Electronic Supplementary Information:

Highly sensitive, temperature-dependent gas sensor based on hierarchical ZnO nanorod arrays

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Materials

Zinc acetate (ZnAc, $Zn(CH_3COO)_2 \cdot 2H_2O$**,** AR), zinc nitrate ($Zn(NO_3)_2$, AR) hydrate and hexamethylenetetramine (HMTA, $(CH_2)_6N_4$) were purchased from Sinopharm Chemical Reagent Co., Ltd.. Polyethylene oxide (PEO) used in this study was purchased from Aldrich. An aqueous solutions containing PEO (600,000, 6wt%) and ZnAc (0.01 M-0.1 M) were fabricated by magnetic stirring for 10 hours. Aqueous solutions of $Zn(NO_3)_2$ (0.2 M) and HMTA (0.2 M) were prepared by magnetic stirring for >0.5 h, respectively, then were mixed with equal volume and stirred evenly to fabricated mixed solution of 0.01 M-0.2 M $Zn(NO_3)_2$ and 0.01 M-0.2 M HMTA as growth solution.

Details of mechanoelectrospinning equipment

The experimental setup of mechanoelectrospinning (MES) is shown in Figure S1 (a). MES process needs two electrodes: 1) a stainless steel nozzle (inner diameter 160 um and external diameter 310 um) is adopted as one electrode, connecting with a High voltage DC power supplier (DW-P403, Dongwen Inc.) and a syringe pump (11 Pico Plus, HARVARD, Inc.); and 2) another electrode is the ground collector (a metal plate) which is fixed on the X-Y moving stage (THK Inc. and Parker Inc). The substrate is mounted on the ground collector underneath the nozzle. The nozzle-to-substrate distance maintains 2-5 mm, which is much shorter than conventional electrospinning. A high-speed camera (Basler A504k with microlens) is used to observe the dynamic process of the jet. The motion stage moves rapidly in one direction to generate the mechanical drawing force, and moves in a perpendicular direction in an intermittent manner to adjust the gap. [1, 2]

The schematic diagram of the direct-writing process by MES is shown in Figure S1 (a). Initially, the nozzle is filled with ZnAc precursor solution. When appropriate voltage (1.5-2.75 kV) and flow rate (450-900 nl/min) are applied, the solution is sucked out from the needle, attaches to the nozzle orifice, and forms Taylor cone at the apex of the nozzle (Figure S1 (a) I). Then the applied voltage increases gradually up to the onset voltage. As the electrostatic force is sufficient to overcome the surface tension of the sucked solution, a thin jet ejects from the apex of the Taylor cone, and forms a fiber between the nozzle and the substrate (Figure S1 (a) II). Then, the applied voltage is reduced to 2.25 kV gradually and appropriately just to keep the jet stable. The Si substrate is mounted on the x–y moving stage, to realize high-precision positioning. The

liquid jet undergoes extensive stretching forming linear fibers on the substrate orderly by the mechanical drawing force in one direction through the moving substrate (Figure S1 (a) III). Meanwhile, the jet diameter becomes controllable due to the mechanical drawing force resulted from the digitally controllable high-speed motion. The velocity of the motion stage and the flow rate are 200 mm/s and 500-750 nl/min in this paper.

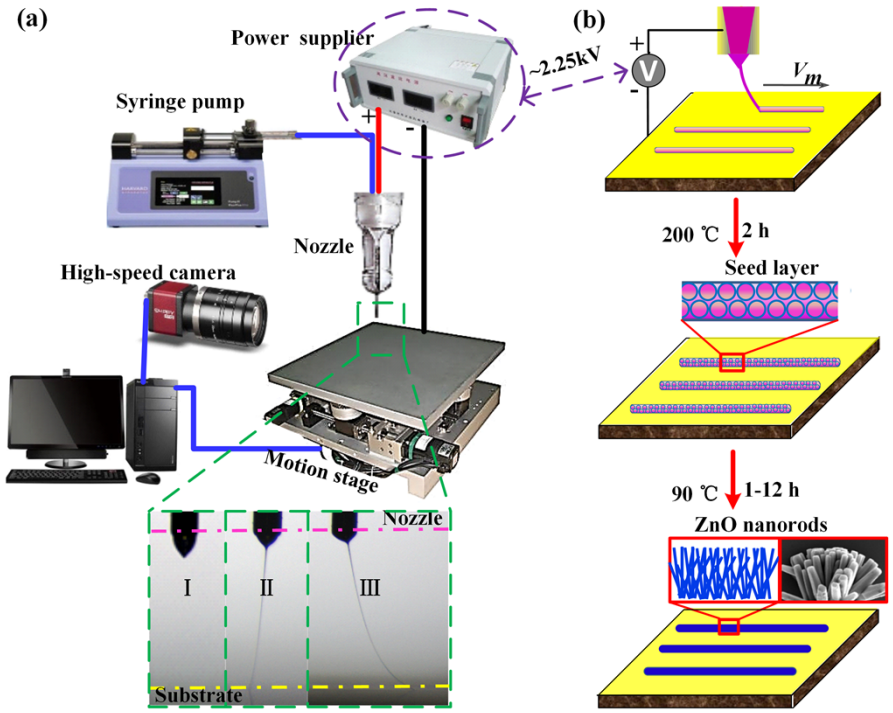

Figure S 1 (a) Schematic diagram of MES setup. I, II and III are the images of the jet in deferent stages indicated by dashed line box. (b) Growth process of the directly patterned ZnO nanorod arrays.

Synthesis of ZnO nanorod arrays

An aqueous solution containing PEO making electrospinning easier and ZnAc was direct-written on the substrate to form parallel fibers by mechanoelectrospinning (MES) [3]. Then the obtained samples were annealed at 200 ºC for 2 hours (h) to form ZnAc nanoparticles nuclei and to ensure the seed particle adhesion to substrate formed the seed layer, as shown in Figure S1 (b). Direct patterned ZnO nanorod arrays (ZnO-NAs) (Figure S2) were selectively grown from ZnAc nanoparticle nuclei through the hydrothermal decomposition of a zinc complex.

Selective growth of ZnO-NAs was formed by suspending the substrate upside-down in a teflon-bottle filled with the growth solution which was the mixture of 0.01-0.2 M $Zn(NO_3)$ and HMTA (with equal concentration), and teflon-bottle was placed in the reaction kettle for 1-12 h, with an ambient temperature of 90 ºC. The whole experimental process schematics was shown in

Figure S1 (b). In the hydrothermal growth process, the possible chemical reactions in the aqueous solution can be described as follows:

$$(CH_2)_6N_4 + 6H_2O \rightarrow 6HCHO + 4NH_3 \quad (1)$$

$$NH_3 + H_2O \rightarrow NH_{4+} + OH^- \quad (2)$$

$$Zn^{2+} + 2OH^- \rightarrow Zn(OH)_2 \quad (3)$$

$$Zn(OH)_2 \rightarrow ZnO + H_2O \quad (4)$$

After growth, the substrate were removed from the grown solution, rinsed with deionized water, and then dried at 60 ºC in clean air.

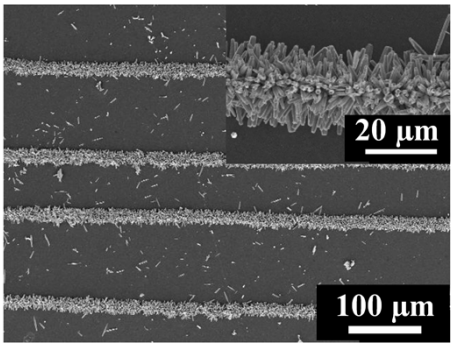

Figure S 2 Field emitting scanning electron microscope (FESEM) image of ZnO-NAs. The inset is an enlarged view.

Diameter distributions of ZnO nanorod arrays by different process parameters

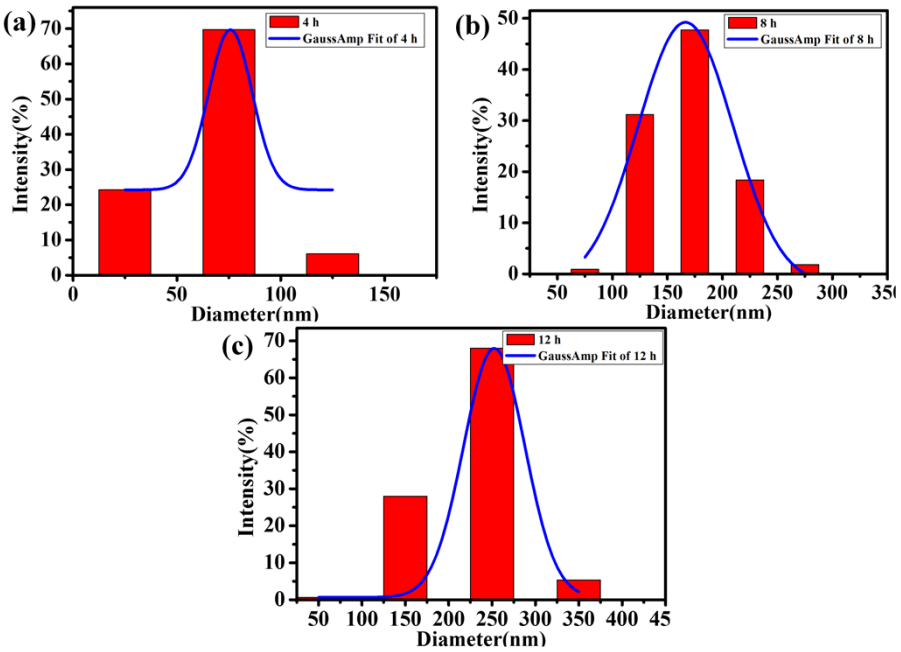

Figure S 3 Diameter distributions of ZnO nanorods growing for (a) 4 h; (b) 8 h; (c) 12 h.

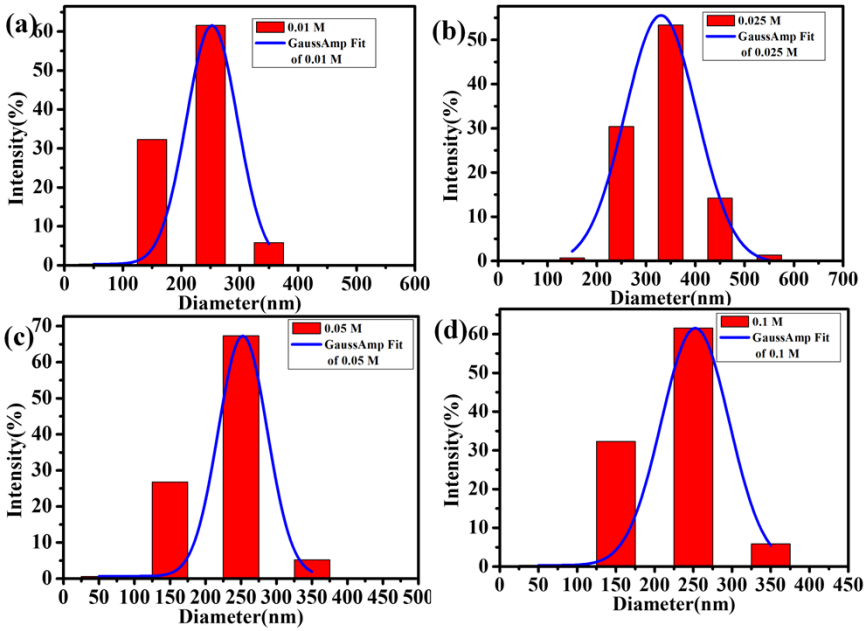

Figure S 4 Diameter distributions of ZnO nanorods growing from (a) 0.01 M ZnAc; (b) 0.025 M ZnAc; (c) 0.05 M ZnAc; (d) 0.1 M ZnAc as seeds by MES

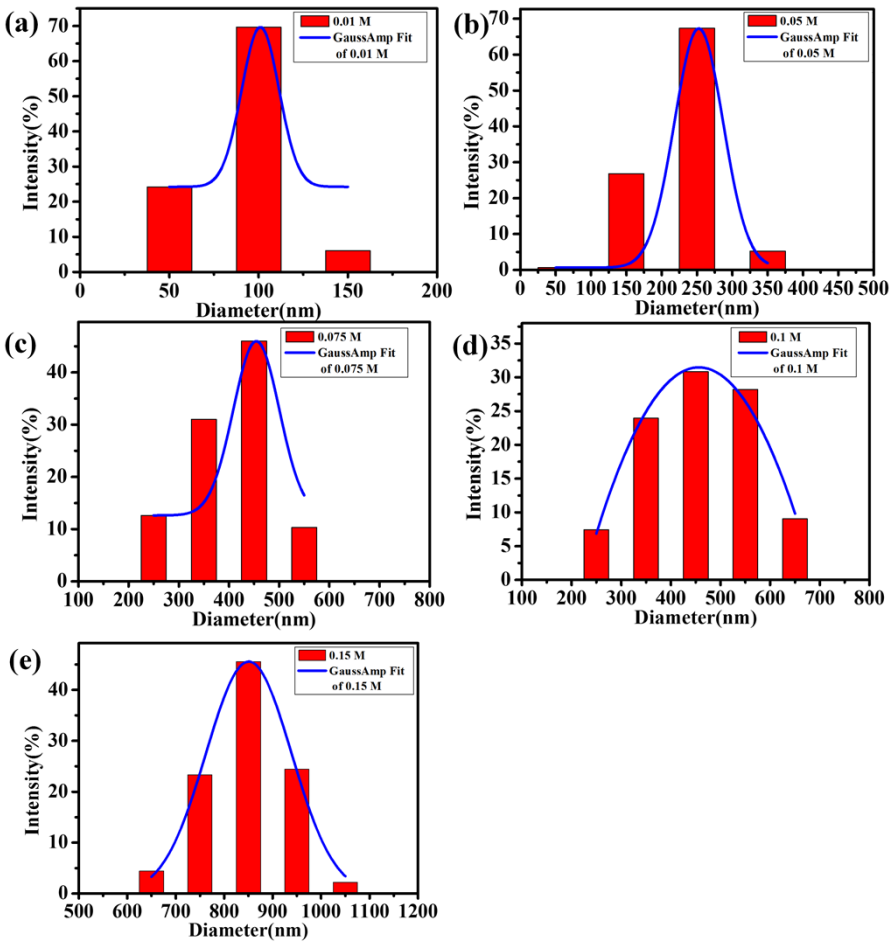

Figure S 5 Diameter distributions of ZnO nanorods growing with (a) 0.01 M $Zn(NO_3)_2$; (b) 0.05 M $Zn(NO_3)_2$; (c) 0.075 M $Zn(NO_3)_2$; (d) 0.1M $Zn(NO_3)_2$; (e) 0.15 M $Zn(NO_3)_2$; (f) 0.2 M $Zn(NO_3)_2$ in growth solution.

Resronse of ZnO samples at room temperature

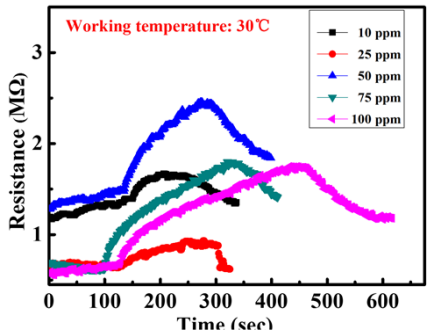

Figure S 6 (a) shows the dynamic responses of ZnO sample exposed to different concentrations of NO_2 (10 -100 ppm) at room temperature (30 ºC).

References

(1) Bu, N.; Huang, Y.; Wang, X.; Yin, Z. Continuously Tunable and Oriented Nanofiber Direct-Written by Mechano-Electrospinning. *Mater. Manuf. Processes* **2012,** *27,* 1318-

1323.

(2) Huang, Y.; Wang, X.; Duan, Y.; Bu, N.; Yin, Z. Controllable self-organization of colloid microarrays based on finite length effects of electrospun ribbons. *Soft Matter* **2012,** *8,* 8302-8311.

(3) Wang, X.; Sun, F.; Huang, Y.; Duan, Y.; Yin, Z. A patterned ZnO nanorod array/gas sensor fabricated by mechanoelectrospinning-assisted selective growth. *Chem. Commun.* **2015,** *51,* 3117-3120.