Supporting Information

For

Fabrication and Characterization of Nanostructured ZnO Thin Film Microdevices by Scanning Electrochemical Cell Microscopy

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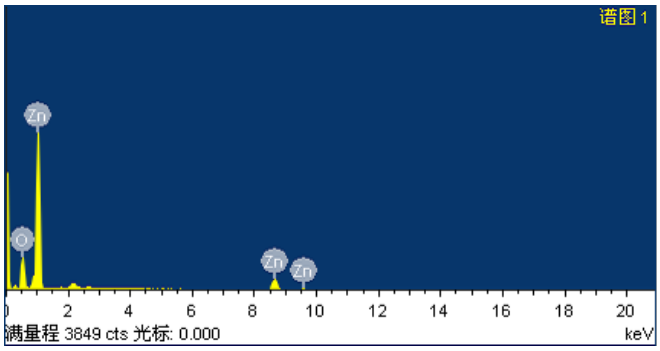
S1 Experimental details

The chemicals used in the experiments ($Zn(NO_3)_2$ and Hexamethylene tetraamine) were analytical grade or better (Sigma-Aldrich Co.). All aqueous solutions were prepared with deionized water (18.2 MΩ, Milli-Q, Millipore Corp.). The borosilicate micropipettes (o.d.: 1.2mm, i.d.: 0.8mm) with orifice of 10~100 μm diameter were prepared with a programmed laser puller PS-2000 (Sutter Co., USA). The Au film coated glass slides were prepared through magnetron sputter plating (JC500-3/D, Chengdu Vacuum Equipment Co., China). The ITO glass slides are a kind gift from Prof. Bin Ren at Xiamen University. Before experiments, the slides were cleaned with acetone and deionized water for several times and dried with pure nitrogen gas. A scanning electron microscope (SEM, Hitachi High-Technologies Co., Japan) was employed to obtain geometric topography and elementary analysis of the single microcrystals. Confocal Raman spectrum experiments were performed with a Renishaw inVia Raman microscope (Renishaw Co., British) to confirm the composition of the microcrystalline solution. All electrochemical experiments were

performed with the SECM workstation CHI920c (CHI Instrument Co., USA).

It should be noted that ITO also has a big double-layer capacitance. To eliminate the interference of ITO, the gold thin film coated glass slide was used to study the electrochemical capacitance of the nanostructured ZnO thin films.

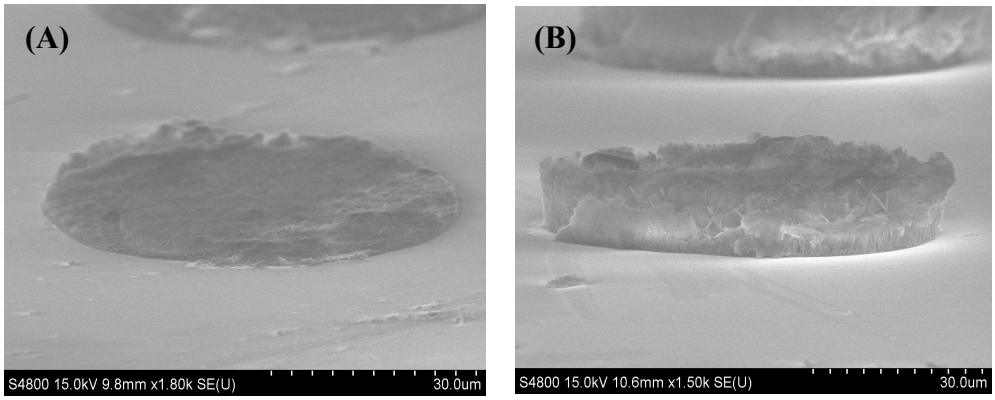
S2 The EDS results of the nanostructured ZnO thin film



Element	Weight percentage	Atomic percentage
O K	21.86	53.34
Zn K	78.14	46.66
total	100.00	

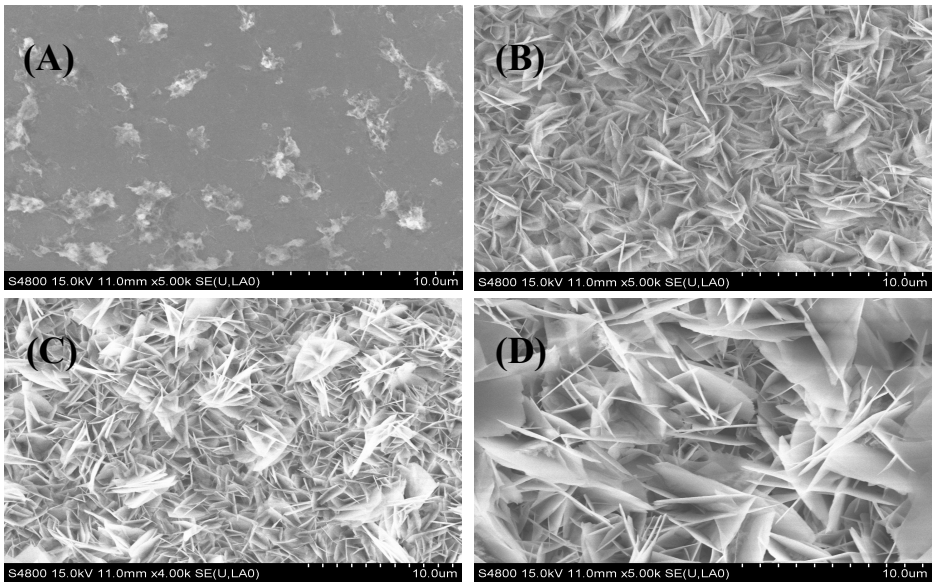
In order to reduce oxygen interference from the ITO substrate, nanostructured ZnO thin films were synthesized on newly prepared gold thin film coated glass slides through SECCM for SEM and EDS experiments. Comparing to the results on ITO substrate (O/Zn: 60/40), the nanostructured ZnO thin films with similar thickness (-1.5 V for 200 s) have an O/Zn ration of 53:47. Even if the depositing time was extended to 400s to form thicker films (See S3), the O/Zn ration would not change too much. The oxygen was always a little bit higher than Zn. The nonstoichiometric ratio of O/Zn indicates that there exist the lattice defects in nanostrutured ZnO thin film. Oxygen dopant promotes the application of ZnO into energy storage devices and electronic components (*J. Appl. Phys., 2005, 98, 041301*).

S3 The thickness dependence of the film on electrodepositing time



The aqueous solution in the microcapillary contains 1.0 mol/L $Zn(NO_3)_2$ and 0.01 mol/L Hexamethylene tetraamine (HMT), electrodepositing potential: -1.5 V; electrodepositing time: (A) 200s; (B) 400s. With the extending time, the thickness of ZnO thin film increases.

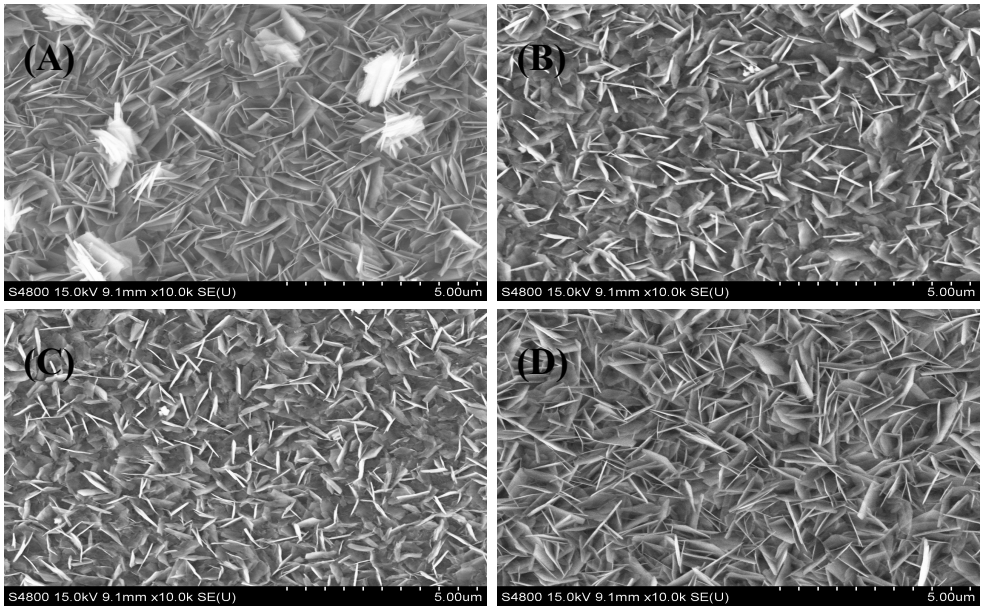
S4 The SEM images of the film at different electrodepositing time



The aqueous solution in the microcapillary contains 1.0 mol/L $Zn(NO_3)_2$ and 0.01 mol/L Hexamethylene tetraamine (HMT), electrodepositing potential: -1.5 V; electrodepositing time: (A) 10s; (B) 100s; (C) 200s; (D) 300s. It's very difficult to get reproducible SEM images before a "monolayer" is formed, i.e., the deposition time is less than 100s in the experimental condition declared in the text (orifice diameter: 50

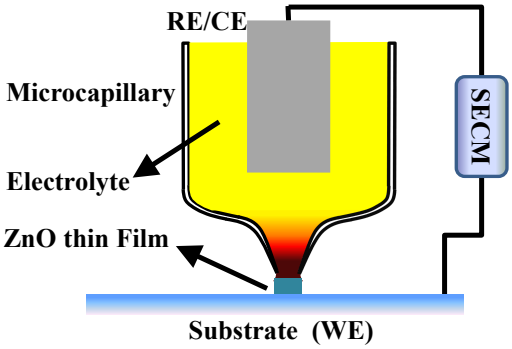
μm, applied potential: -1.5 V, solution: 1.0 mol/L Zn(NO3)2 and 0.01 mol/L Hexamethylene tetraamine (HMT), humidity: 85%). We think that is because the nucleation and growth of ZnO are simultaneous and in random. However, after a "monolayer" is formed, the growth rate slows down. Because the substrate is covered by the semiconductive ZnO film, the electrochemical reduction of nitrate is hindered, thus, the growth rate decreased.

S5 The SEM images of the film at different electrodepositing potentials



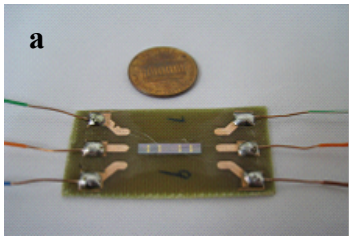
The aqueous solution in the microcapillary contains 1.0 mol/L $Zn(NO_3)_2$ and 0.01 mol/L Hexamethylene tetraamine (HMT), electrodepositing time: 200s; electrodepositing potential: (A) -1.2 V, (B) -1.3 V, (C) -1.4 V, (D) -1.5 V. As discussed in S4, the nucleation and growth of ZnO are spontaneous and in random. The nucleation may be accelerated at more negative potential. Due to the high nucleation rate, the nanostructured ZnO thin film formed at -1.5 V seems more uniform. That's why we choose the experimental potential (-1.5 V) in our experiment.

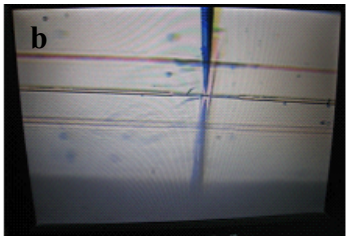
S6 The setup for the electrochemical capacitor experiments



The setup used for electrochemical capacitor experiments is the same as that for ZnO microsynthesis. The difference is that the electrolyte in the microcapillary contains only 0.1 mol/L NaCl. To eliminate the interference from ITO substrate, a newly prepared gold slide was adopted since gold/0.1 mol/L NaCl interface has much smaller double layer charging/discharging background as shown in Fig. 2a of the text.

S7 The microchip for preparing ZnO micro-varistor





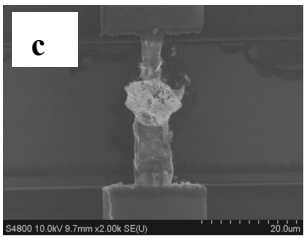


Fig a: The microchip (in the central area of the bakelite plate,) was fabricated through lithography microfabrication. The substrate material is silicon. Three pairs of gold microwires were deposited through lithography. Then the microchip was insulated by deposition a kind polymer. In each pair of gold microwire, one is 2 μm and the other is 4μm, the gap between them is 2 μm. Gold wire with a diameter of 60 μm was used to connect the microchip to the extern circuit. However, this polymer insulator can't endure high temperature. In order to promote the I-V property of ZnO micro-varistor, we replace the insulator as silicon nitrate so that the ZnO thin film can be sintered at high temperature (400ºC for 30 min in our experiment as declared in the text).

Fig b: the video camera used for the manipulation of SECCM system.

Fig c: the SEM image of the sintered microdevice.