# Zeolitic Imidazolate Framework Coated ZnO Nanorods as Molecular Sieving to Improve Selectivity of Formaldehyde Gas Sensor

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ABSTRACT

ZnO@ZIF–8 nanorods with core–shell heterostructures were obtained by using the self–template strategy. The ZnO@ZIF–8 heterostructure was composed of ZnO as core and ZIF–8 as shell. The ZIF–8 shell was uniformly deposited to form ZnO@ZIF–8 nanorods with core–shell heterostructures at 70 °C for 24 h by the hydrothermal synthesis. As a porous material, ZnO@ZIF–8 nanorods with core–shell heterostructures exhibited distinct gas response for reducing gases with different molecule sizes. The sensor of ZnO@ZIF–8 nanorods with core–shell heterostructures is potentially applied to detect the formaldehyde concentration in our living environment.

**Supporting information**

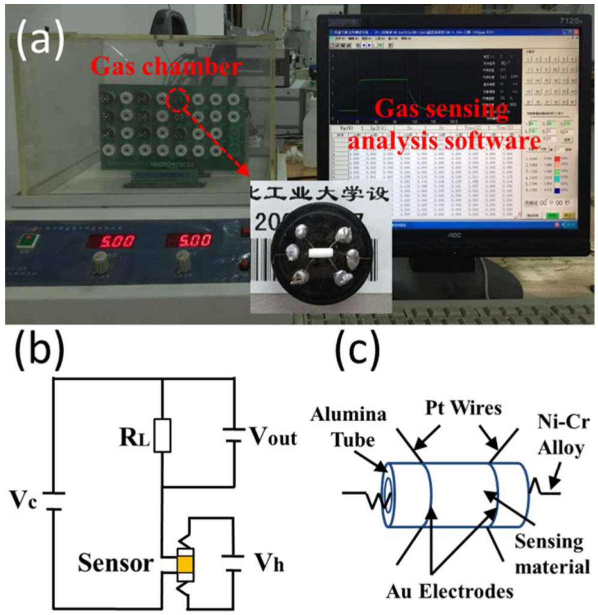


**Figure S1.** (a) Photograph of the gas–sensing system (Inset: a gas sensor by using the ZnO@ZIF–8 nanorods). (b) The measuring electric circuit of the gas–sensing instrument. (c) Schematic diagram of the compositions of a gas sensor.

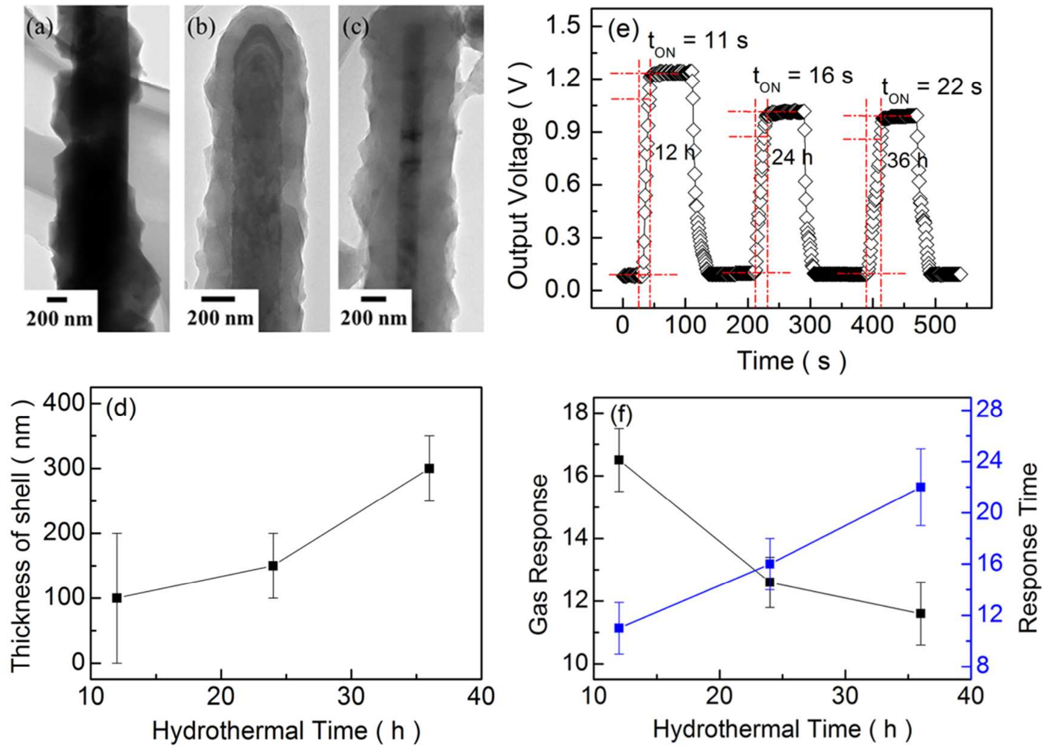


**Figure S2.** (a–c) Low–magnification TEM images of the ZnO@ZIF–8 nanorod obtained at the hydrothermal time of 12, 24 and 36 h, respectively. (d) The thickness of the ZIF–8 shell at different reaction times. (e) Gas response transient curves of the ZnO@ZIF–8 nanorods sensor at 300 ºC for formaldehyde in 100 ppm at different hydrothermal times. (f) The gas response and response time as a function of the hydrothermal time.

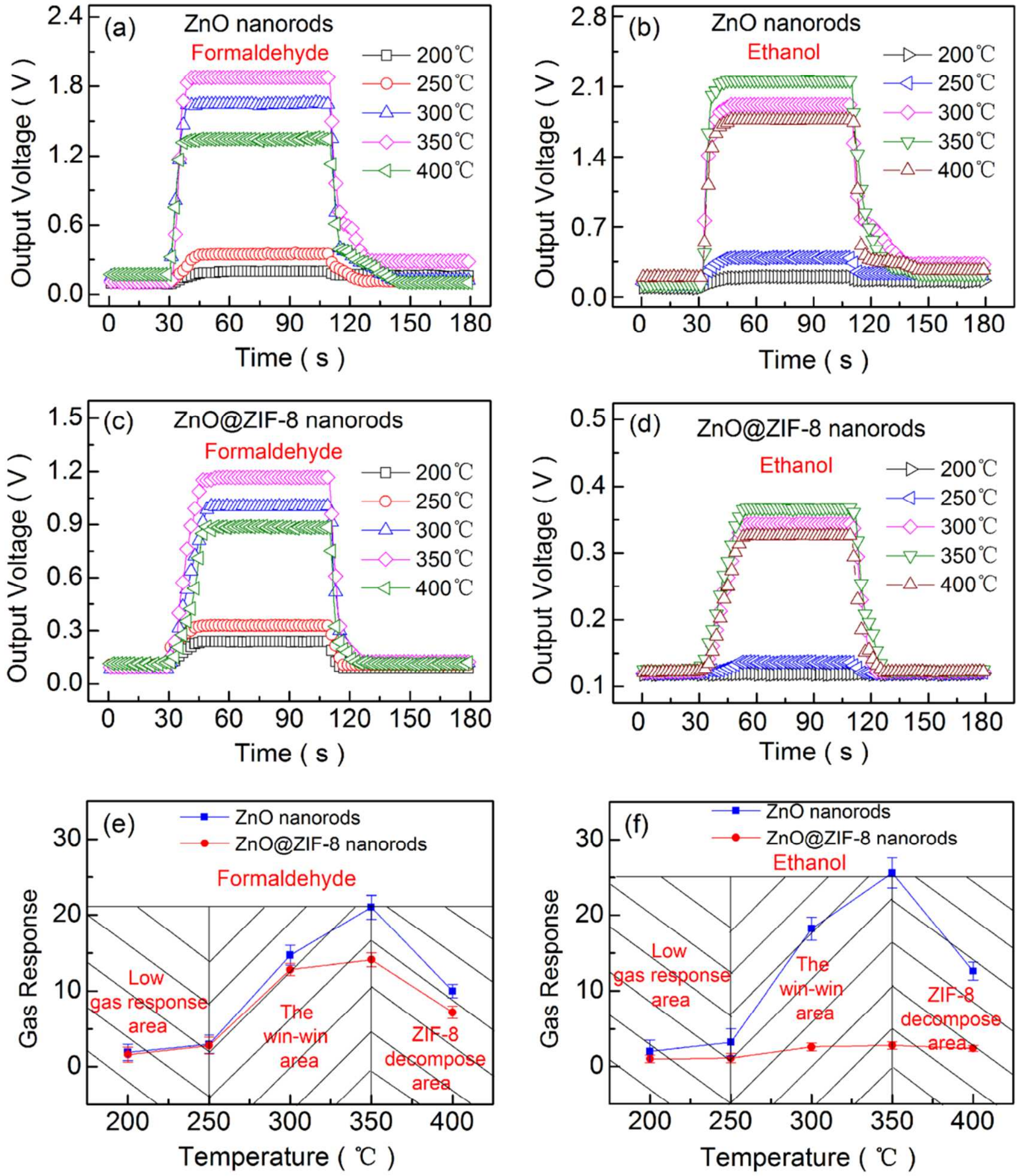


**Figure S3.** (a–b) Dynamic response and recovery curves of the ZnO nanorods sensor to 100 ppm formaldehyde and ethanol at the temperature range of 200–400 °C. (c–d) Dynamic response and recovery curves of the ZnO@ZIF–8 nanorods sensor to 100 ppm formaldehyde and ethanol at the temperature range of 200–400 °C. (e–f) The gas response of the ZnO nanorods sensor and the ZnO@ZIF–8 nanorods sensor to 100 ppm formaldehyde and ethanol at different working temperatures.

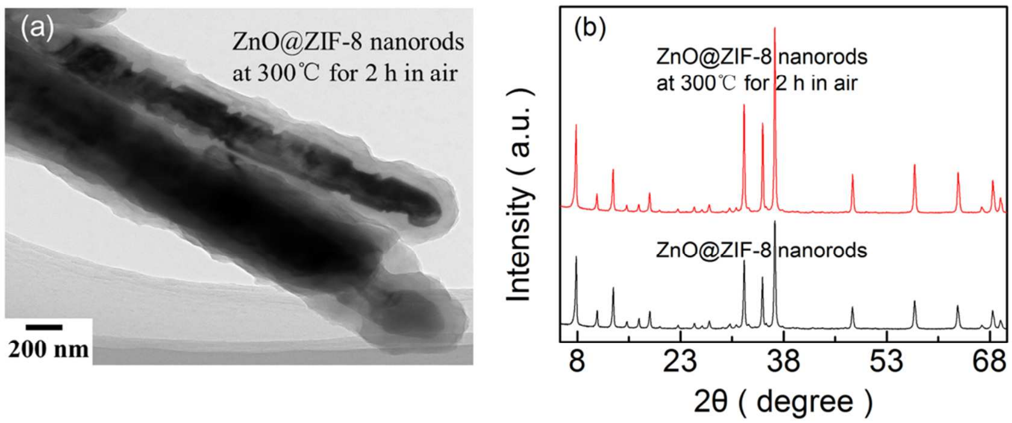


**Figure S4.** (a) TEM image of the ZnO@ZIF–8 nanorods at 300 °C for 2 h in air. (b) XRD patterns of the ZnO@ZIF–8 nanorods at 300 °C for 2 h in air and the ZnO@ZIF–8 nanorods.

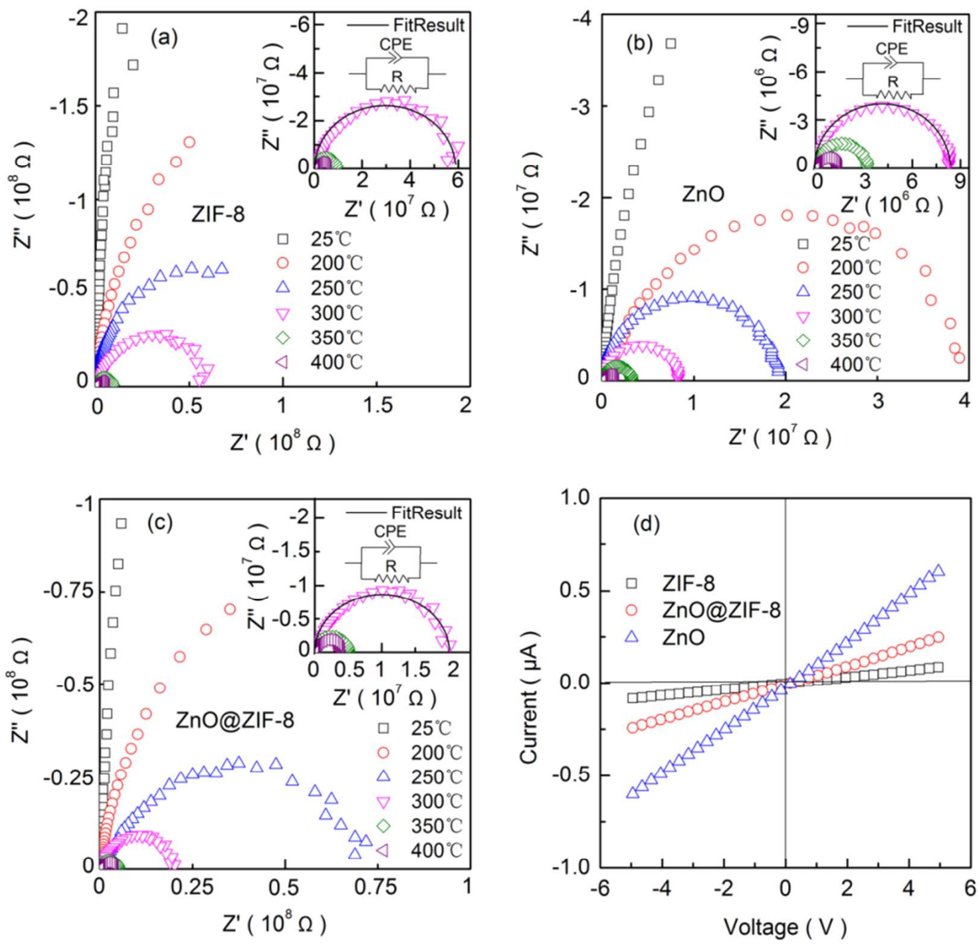


**Figure S5.** Ac impedance responses obtained at different temperatures for (a) ZIF–8, (b) ZnO and (c) ZnO@ZIF–8; (Inset: Fitting of impedance response with an RC circuit) (d) dc I–V characteristics of three samples acquired at 300 ºC in the voltage range from -5 V to 5 V.

**Explanation of Figure S5:**

Ac impedance measurements of the sensor were conducted by using an impedance analyzer (4294A, Agilent, CA, USA) with a gas response instrument (HW–30A, Hanwei Ltd., Zhengzhou, China) where the temperature of the sensor could be controlled. The measurement frequency range was from 100 Hz to $1\times10^7$ Hz.

As can be seen from Figure S5, where ac impedance response is presented as a Nyquist plot, the prepared ZIF–8, ZnO and ZnO@ZIF–8 sensors behave huge electrical resistance at room temperature (25 ºC). Only a part of the semicircle can be observed at higher frequencies, while the response signal reduces below sensitivity level of the apparatus. A cloud of random values are obtained at lower frequencies. So, they are omitted in Figure S5 for the sake of clarity. However, the semicircle is decreased at elevated temperature due to thermal activation of charge carriers. In Figure S5(a), the impedance response of the ZIF–8 sensor exhibits the small depressed semicircle in the complex plane, particularly above 350 ºC. The similar response can be observed for ZnO@ZIF–8 in Figure S5(c). According to the reported papers [ref.26,27], the framework of ZIF–8 began to decompose at 350 ºC. It is quite probable that the thermolysis product of ZIF–8 may participate in charge transfer at a high temperature. Therefore, we fitted the impedance responses of three samples with semicircles at 300 ºC, which the temperature is selected for the gas sensing measurement in our work. The results are presented in the insets of Figure S5. The data can be well fitted with one semicircle, which means that the impedance is dominated by the dc bulk resistance of the sample. The fitting model was described with the equivalent circuit model which corresponds to a capacitor in parallel with a very high resistance. The capacitor was replaced by a constant phase element (CPE) [ref.S1]. This substitution is stipulated by the shape of the responses that differs from perfect semicircles, reflecting the fact that the sample material is not uniform and its microscopic bulk properties are space distributed [ref.S2]. The resistance of the sample can be calculated from the value of $Z'$ in the low–frequency end of the semicircle. The resistance of ZnO@ZIF–8 decreased about 3 times than that of ZIF–8 with heating to 300 ºC due to a synergistic effect with ZnO (Figure S5(b)). In addition, we measured dc I–V characteristics of the sensor by using a source meter (Model 2410, Keithley, Cleveland, USA) at working temperature of 300 ºC. Figure S5(d) illustrated that the current response of the sensor at the voltage range from -5 V to 5 V.

**Reference:**


[S1] Liu, X.; Fan, H. Q.; Shi, J.; Dong, G. Z.; Li, Q. High oxide ion conducting solid electrolytes of bismuth and niobium co–substituted $La_2Mo_2O_9$. *Int. J. Hydrogen. Energy* **2014**, *39*, 17819–17827.

[S2] Mikhailenko, S. D.; Afsahi, F.; Kaliaguine, S. Complex impedance spectroscopy study of the thermolysis products of metal–organic frameworks. *J. Phys. Chem. C* **2014**, *118*, 9165–9175.