Supplementary Information

Synthesis of ZnO nanosheets arrays with exposed (100) facet for gas sensing applications

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Figure S1. Schematic diagrams of the electrodeposition setup with an ultrathin electrolyte layer by freezing the electrolyte solution.1) anode; 2) Top glass plate;3) and 5) the ultrathin electrolyte layer trapped between the ice of electrolyte and the substrate 4) cathode;6) bottom silicon substrate and 7) deposit.



Figure S2. The the I-V characteristics of the ZnO NSs under NO₂ and air.

The I-V measurement for the channels of ZnO NSs array bridged between two Au electrodes was carried out in both ambient air and NO₂. The curves are nearly linear, indicating excellent Ohmic contact nature. Ohmic behavior is crucial to the gas sensing characteristics, since the sensitivity of gas sensors is maximized when the metal-semiconductor junction is in Ohmic contact with a negligible junction resistance.¹



Figure S3. TEM images and its SAED of three different samples.



Figure S4. The pole figure and TEM image.

The grain size estimated by using the Scherrer's equation:

D = $K\lambda/\beta \cos\theta$, where K = 0.89, D is the grain size (nm), λ = 0.15406 nm, β is FWHM (unit in radians), and θ is Bragg's angle (unit in degrees). The grain sizes were found to be 28 nm.

Growth mechanism of ZnO NSs array:

There are two processes in the formation of ZnO NSs array: the formation of NSs and assembling of arrayby the NSs. In quasi-two-dimensional ultra-thin liquid layer electrochemical deposition, Zn²⁺ ions are driven to the cathode by the electric field and electrons gather in the deposit forefront surface. When the electrode potential reaches the deposition potential of ZnO, multiple nucleation and growth of the ZnO NSs occurs. The deposition equations of ZnO NSs arrayin the ultra-thin layer are as follows:^{2,3}

$$NO_3^{-+} H_2O^{+}2e^{-} \rightarrow NO_2^{-+}2OH^{-}$$
 (1)

$$O_2 + 4e^- + 2H_2O \rightarrow 4OH^-$$
 (2)

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

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

In this process, Zn²⁺ concentration decreases gradually, the growth of ZnO tends reach a metastable state making it grow along the (001) direction. The ZnO NSs stop growing until the Z axis direction (the thickness of ultrathin layers) is close to the height of the quasi 2D. Subsequently, the action of an electric field gathers Zn²⁺ ions at the cathode, resulting in multi-nucleation and growth of the ZnO NSs again. In this way, ZnO NSs gradually grow forward and form the NSs arrayin the quasi 2D ultrathin space.

References:

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