Supporting information

CdO Nanoflake Arrays on ZnO Nanorod Arrays for Efficient Detection of Diethyl Ether

*Sheng-guang Ban, Xiao-Hua Liu, Tao Ling, Cun-Ku Dong, Jing Yang and Xi-Wen Du**

Key Laboratory of Advanced Ceramics and Machining Technology, Ministry of Education (Tianjin University), Institute of New-Energy Materials, School of Materials Science and Engineering, Tianjin University, Tianjin 300072, People's Republic of China

* Address correspondence to xwdu@tju.edu.cn

Experimental

1. Synthesis of ZnO NRAs

ZnO NRAs were fabricated on glass substrate via a hydrothermal route. First, a ZnO seed layer was deposited on a glass substrate by immersing the substrate in a 2-methoxyethanol solution of zinc acetate dehydrate (0.1 M) and ethanolamine (0.2 M), and then the substrate was dried with compressed air. Immersion and drying steps were repeated for three times. Afterwards, ZnO seed layer on the substrate was annealed at 500 °C for 1 hr. To grow NRAs, the substrate coated with ZnO seed layer was floated face down in an aqueous solution of zinc nitrate hexahydrate (25×10^{-3} M) and hexamethylenetetramine (25×10^{-3} M) at 100 °C for 9 hrs. Then the substrate was thoroughly rinsed with deionized water and dried with flowing nitrogen.

2. Synthesis of CdO nanostructures on ZnO NRAs

The synthesis of Cd NFAs followed the procedure reported in our previous works.[28,29] First, cadmium NFAs were grown on the top of the ZnO NRAs by thermal reduction. Specifically, 0.05 g CdS powder was put in the middle of a tube furnace, while the glass substrate with ZnO NRAs was placed downstream in a low temperature zone (about 30 cm from the CdS powder) where the temperature is around 150 °C. During the heating process, mixed carrier gas consisting of 250 standard cubic centimeter per minute (sccm) N_2 and 45 sccm air was introduced into the quartz tube, and the pressure of quartz tube was maintained at 9 Torr. The synthetic process was lasted for 30 min at 650 °C, afterwards, the tube furnace was cooled down to room temperature naturally. Next, the Cd NFAs were oxidized in air at 360, 400 and 440 °C, respectively, for 1 hr to obtain different nanostructures.

3. Assembly of gas sensor

The structure of the sensor device is shown in the abstract. First, silver paste was coated on the DL structure (size 0.5 cm×1.5 cm) to form two electrodes with diameter of 2 mm and spacing of 10 mm. Then, the electrodes were dried in air at 100 °C for 3 hrs. The obtained device was used directly for measuring gas sensing properties.

4. Characterization and testing

The morphologies of materials were observed using a Hitachi S-4800 scanning electron microscope (SEM). The detailed microscopic structure was characterized with a FEI Technai G2 F20 transmission electron microscope (TEM). The composition was analysed by an EDS module attached to the TEM. X-ray diffraction (XRD) analysis of the crystal structure was conducted in a Bruker-D8 Advanced X-ray diffractometer. Surface area was measured at 77 K with an ASAP 2020 physisorption analyzer. The Mott-Schottky plots were measured with an AC amplitude of 10 mV at a frequency of 1000 Hz in

the dark, using a Par 2273 Potentiostats-Electrochemistry workstation. The gas-sensing properties were detected in an intelligent gas sensing analysis system (CGS-1TP, Beijing Elite Tech Co., Ltd) that offered an external temperature control from room temperature to 500 °C with a precision of 1 °C. The sensor was placed on a planar holder with two copper needles penetrating into the two silver electrodes of the sensor, respectively.[25] Target gases were introduced into the test chamber via a syringe. Two electrical fans installed in the chamber made the test gas homogeneous. The sensitivity of the sensor was defined as $S = |Rg - Ra|/Ra \times 100\%$, where Ra is the resistance in atmospheric air, and Rg the resistance of the sensor device exposed in the detecting gas. The response time is defined as the time required to reach 90% of the final response upon gas exposure, and the recovery time as the time interval over which the sensor response drops in air to 10% of the stabilized response in the target gas. The electrical resistances of the sensors were measured directly in the gas analysis system.

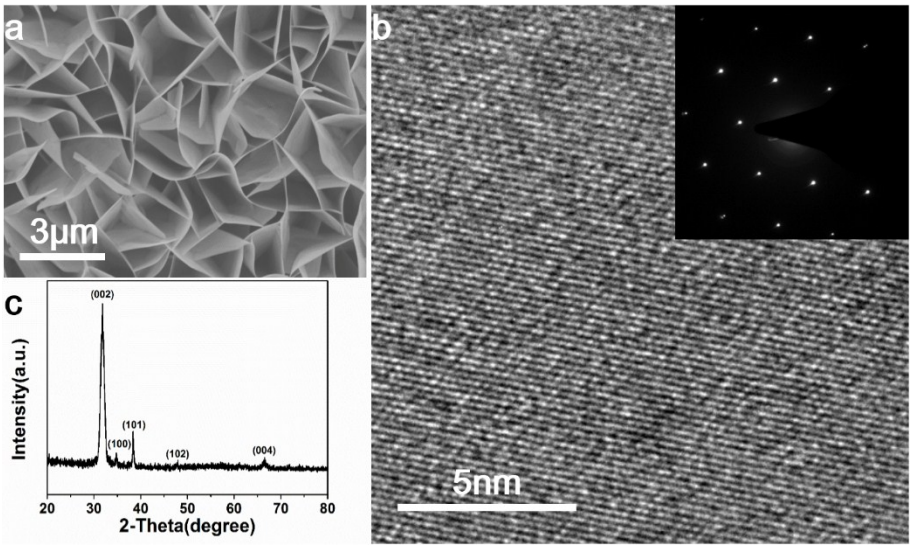

Figure S1.Characterizations of Cd NFAs. (a) SEM images of Cd NFAs from the top view, (b) HRTEM image and SAED pattern (insert), (c) XRD pattern of Cd NFAs.

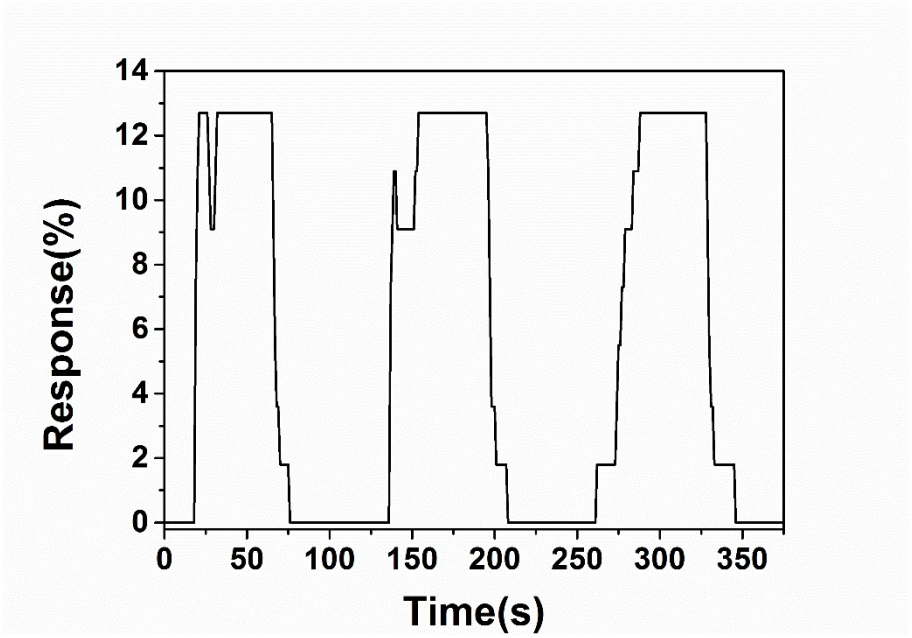

Figure S2. Gas response plot of CdO NFAs on glass substrate to 100 ppm DEE at the temperature of 215 °C

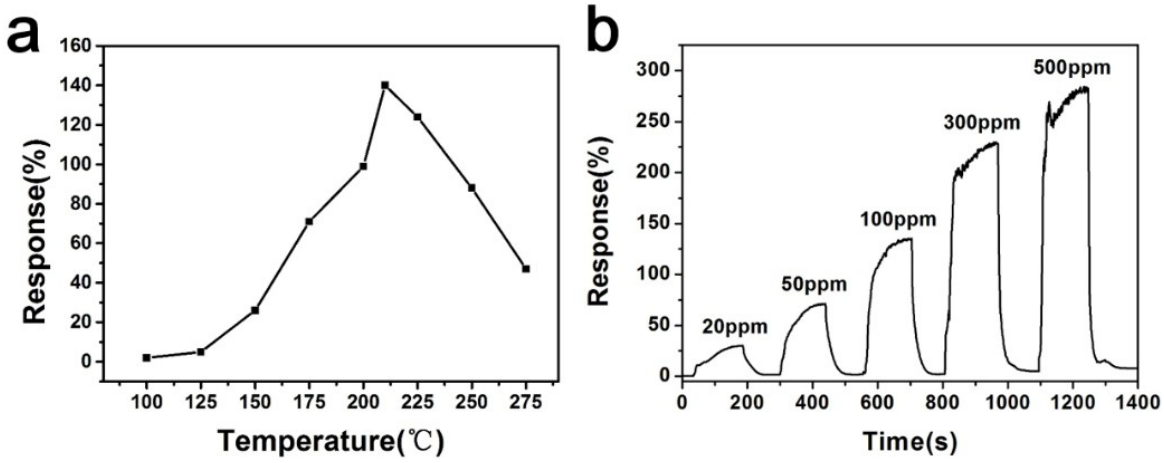

Figure S3. The gas sensing properties of DL400. (a) Response to 100 ppm DEE at different operating temperatures, (b) dynamic response to DEE at different concentrations ranging from 20 to 500 ppm at 215 °C.

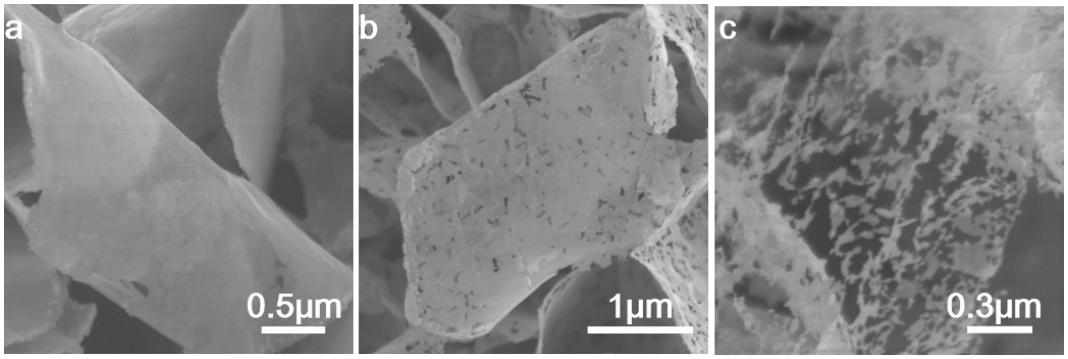

Figure S4. The SEM images of single nanoflake in (a) N-NFAs, (b) P-NFAs, and (c) S-structure.

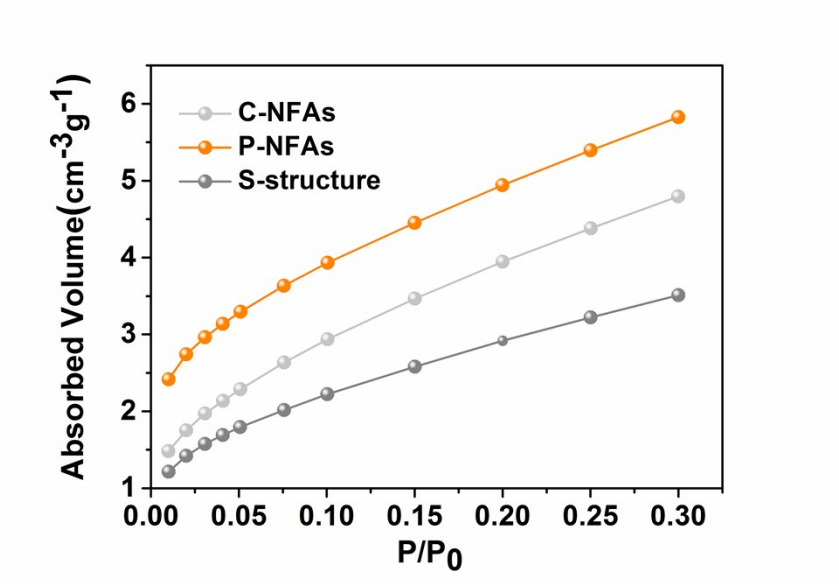

Figure S5 Nitrogen physisorption isotherms for N-NFAs, P-NFAs and S-structure.

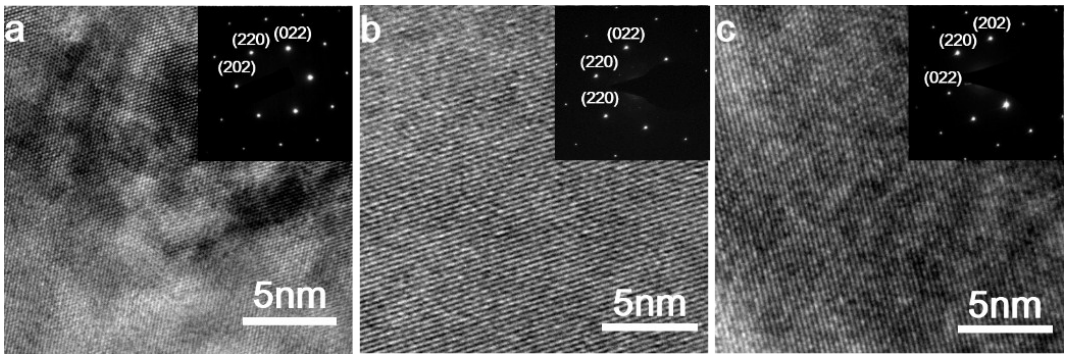

Figure S6. HRTEM images of (a) N-NFAs, (b) P-NFAs, and (c) S-structure and their diffraction patterns (insets).

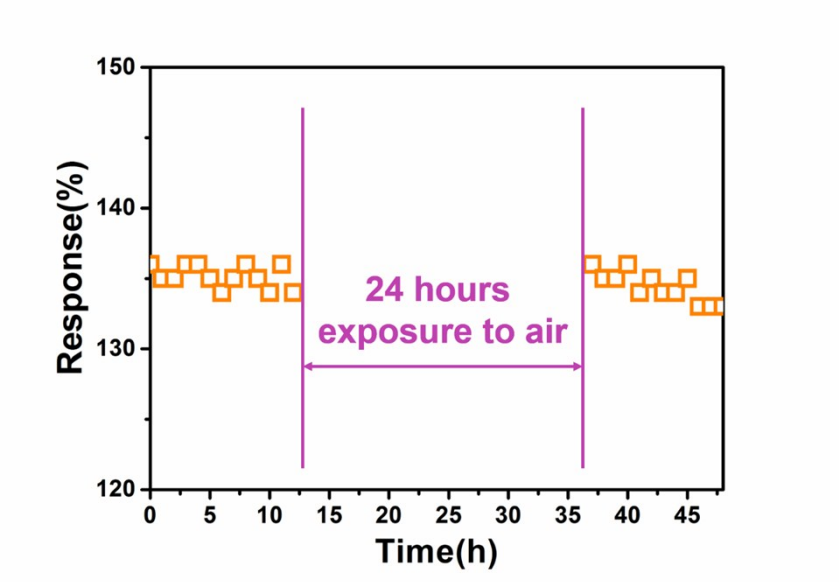

Figure S7. Stability performance of the DL400 gas sensor.

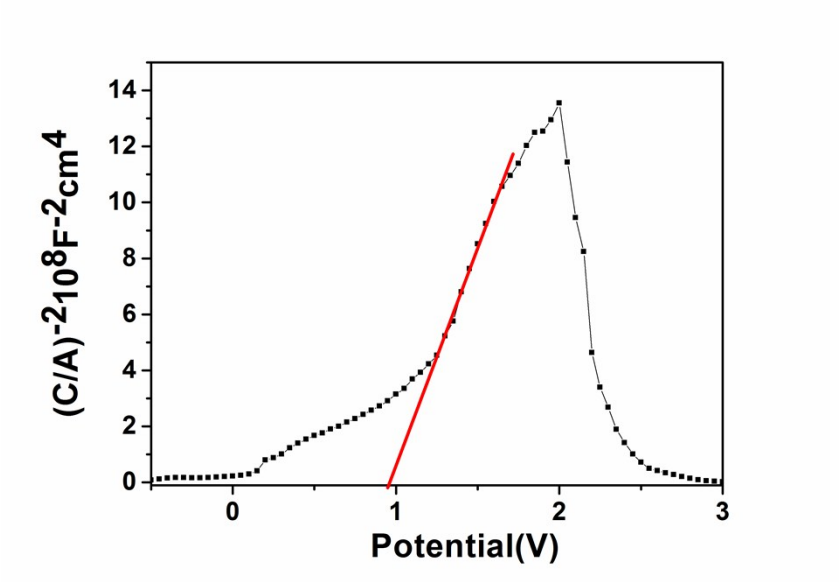

Figure S8. Mott–Schottky plots for CdO NFAs on a FTO substrate

Mott–Schottky (MS) analysis was conducted to investigate the carrier concentration. MS equation of n-type semiconductors can be expressed as following [1],

$$\frac{1}{C^2} = \frac{2}{\varepsilon\varepsilon_0 q N_d}(U - U_{fb} - \frac{kT}{q})$$

where C is the depletion-layer capacitance per unit surface area, N_d the donor densities, ε_0 the permittivity of vacuum, ε the dielectric constant of the semiconductor, U the electrode potential, U_{fb} the flat-band potential, k the Boltzmann constant, T the absolute temperature, and q the elementary charge. The carrier concentration determined by Figure S8 and the above equation is about 1.2×10^{20} cm^{-3}, which is the same with that reported in literature.

Reference

1) M. J. Jin, X. Y. Chen, Z. M. Gao, T. Ling and X. W. Du. *Nanotechnology.*, 2012, **23**, 485401