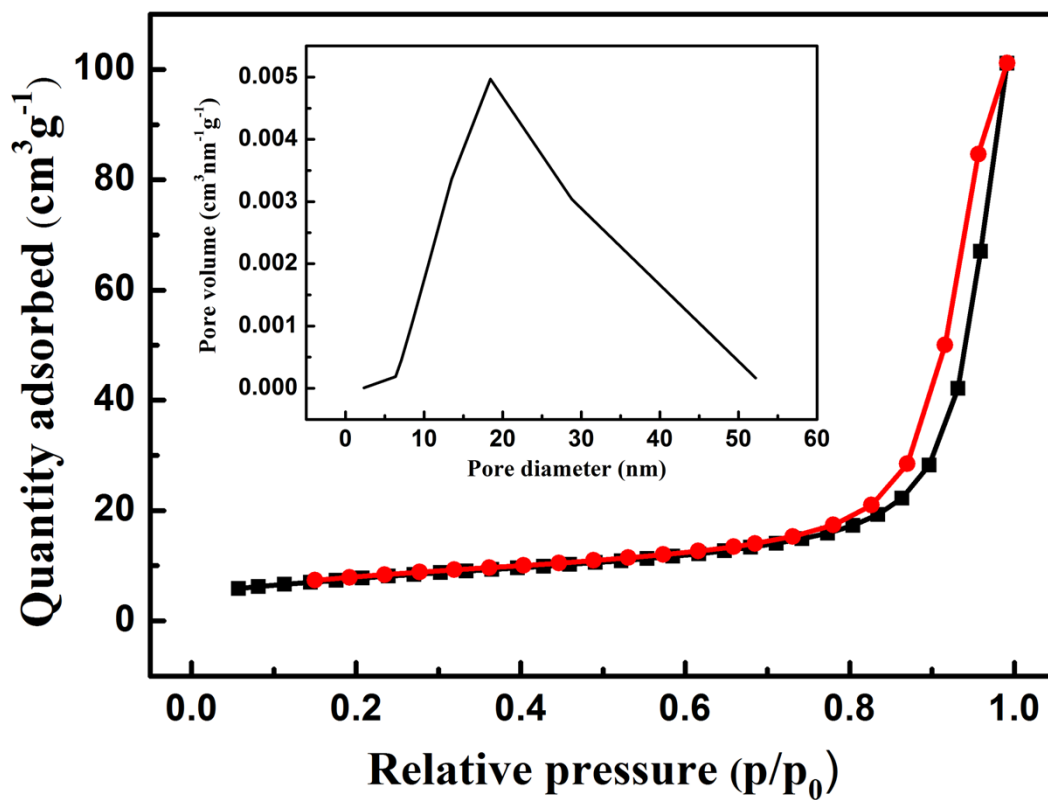
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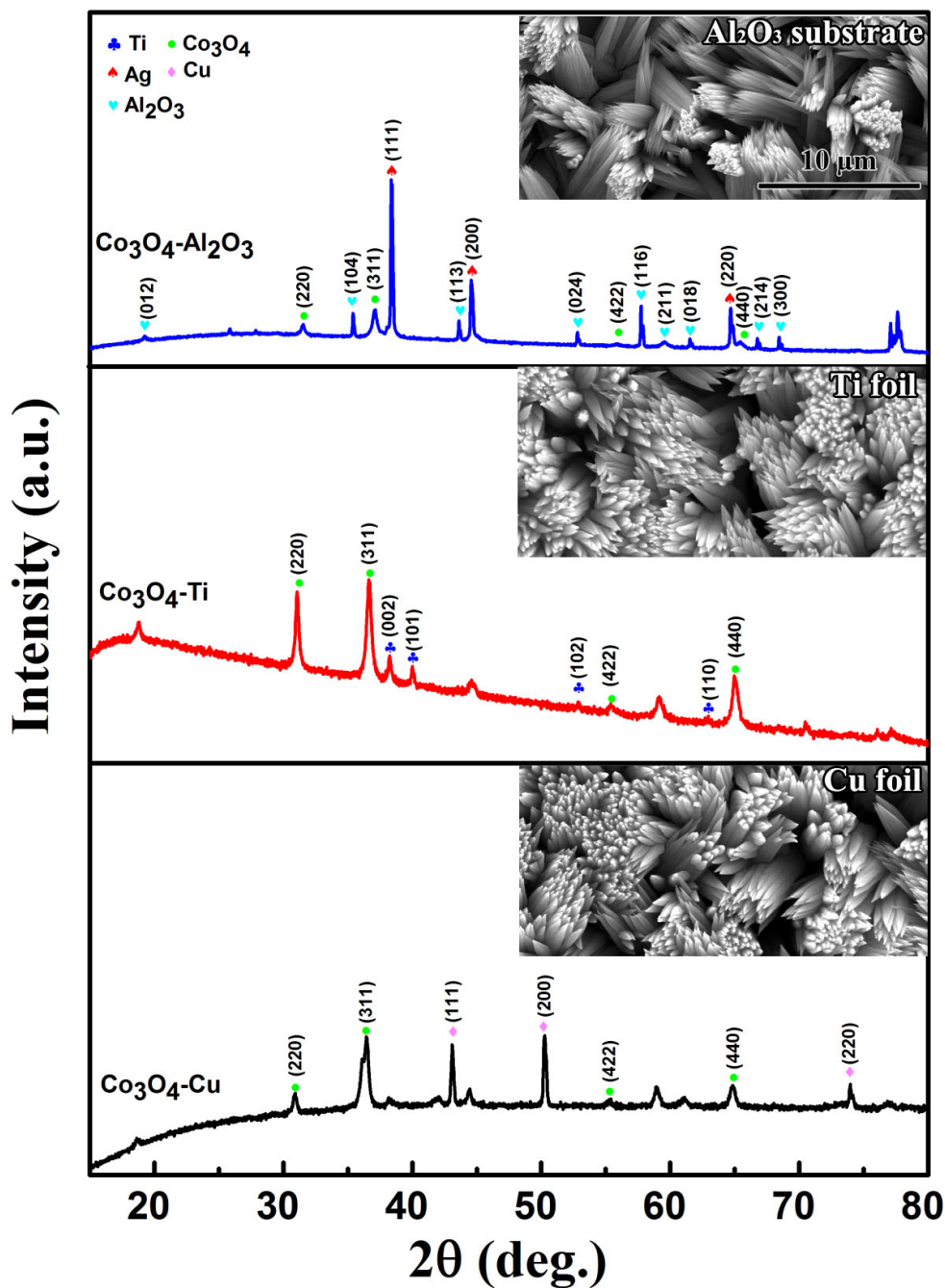
**Figure S1.** SEM image of cobalt-precursor nanostructure growing on the Al<sub>2</sub>O<sub>3</sub> substrate at different hydrothermal temperature: (a) 85 °C; (b) 95 °C; (c) 125 °C; (d) 145 °C.



**Figure S2.** The optical micrographs of the Al<sub>2</sub>O<sub>3</sub> substrates, the as-synthesized precursor, pristine Co<sub>3</sub>O<sub>4</sub> and TiO<sub>2</sub>/Co<sub>3</sub>O<sub>4</sub> NW arrays.



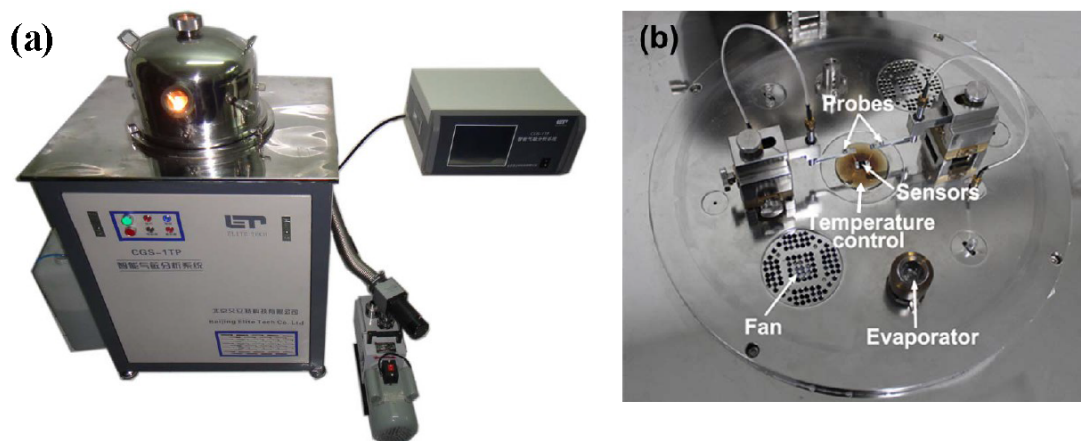
**Figure S3.** N<sub>2</sub> adsorption/desorption isotherm curve of the acicular-like TiO<sub>2</sub>/Co<sub>3</sub>O<sub>4</sub> NWs and porous volume distribution of the pore size.



**Figure S4.** XRD patterns and SEM images of: Co<sub>3</sub>O<sub>4</sub> nanowire with an acicular-like structure grown on the polycrystal Al<sub>2</sub>O<sub>3</sub> plate, Ti foil and Cu foil, respectively.

In this study, we found that the Co<sub>3</sub>O<sub>4</sub> nanowire grown on the titanium foil or copper foil substrate can also form an acicular-like structure, which are shown in Figure S4. At the beginning, the Co<sup>2+</sup> ions interact with F<sup>-</sup> ions to form CoF<sup>+</sup> complexes. And then, the carbonate anions originated from the Urea reacts with CoF<sup>+</sup> to form Co(CO<sub>3</sub>)<sub>0.5</sub>(OH)0.11H<sub>2</sub>O crystals. There are plenty of functional groups exist on the surface of the supporting substrates

containing chemical defects, hydroxyl and carboxyl or carbonyl groups, which are beneficial to heterogeneous nucleation. With the assistance of hydrogen bonding, the dangling functional groups act as anchor sites to capture  $\text{Co}(\text{CO}_3)_{0.5}(\text{OH})0.11\text{H}_2\text{O}$  crystal seeds and make the as-formed crystal seeds stick firmly to the supporting substrate. These crystals agglomerate into  $\text{Co}(\text{CO}_3)_{0.5}(\text{OH})0.11\text{H}_2\text{O}$  crystalline particles on the surface, and naturally form into acicular like NR arrays. The acicular structure is greatly influenced by the chemicals and respective processes during the hydrothermal reaction. Thus in this study, we can select Ti foil as the substrate for collecting more powders for the BET characterization, which has been applied in our previous studies. (Wen et al. *J. Mater. Chem. A*, 2013, 1, 7511).



**Figure S5.** (a) CGS-1TP intelligent gas sensing analysis system. (b) A photograph of the control platform of the gas sensing analysis system.

In the experiment, the gas-sensing measurements were performed on an intelligent gas sensing analysis system (CGS-1TP, Beijing Elite Tech Co., Ltd, China), shown in Fig. R2. The saturated target gas was injected into the test chamber (18 L in volume) by a micro-injector through a rubber plug. The resistance of sensors is collected and analyzed by the system in real time. The volume of the ethanol can be calculated by the following formula:

$$Q = (V \times C \times M) / (22.4 \times d \times \rho) \times 10^{-9} \times (273 + T_R) / (273 + T_B)$$

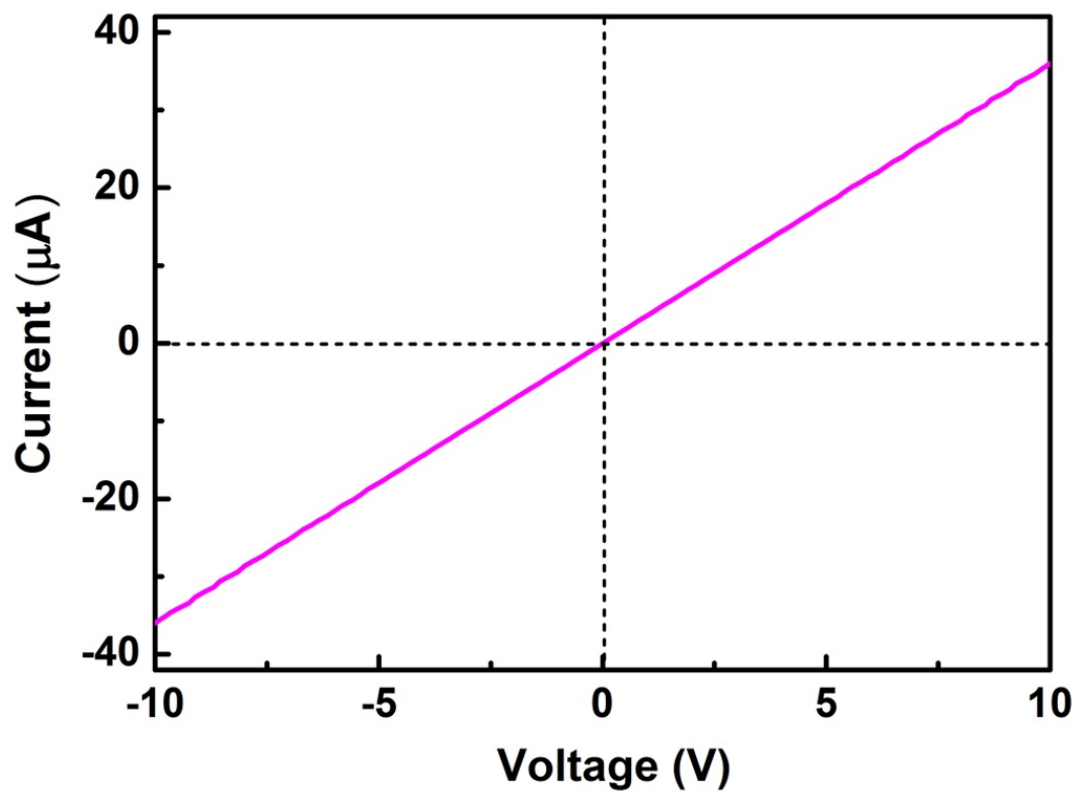
Q—Liquid Volume (mL)      V—Test Chamber Volume (mL)

M—Molecular Weight (g)       $\rho$ —Liquid Purity

C—Gas Concentration (ppm)      d—Liquid Density( $\text{g}/\text{cm}^3$ )

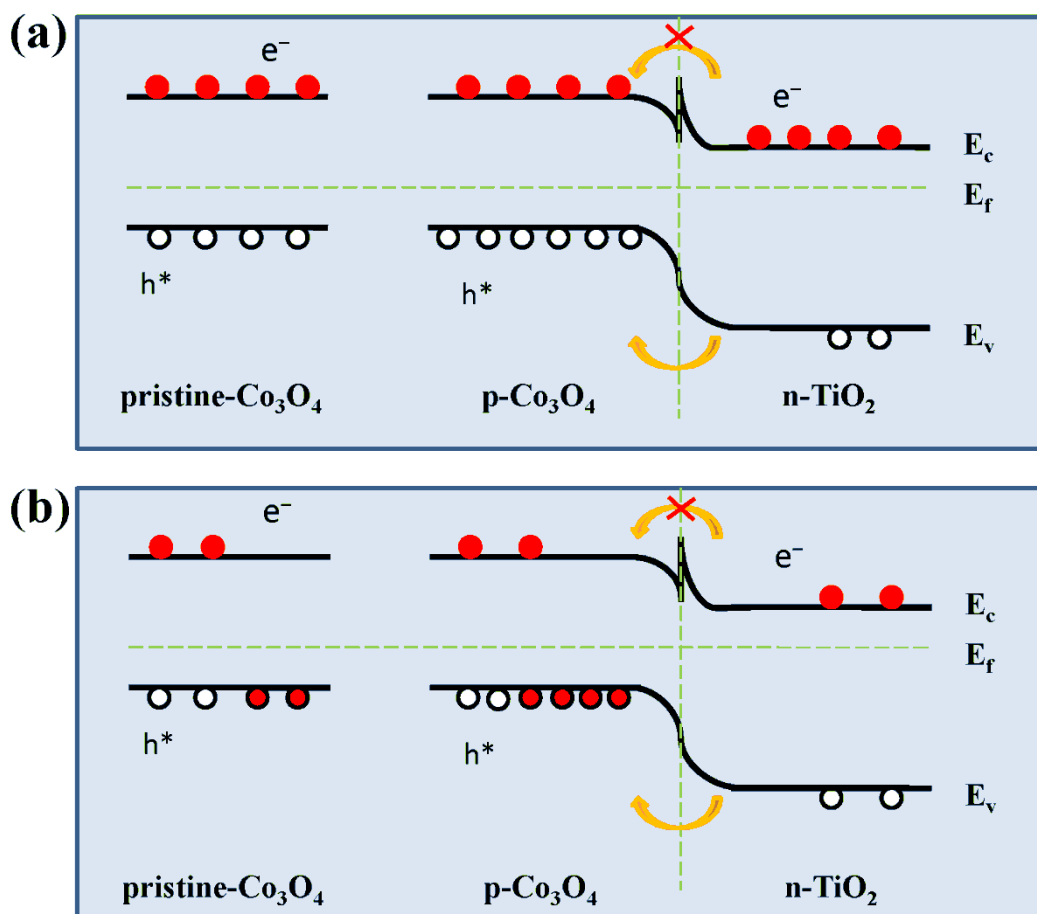
$T_R$ —Environment Temperature ( $^{\circ}\text{C}$ )       $T_B$ —Testing Temperature ( $^{\circ}\text{C}$ )

This gas-sensing test method, so-called Static Volumetric Method, is widely used by many researchers. On the other hand, the analysis system offered an external temperature control (from room temperature to  $500^{\circ}\text{C}$ ), which could conductively adjust the sensor temperature with a precision of  $1^{\circ}\text{C}$



**Figure S6.** The I-V characteristics of TiO<sub>2</sub>/Co<sub>3</sub>O<sub>4</sub> sample between the two neighboring electrode.



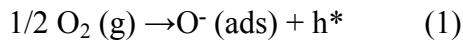


**Figure S7.** The energy band structure diagram for the pristine  $\text{Co}_3\text{O}_4$  and  $\text{TiO}_2/\text{Co}_3\text{O}_4$ . (a) The pristine state. (b) Exposed in the ethanol.

### The superiority of p-n junction sensor than conventional chemi-resistive sensor:

Fig. S7 described the energy band structure diagram for the  $\text{Co}_3\text{O}_4$  and  $\text{TiO}_2/\text{Co}_3\text{O}_4$  heterojunction in the pristine state. As a p-type semiconductor, the resistance of  $\text{Co}_3\text{O}_4$  is based on the concentration of the hole. For the  $\text{TiO}_2/\text{Co}_3\text{O}_4$ , the holes in p-type  $\text{Co}_3\text{O}_4$  and the electrons in n-type  $\text{TiO}_2$  generate a self-built electric field, which could establish a depletion layer until they get an equalization of the Fermi level. The heterojunction region of  $\text{TiO}_2/\text{Co}_3\text{O}_4$  is believed to easily attract reductive and oxidative gases. When exposed in the air (1), the hole density on the surface of  $\text{Co}_3\text{O}_4$  increases while the electrons on the surface of  $\text{TiO}_2$  decrease due to the ionization of absorbed oxygen species, during which, the holes can

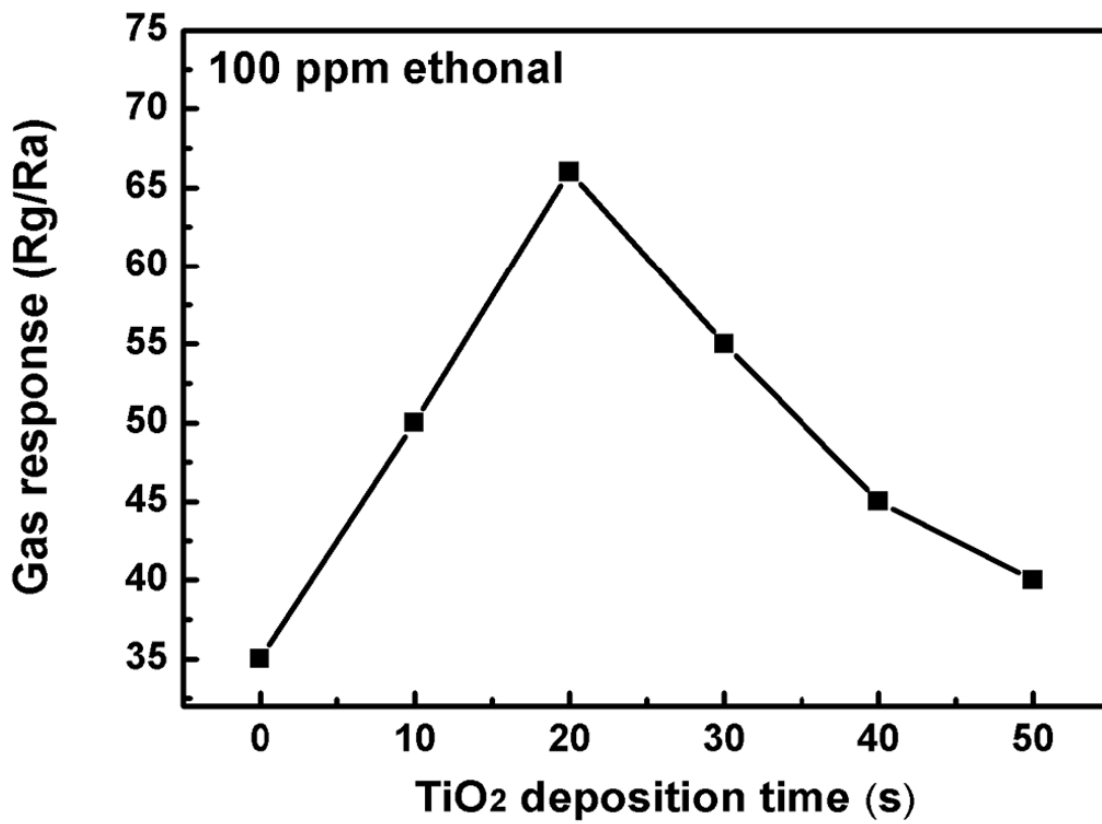
easily transfer to p-type  $\text{Co}_3\text{O}_4$  semiconductor, leading to a lower resistance of the sensor.



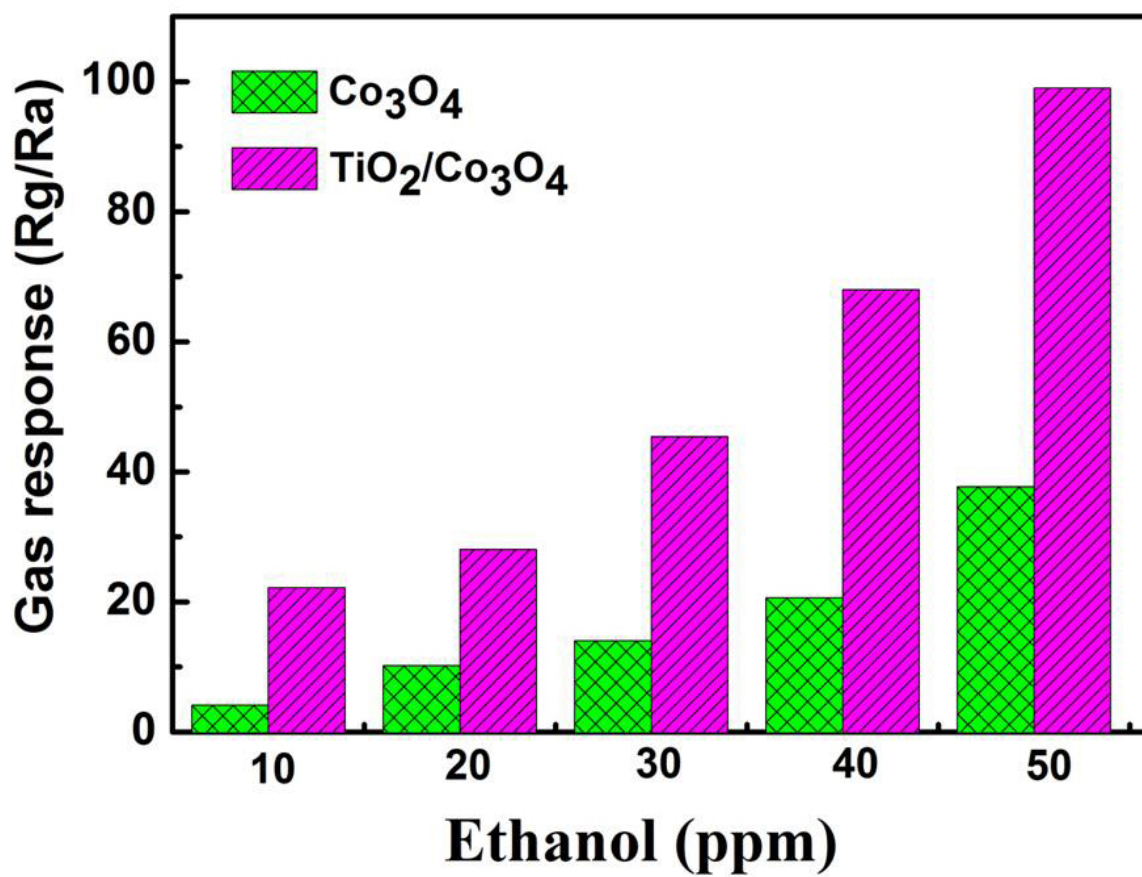
As shown in Fig. R1(b), when ethanol was introduced into the chamber, the new generated free electrons from the reaction (2) would neutralize the holes in the  $\text{Co}_3\text{O}_4$ . As a consequence, its resistance would demonstrate an increase. The resistance transient is applied to reflect its gas response. For the  $\text{TiO}_2/\text{Co}_3\text{O}_4$ , the charged carrier accumulation layer near the surface is thinned by the electrochemical interaction between  $\text{O}^-(\text{ads})$  and  $\text{C}_2\text{H}_5\text{OH}$  molecules (2), which releases free electrons and neutralizes the holes in the  $\text{Co}_3\text{O}_4$ . However, the electrons transfer from n-type semiconductor to the p-type semiconductor are impeded at this moment, which makes the resistance of the device increases more rapidly. As a consequence, the  $\text{TiO}_2/\text{Co}_3\text{O}_4$  demonstrates a higher gas sensitivity than the pristine  $\text{Co}_3\text{O}_4$ . The reaction process can be described as follows:



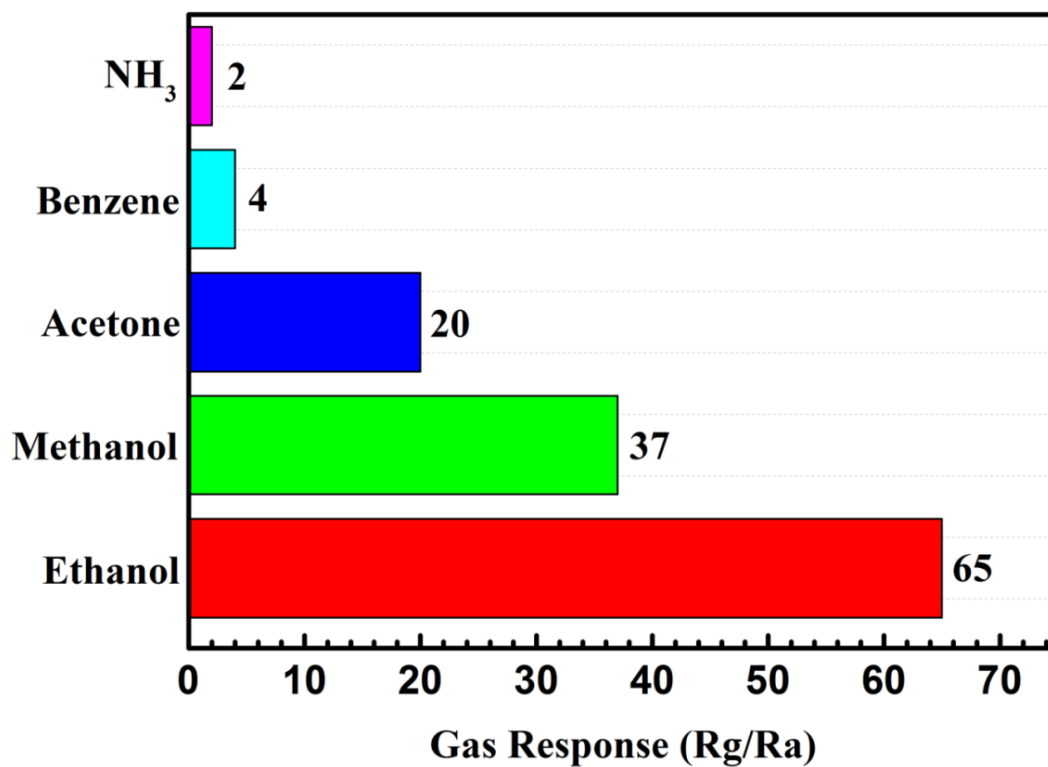
As shown in the schematic diagram, it is supposed that there exists only four holes in the pristine  $\text{Co}_3\text{O}_4$ , two of them are neutralized when ethanol is introduced, and its response would be two. As a p-type semiconductor, the resistance is significantly influenced by the hole density, where  $R_i \propto 1/N_i$ ,  $R_f \propto 1/N_f$  ( $R_i$  and  $N_i$  represent the initial resistance and the initial number of holes in  $\text{Co}_3\text{O}_4$ ;  $R_f$  and  $N_f$  represent the resistance and the number of left holes in  $\text{Co}_3\text{O}_4$  after neutralization). Thus, the resistance of  $\text{Co}_3\text{O}_4$  can be calculated as  $R_f/R_i = N_i/N_f = 4/2 = 2$ . While for the  $\text{TiO}_2/\text{Co}_3\text{O}_4$ , the holes in p-type semiconductor  $\text{Co}_3\text{O}_4$  and the electrons in n-type semiconductor  $\text{TiO}_2$  form a self-built electric field, which could establish a depletion layer until they get an equalization of the Fermi level. It would attract six holes in the  $\text{Co}_3\text{O}_4$  region in the initial state. In addition, the heterojunction region of  $\text{TiO}_2/\text{Co}_3\text{O}_4$  is believed to easily attract reductive and oxidative gases. When ethanol is introduced, four holes would be neutralized and two are left in  $\text{Co}_3\text{O}_4$  region, as a result, it demonstrates a response of three ( $R_f/R_i = N_i/N_f = 6/2 = 3$ ), which is larger than that of the  $\text{Co}_3\text{O}_4$ . The superiority of p-n junction sensor than conventional chemi-resistive sensors has been widely confirmed in the sensors such as n- $\text{Fe}_3\text{O}_4/\text{p-Co}_3\text{O}_4$  (Qu et al, *Sens. Actuators B Chem.*, 2010, **148**, 478-485.), and n- $\text{ZnO}/\text{p-Co}_3\text{O}_4$  (D. Bekermann, et al., *ACS Appl. Mater. Interfaces*, 2012, **4**, 928-934.).



**Figure S8.** The gas responses of TiO<sub>2</sub>/Co<sub>3</sub>O<sub>4</sub> sensor to a series content of TiO<sub>2</sub>.



**Figure S9.** The maximum gas responses of the TiO<sub>2</sub>/Co<sub>3</sub>O<sub>4</sub> and Co<sub>3</sub>O<sub>4</sub> sensor to a series concentration of ethanol at 160 °C.

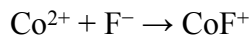


**Figure S10.** The responses of the TiO<sub>2</sub>/Co<sub>3</sub>O<sub>4</sub> sensor to several gases with concentration of 100 ppm at 160 °C.

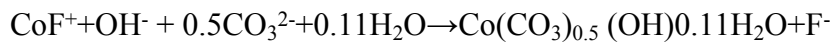
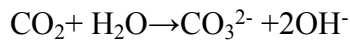
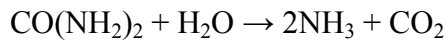
## The formation process of the TiO<sub>2</sub>/Co<sub>3</sub>O<sub>4</sub> acicular NW arrays:

The chemicals and the respective processes greatly influence the morphology of the final products. In this study, Urea can release ammonia at a low hydrolysis rate, which provides carbonate anions simultaneously during the hydrolysis. Carbonate anions can be gradually intercalated into the interlayers by replacing F<sup>-</sup> and OH<sup>-</sup> anions due to the strong affinity to Co<sup>2+</sup>. The anion exchange process is kinetically driven and induced a dissolution-recrystallization in which carbonate anions act as a structure-directing agent, producing acicular-like cobalt hydroxide carbonate. (Xie et al. *J. Phys. Chem. C* 2010, 114, 2116, Xu et al. *J. Phys. Chem. B* 2003, 107, 12643). We have added the related discussion in the revised manuscript.

In the presence of NH<sub>4</sub>F, Co<sup>2+</sup> ions form complexes with F<sup>-</sup>:



When using urea as a hydrolysis reagent, cobalt hydroxide carbonate forms:



After the treatment:

