Electronic Supplementary Information

Crystal growth and piezoelectric characterization of mechanically stable ZnO nanostructure arrays

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1. Materials

FTO substrate (~8 Ω/sq, 80% transmittance) and Zn powder (99.995%, <150 μm) were purchased from Sigma-Aldrich. Nitrogen (99.999%) and oxygen (99.5%) were purchased from Praxair and Airgas, respectively. Hydrochloric acid (37% in water) was purchased from Acros Organics.

2. Instruments

A three-zone horizontal tube furnace (OTF-1200X-III, MTI Corporation) was used for the ZnO chemical vapor deposition (CVD) synthesis. The nitrogen gas flow was controlled and measured by a FM-1050 tube flowmeter from Matheson Tri-Gas and a TopTrak 822 Mass flow controller from Sierra Instruments, respectively. CPX 2800 ultrasonic cleaner from Branson Ultrasonics was used for the ultrasonic cleaning and testing of the mechanical stability of the nanopyramids. KSL-1100X muffle furnace from MTI Corporation was used for the oxygen annealing treatment. FEI Nova NanoSEM 450 and PANalytical Empyrean were used for scanning electron microscopy (SEM) imaging and X-ray diffraction (XRD) characterization. Piezoelectric force microscopy (PFM) was conducted by MFP-3D from Asylum Research with the highly conductive AFM cantilever (OMCL-AC240TM from Olympus). Horiba LabRAM was used for Raman spectroscopy.

3. Experimental procedure

The FTO substrate was precut in 2 x 2 cm^2 and cleaned by ultrasonication in detergent solution, acetone and 2-propanol for 15 mins, respectively. 0.2 g Zn powder was loaded in a small quartz test tube and placed in a horizontal tube furnace. The prepared substrate was placed next to the test tube precursor boat. The tube furnace was purged by a mixture gas of

100 SCCM N_2 and 4 SCCM O_2 for 30 mins under low vacuum status by a mechanical pump to remove unwanted gas impurities. The furnace was heated up to 450 ℃ for 30 min and maintained for another 30 min to allow the synthesis of ZnO. After the furnace cooled down, the ZnO synthesis was completed. To improve piezoelectric properties, the as-synthesized ZnO on FTO was annealed under an oxygen condition in a muffle furnace. The muffle furnace was purged by 30 SCCM O_2 under atmospheric pressure for an hour and heated up to 500 ℃ and maintained for an hour. After the synthesis and annealing of ZnO was completed, some portion of the ZnO was removed by HCl to expose the underlying FTO surface for electrical connection and grounding.

The product was characterized in terms of morphology, crystal structure, crystal defect and piezoelectric properties by SEM, XRD, Raman spectroscopy and PFM, respectively. During the piezoelectricity measurement, the cantilever tip was placed at the apex of a pyramidal ZnO nanostructure. An electric field was applied and swept in forms of triangle and alternating step to measure the piezoelectric response from the sample.

4. FTO surface roughness

The evident high surface roughness of the FTO substrate used to grow the ZnO nanopyramids is shown in Figure S1.

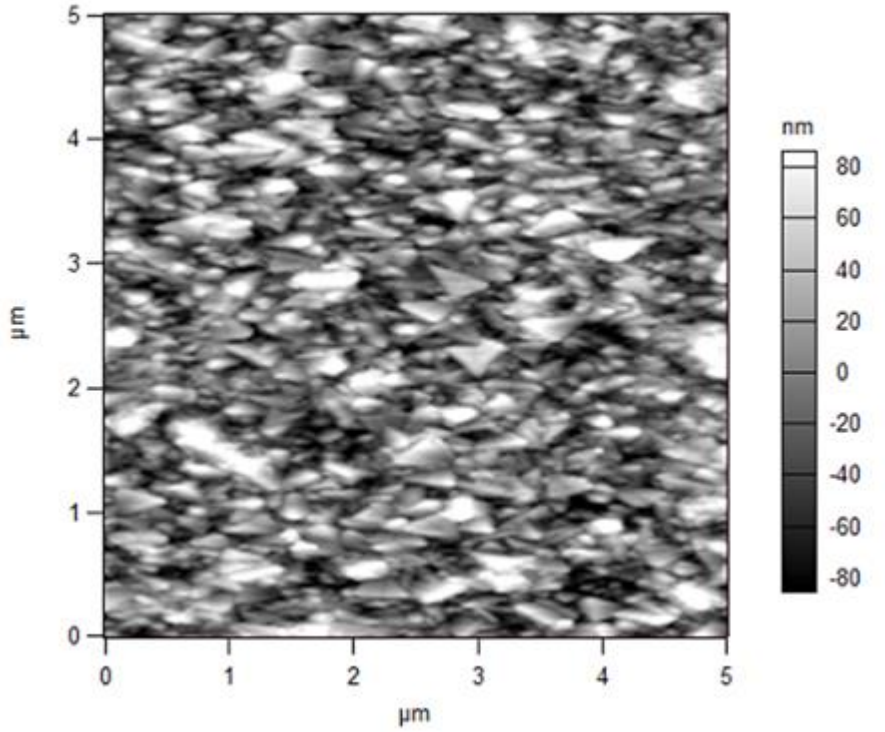

Fig. S1 AFM surface topography of FTO substrate.

5. Mechanical stability test

To demonstrate the mechanical stability of the synthesized ZnO nanopyramids, they were ultrasonicated at 110 W and 40 kHz for 3 hours. To compare the mechanical stability of nanopyramids, the ZnO nanorods were synthesized at 550 ℃ and ultrasonicated under the same conditions. In Figure S2, before and after ultrasonication of ZnO nanopyramids (a and b, respectively) and nanorods (c and d, respectively) are shown. Most of the ZnO nanorods were broken and removed from the surface, while nanopyramids are not damaged and remained intact. This result provides evidence that the ZnO nanopyramids have superior mechanical stability compared to the nanorods structure.

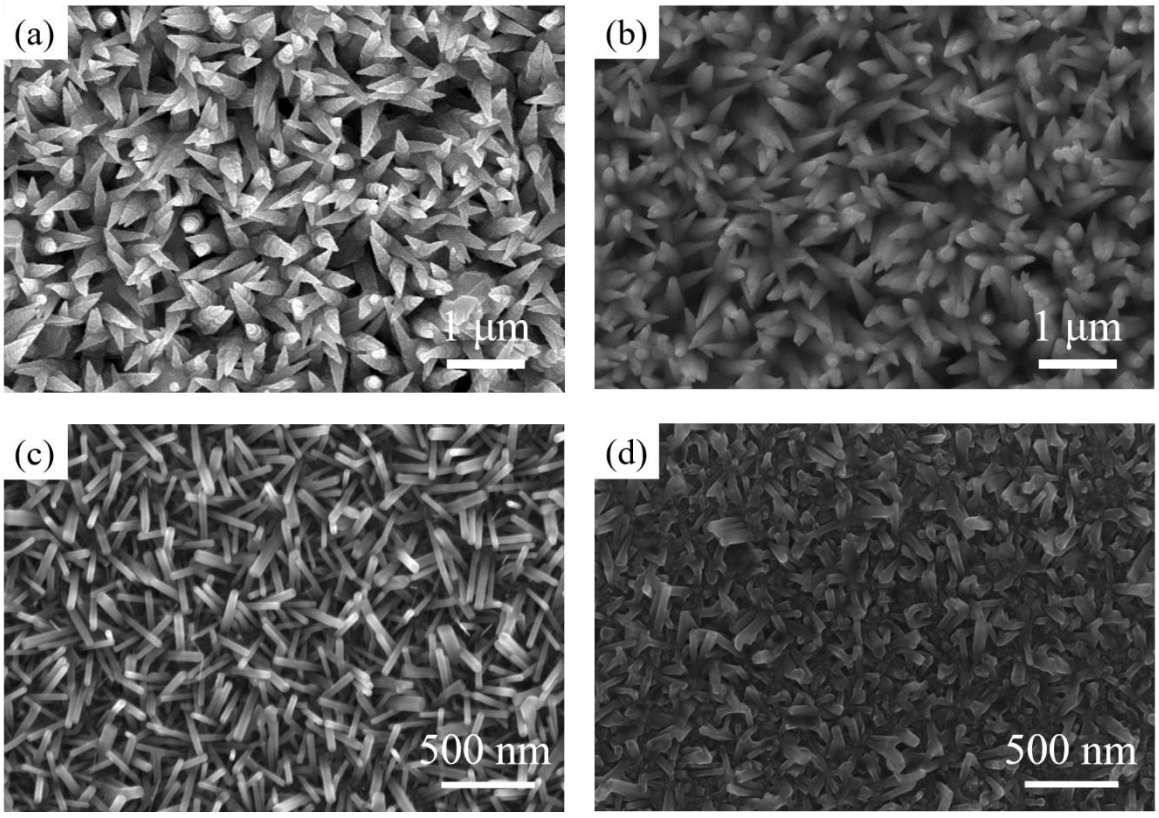

Fig. S2 SEM surface image of ZnO nanopyramids (a) before and (b) after ultrasonication; ZnO nanorods (c) before and (d) after ultrasonication.

6. Statistic data of piezoelectric coefficient

The statistics of measured piezoelectric coefficient is shown in Figure S3. In the as-synthesized ZnO, the average, median, and standard deviation of d_{33} are 10.58, 10.80, and 1.99 pm/V, respectively. In the oxygen annealed ZnO, the average, median, and standard deviation of d_{33} are 23.08, 23.31, and 1.84 pm/V, respectively.

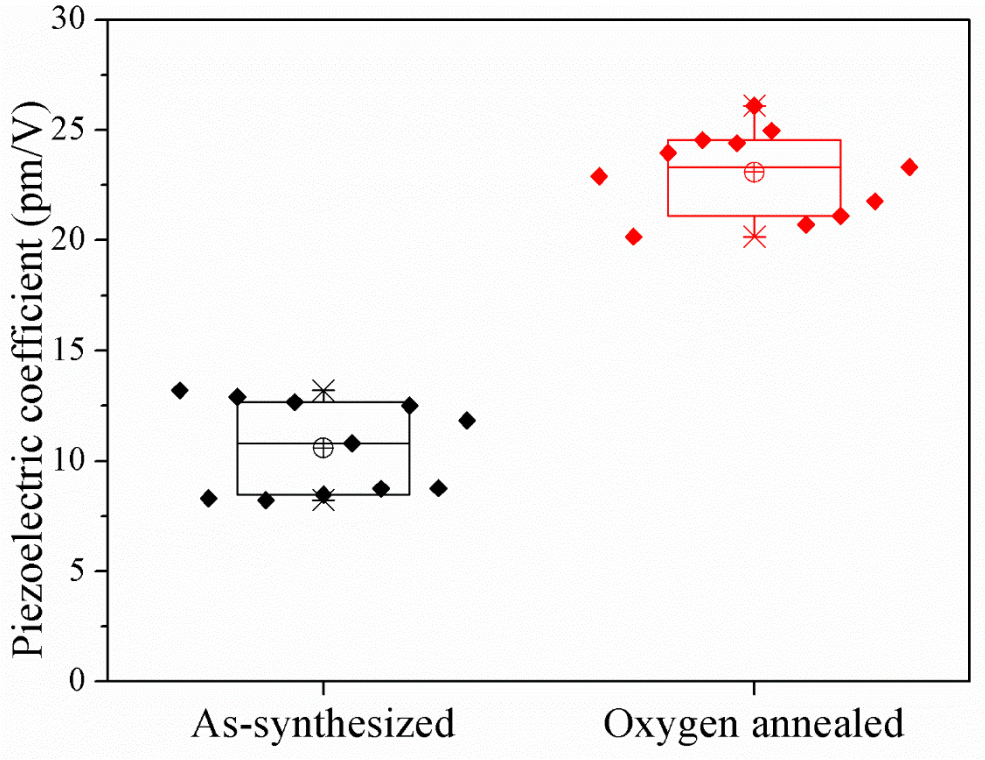

Fig. S3 Statistics of measured piezoelectric coefficient before and after oxygen annealing.