Toward Practical Gas Sensing with Rapid Recovery Semiconducting Carbon Nanotube Film Sensors

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Supplementary information

Fabrication and Measurement

Fabrication Process: We use the prepared carbon nanotube solution with a semiconductor purity higher than 99.99%, and dilute the carbon nanotube solution with toluene. The 4-inch Si/SiO_2 substrate was soaked in the diluted solution for 48 hours, and then the substrate was taken out of the solution and cleaned with 99.999% N_2. A 3 nm Y film was deposited by electron beam evaporation and thermally oxidized at 250 °C to make it tightly combined with the PCz polymer. The CNT-TFT gas sensors are fabricated in the following steps. (1) The source and drain regions are formed by photolithograph, EBE of Ti/Au (20 nm/40 nm) film and standard lift-off process. (2) The redundant CNTs are etched to form the channel with the length of 10 μm and width of 90 μm by Reactive Ion Etching (RIE). (3) Expose the channel area through photolithograph. (4) Finally, 1 nm Pd NPs are deposited by EBE to form our sensing layer. (5) Repeat steps (3) and (4) to modify the 0.3 nm Pd/1 nm Au NPs and 1 nm Sn NPs (oxidized at 250 °C for 30 minutes to form SnO_2 NPs) on the surface of CNT as the sensing materials. Microheaters are

formed by magnetron sputtering Ti / Pt (5 nm/90 nm). In addition, we used FlIR's infrared thermometer to analyze the relationship between the chip temperature and the power of the microheater.

Measurement of gas Sensing Performance: The measurement of the gas sensor is to place the sensor device in the constructed gas environment. The gas test chamber is a 375 ml quartz glass tube. We place the sensor on a PCB that can be connected to the electrical measurement equipment by bonding and collect the data of the sensors through the Kethily 4200 semiconductor analyzer. Taking the test of H_2 as an example, the test process of H_2S and NO_2 is the same. The specific test process is as follows. We first pass 2000 sccm of high purity nitrogen for 5 minutes to exhaust the air in the chamber and the pipeline. Then turn on the H_2 gas flowmeter to set the target flow rate for preparing different target gas concentrations. Here we set the H_2 concentration to 20, 40, 60, 80, and 100 ppm. The gas flow rate is all controlled by the mass flow controller. The target gas was turned off after passing the target H_2 gas for 100 s. Finally, switch to air and observe the normal recovery of the sensor at room temperature. Meanwhile, we can load the back gate voltage V_{gs}= +60 V for fast recovery and the recovery time is 50 s. Since the sensor's response to NO_2 gas changes in the opposite direction to H_2 and H_2S gas, the back gate voltage we use is V_{gs}= −60 V for fast recovery.

S1. The Raman characteristics of sensitive materials-modified CNT film-based sensors.

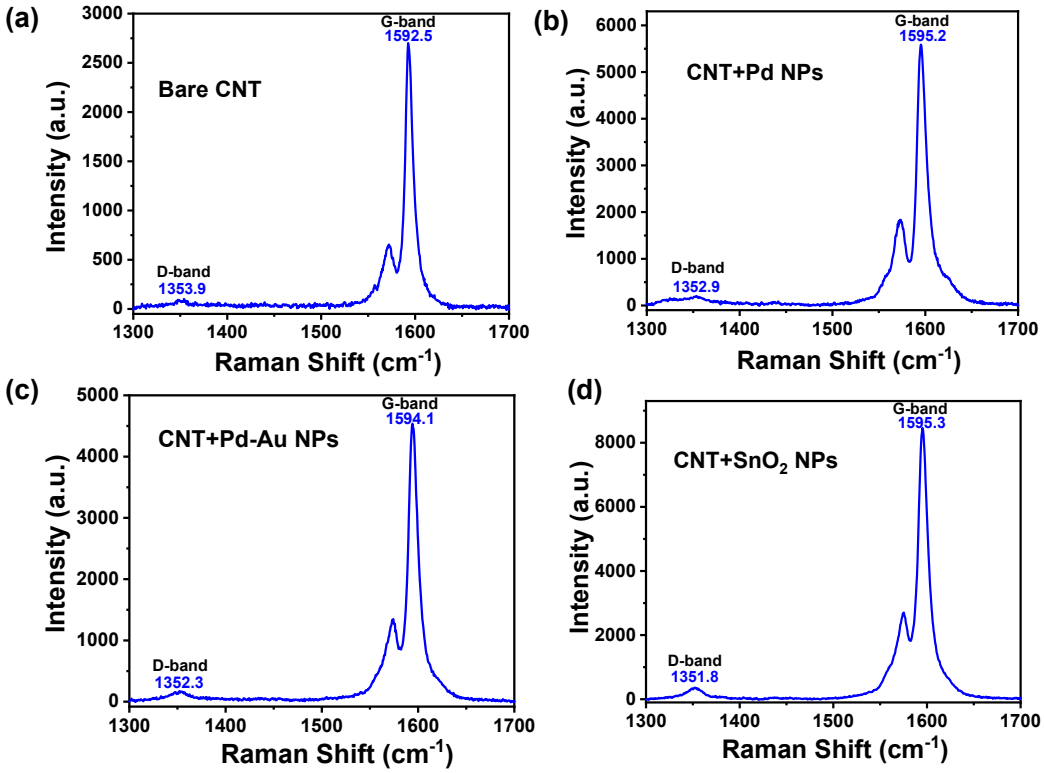


Figure S1 Raman characteristics of (a) bare CNT, (b) (c) (d) sensitive materials-modified CNT film-based sensors. High I_G/I_D ratio suggests few defects in CNTs used here. The red shift or blue shift indicates the charge transferring effect between the nanoparticles decoration and CNT film.

S2. The selectivity of Pd-modified CNT film-based sensor.

We measured the selectivity of Pd-modified CNT film-based sensor. The selectivity of CNT film-based gas sensors depends on the modification materials. In this experiment, the response of the Pd-modified CNT film-based gas sensor to H_2, H_2S, and NO_2 is shown in Fig. S2. The sensor has a response of 1.01 for 5 ppm H_2, 0.63 for 10ppm H_2S, and -0.23 for 10 ppm NO_2.

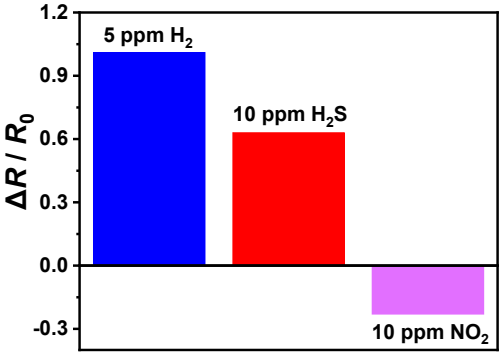


Figure S2 The selectivity of Pd modified CNT film-based sensor to 5 ppm H_2, 10 ppm H_2S and 10 ppm NO_2.

S3. Temperature characterization of on-chip microheaters and its use for gas recovery.

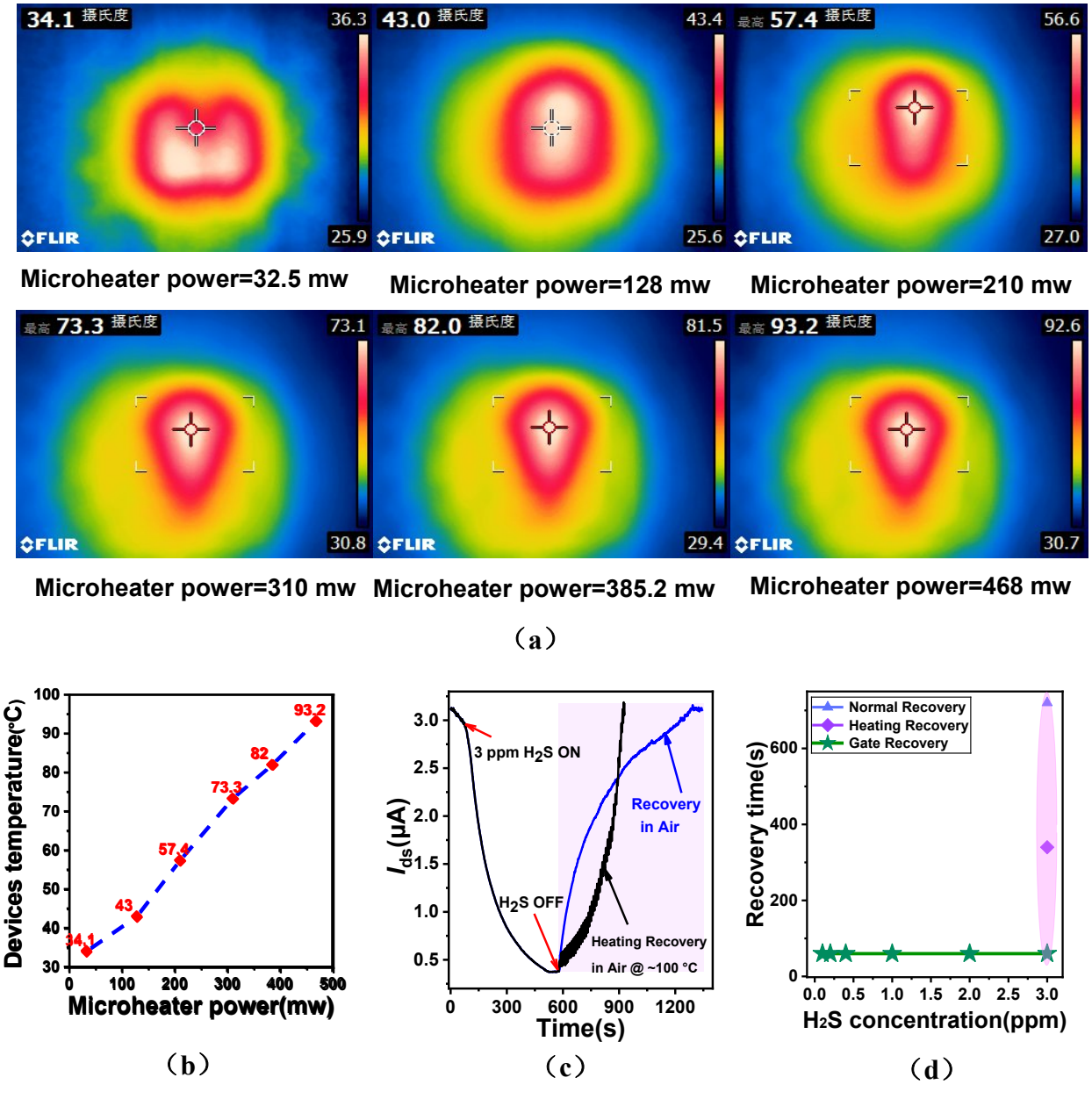


Figure S3 Characterization of microheater and its effect on H_2S gas recovery.(a)Infrared imaging at different microheater powers.(b) Plot of chip temperature vs microheater power, and temperature and power are approximately linear.(c) Comparison of natural recovery and heating recovery of CNT-TFT devices modified with 0.3 nm Pd/1 nm Au NPs in response to 3 ppm H_2S gas.(d) For 3 ppm H_2S gas, the comparison of the recovery time used by the three methods.

S4. Schematic diagram of the core circuit of hydrogen detection system.

The H_2 measurement system mainly includes sensor array module, RTF circuit module and control module, ADC module, FPGA module, screen display module. First, through the control module in FPGA, we can choose one sensor or sensors to use to measure H_2 concentration, and then the RTF circuit converts the resistance value of the sensor into the period value, the conversion formula is shown in Formula (1) , where R is the resistance value of the sensor.

$$T = \frac{4C_L R_1}{R_2} \times R \tag{1}$$

Then, sampling through an 8-bit, 50 M/s ADC. In this system the average period value is about 100 μs, that is, the average frequency value is about 10 KHz, it can be concluded that the maximum error does not exceed 4/10000. For H_2 detection, the system fully meets the detection requirements. The digital signal obtained from ADC is preprocessed, filtered and slope calculated to obtain the concentration of H_2. Finally, we realize the display on the screen through the LCD driver module in FPGA.

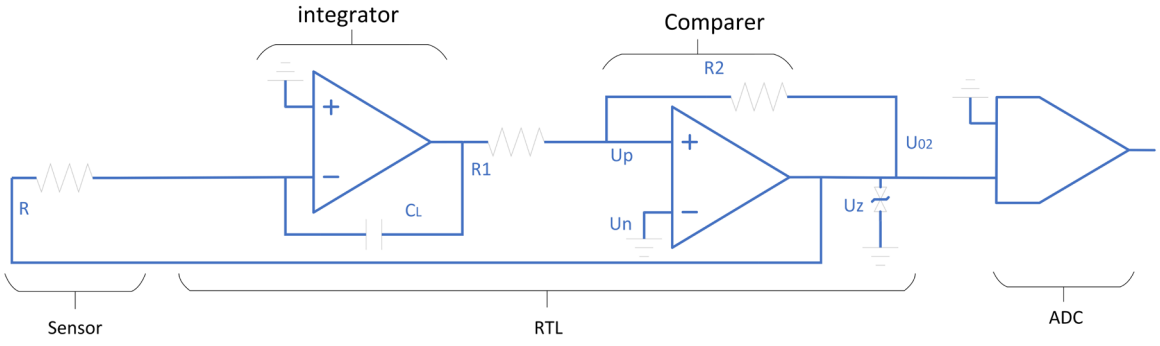


Figure S4 Schematic diagram of signal conversion.

S5. The combination of CNT-TFT gas sensor and detection system can detect different concentrations of H_2 in the actual environment.

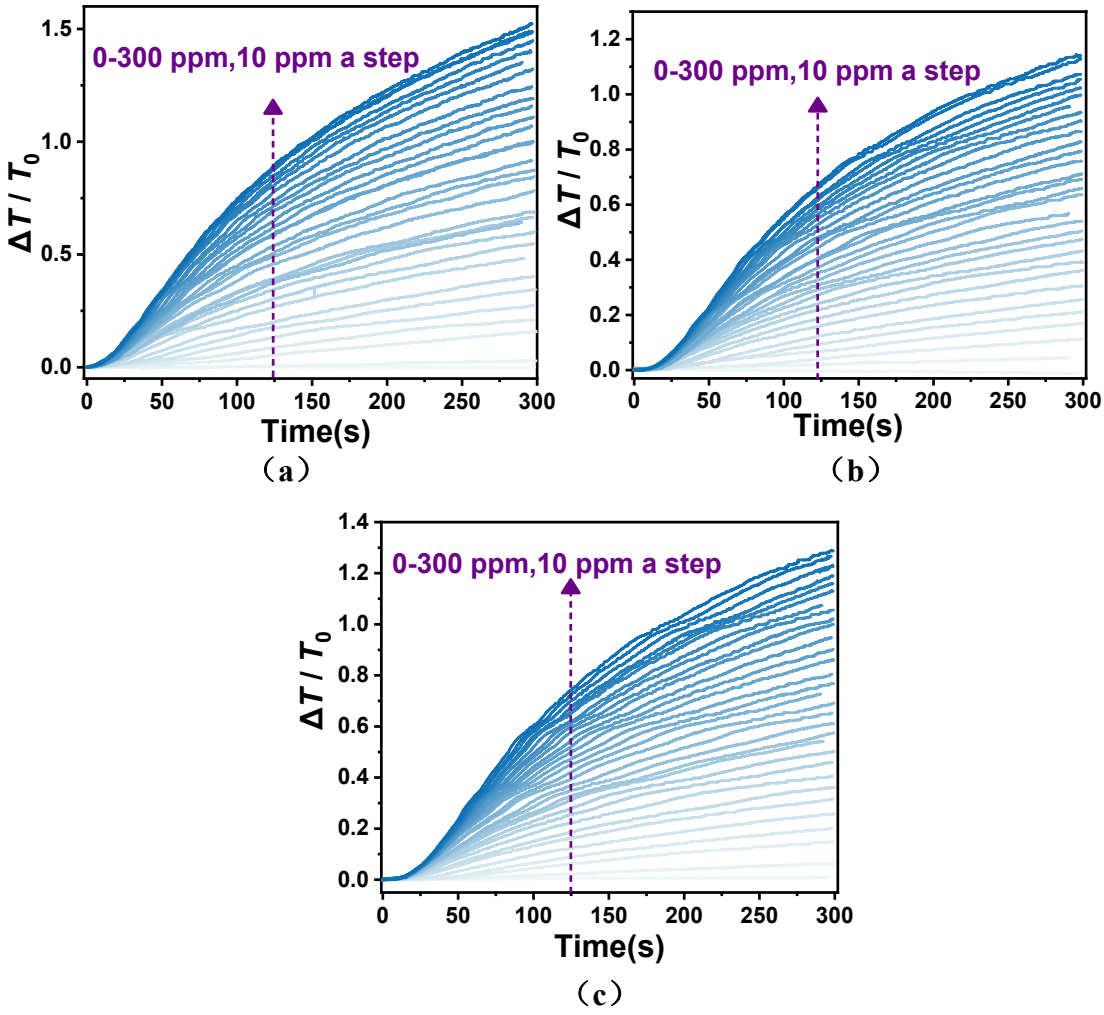


Figure S5 The H_2 sensor detection system detects the period signal changes after 30 concentration gradients of H_2 (0-300 ppm, step: 10 ppm) are injected. (a-c) For the change of the corresponding period signal after 30 concentration gradients of H_2 were injected, we repeatedly tested three sets of data. The system showed good consistency and stability.

S6. The maximum slope value of the oscillation period change curve of H_2 concentration and the corresponding time when the maximum slope value appears.

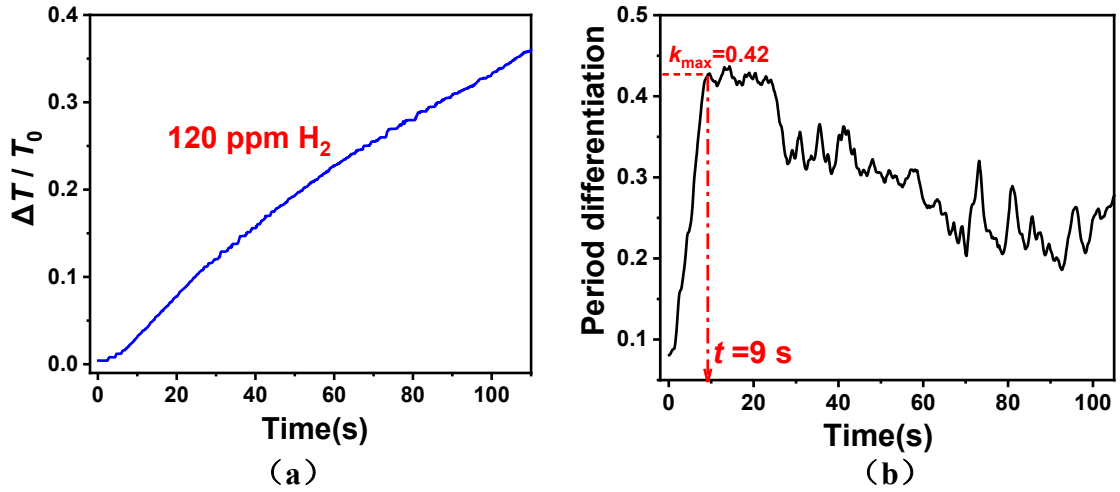


Figure S6 (a) Relative variation of the oscillation period corresponding to 120 ppm H_2.(b) The time VS period curve corresponding to 120 ppm H_2 is differentiated, and the maximum slope value is 0.42 and the maximum slope value is about 9 s.

S7. By using the method of extracting the maximum slope value, real-time monitoring of H_2 concentration is realized.

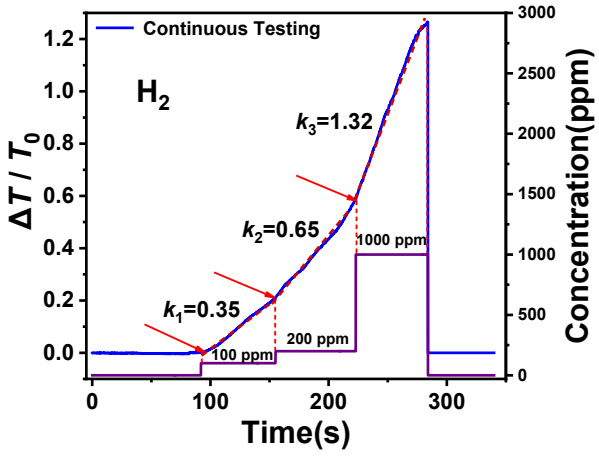
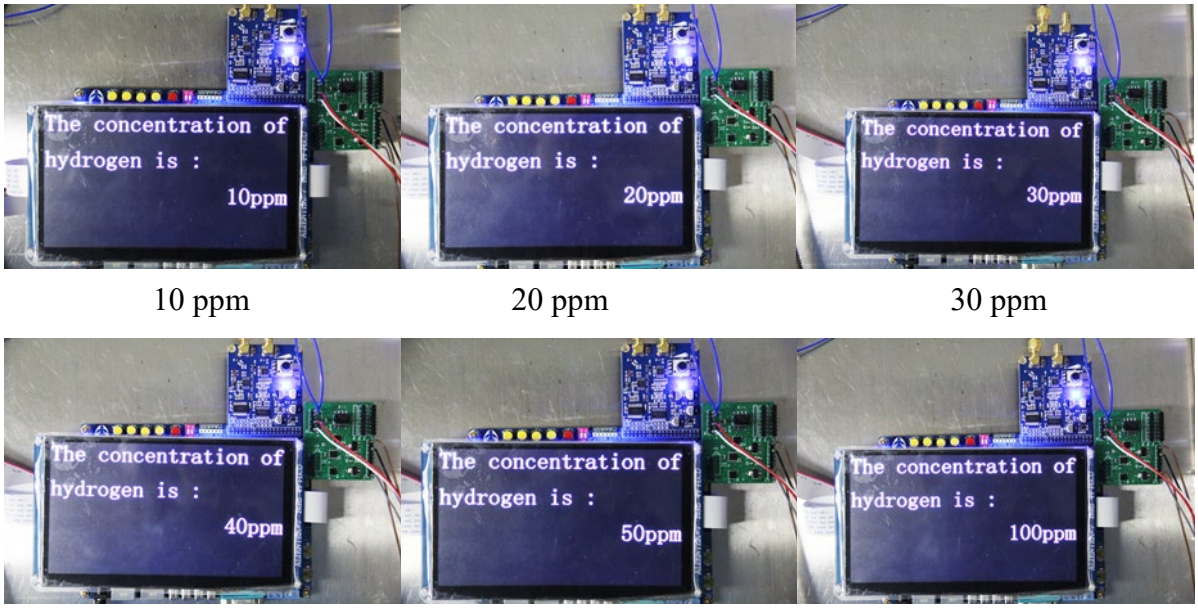


Figure S7 The continuity test of different concentrations of H_2. Three different concentrations of H_2 are continuously introduced in sequence. By extracting the maximum slope value of the oscillation period variation curve, the amount of H_2 concentration introduced can be identified.

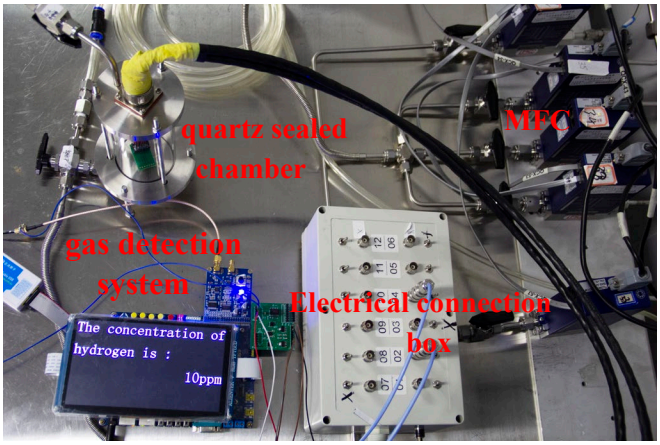
S8. System for rapid detection of H_2 with a resolution of 10 ppm.



10 ppm 20 ppm 30 ppm

40 ppm 50 ppm 100 ppm

(a)



(b)

Figure S8 H_2 detection system.(a)The detection system realizes rapid detection of H_2 with a resolution of 10 ppm in the air environment and the results are reliable and repeatable (the detection accuracy rate has reached 100%).(b) The test environment of the H_2 detection system in the laboratory.