

## Electronic Supplementary Information:

# **Patterned ZnO nanorod array/gas sensor by mechanoelectrospinning-assisted selective growth**

Xiaomei Wang,<sup>a</sup> Fazhe Sun,<sup>b</sup> Yongan Huang,<sup>\*a</sup> Yongqing Duan,<sup>a</sup> and Zhouping Yin,<sup>\*a</sup>

a State Key Laboratory of Digital Manufacturing Equipment and Technology,  
Huazhong University of Science and Technology, Wuhan 430074, China

b Analysis Testing Center, Shandong University of Technology, Zibo 255100, China

## **Materials and equipments**

Zinc acetate ( $\text{ZnAc}$ ,  $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ , AR), zinc nitrate ( $\text{Zn}(\text{NO}_3)_2$ , AR) hydrate and hexamethylenetetramine (HMTA,  $(\text{CH}_2)_6\text{N}_4$ ) are purchased from Sinopharm Chemical Reagent Co., Ltd.. Polyethylene oxide (PEO) used in this study is purchased from Aldrich. An aqueous solution containing PEO (60W, 6wt%) and  $\text{ZnAc}$  (0.01 M) is fabricated by magnetic stirring for 10 h. Aqueous solution of  $\text{Zn}(\text{NO}_3)_2$  (0.1 M) and HMTA (0.1 M) are prepared by magnetic stirring for >0.5 h, respectively, then are mixed with equal volume and stirred evenly to fabricate mixed solution of 0.05 M  $\text{Zn}(\text{NO}_3)_2$  and 0.05 M HMTA as growing solution.

The experimental setup of MES is shown in Figure S1 (a). MES process needs two electrodes: 1) a stainless steel nozzle (inner diameter 160  $\mu\text{m}$  and external diameter 310  $\mu\text{m}$ ) 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) with 3 mm thickness 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.

The schematic diagram of the direct-writing process by MES is shown in Figure S1 (a). Initially, the nozzle is filled with  $\text{ZnAc}$  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<sup>26</sup>. The velocity of the motion stage and the flow rate are 200 mm/s and 500-750 nl/min in this paper.

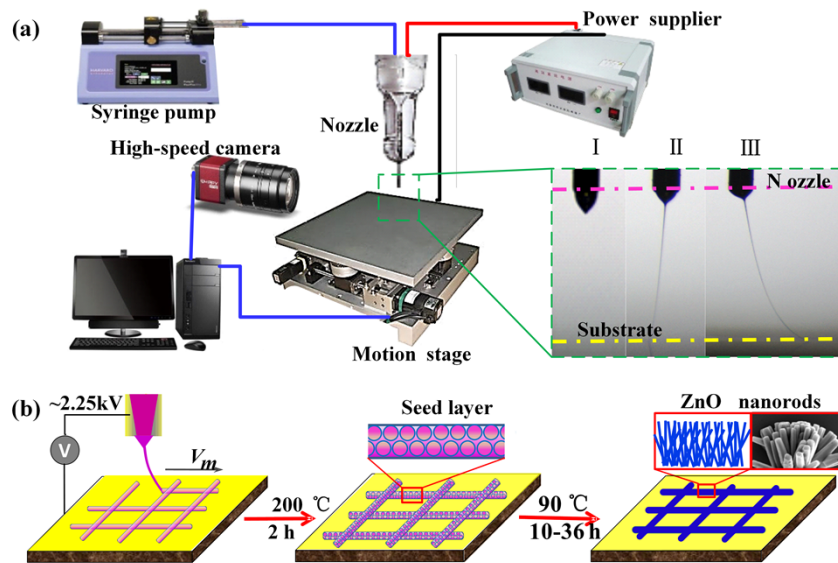
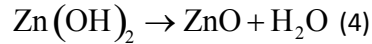
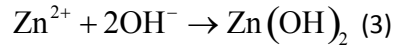
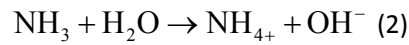
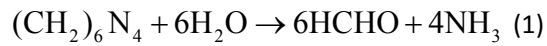


Figure S1 (corresponding to Figure 1 in the paper) (a) Schematic diagram of MES setup. I, II and III are the images of the jet in different stages indicated by dashed line box. (b) Growth process of the directly patterned ZnO nanorod array.

### **ZnAc seed layer synthesis and ZnO nanorod selective growth**

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

Selective growth of ZnO nanorod array was formed by suspending the Si substrate upside-down in a teflon-bottle filled with the growth solution which was the mixture of 0.05 M Zn(NO<sub>3</sub>) and 0.05 M HMTA, and teflon-bottle was placed in the reaction kettle for 10-36 h, with an ambient temperature of 90 °C. 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:



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

## **Characterization**

The morphologies of the samples were characterized using optical microscope (OLYMPUS BX 51) and field emission scanning electron microscope (FESEM, Sirion 200, FEI Company, Holland, operating at 20 kV) sputtering a thin film of gold. The crystalline structure and composition of the samples were analyzed by a X-ray diffraction (XRD, Philips X'Pert PRO diffractometer) with Cu-K $\alpha$  radiation ( $\lambda = 1.5418$  Å) at room temperature. The accelerating voltage was set at 40 kV with 40mA emission current. To determine the crystallinity and crystal planes of the ZnO structures, Nanorod growth direction was analyzed by high-resolution transmission electron microscope (HRTEM, JEM-2100F STEM/EDS, JEOL, Japan). I-V characteristics was measured by Semiconductor Characterization System (Keithley 4200-SCS) and a typical four-point probe station (CASCADE SUMMITI 11000). For the sensor response measurement<sup>1</sup>, a DC voltage of 4.096 V was applied and the voltage across the signal resistor was continuously recorded as the sensor sample was subjected to repeated target gas exposure and removal.

## **References**

- 1 H. Liu, M. Li, O. Voznyy, L. Hu, Q. Fu, D. Zhou, Z. Xia, E. H. Sargent and J. Tang, *Adv. Mater.* , 2014, **26**, 2718-2724.