Supporting Information

Biomimetic ZnO Plate Twin-Crystals Periodical Arrays

Yao-Hung Tseng,[a] Ming-Han Liu,[a] Yu-Wei Kuo,[b] Peilin Chen,[b] Chiang-Ting Chen,[c] Yang-Fang Chen,[c] and Chung-Yuan Mou*[a]

Department of Chemistry and Center of Condensed Matter Science, National Taiwan University, Taipei 10617, Taiwan.

cymou@ntu.edu.tw

Experimental details:

All chemicals, hexamethylenetetramine (HMT) (99%, Acros), Zn $(NO_3)_2 \cdot 6H_2O$ (95%, Acros), and granular gelatin (typeB, 225 Bloom, Sigma), SU8-2015 (Microchem corp.), Polydimethalsiloxane (PDMS) (Dow Corning, Sylgard 184), urea (99.5%, Acros), 11-mercaptoundecanoic acid (95%, Aldrich) and fluorescen isothiocyanate isomer (FITC) (90%, Acros) were used without purification.

Patterning SAMs (self-assembly monolayers) on the substrate:

The masters for μCP were prepared by forming SU8-2015 photoresist patterns on Si substrates. Polydimethalsiloxane (PDMS) is cured over the masters to form stamps with complementary relief structures. For the fabrication of the Au-coated substrate, the Au films (20 nm) were deposited on Si wafers by sputtering deposition through EMITECH K550X sputter coater (Quorum Technologies Ltd). Later, the SAMs solution was prepared by dissolving 11-mercaptoundecanoic acid in ethanol to reach the concentration of 20mM. The PDMS stamp was immersed in the SAMs solution for 30 min. After aging, the PDMS stamp was taken out and rinsed with 95% ethanol solution. A hand held N2 gun was applied to dry the PPDMS stamp. To pattern SAMs on the Au surface, the stamp inked with SAM was placed on the Au films for 30 sec, so that the SAM molecules on the portions of PDMS stamp that came into contact with the surface being transferred and assembled onto Au.

Formation of ZnO hierarchical structure on the SAMs-patterned substrate:

To grow ZnO crystals on the substrate with patterned SAMs , typically a proper amount of gelatin (0.15 or 0.3 g) was dissolved in doubly distilled water (30 mL) to form a gel with various concentrations of gelatin (5 or 10 g/L). Then a mixture of Zn $(NO_3)_2 \cdot 6H_2O$ (3 mmol) and HMT (3 mmol) was added to the gelatin solution. The SAMs-patterned substrate was suspended upside down in the solution to avoid non-specific precipitation on the substrate. The aqueous solution was sealed in the autoclave at 80℃ for 21 h. After reaction, the substrate was washed with large amount of de-ionized water. The substrate was dried at 60℃ for 1 day. For the experiment with the urea as the source of hydroxyl ions, the same synthetic condition was applied except the replacement of 3 mmol HMT by 3mmol urea. For growing ZnO crystals on the substrate with the smaller patterned size (10μm x 10μm), 30 mM Zn $(NO_3)_2 \cdot 6H_2O$ and 30mM HMT were mixed together with the presence of 10g/L gelatin. In the FITC loading experiment, the ZnO crystals were grown on the substrate for 24 h. Later, it was immersed into 1mM FITC solution for 2h.

Instruments:

The FITC loading status was monitored by the confocal microscopy through exciting the sample with 494 nm

laser light and observing its emitted light of 521 nm. X-ray diffraction (XRD) analysis was performed on a Philips X'Pert diffractometer, using Cu KR radiation (λ) 1.5418 Å). SEM observations were done on JEOL-JSM-6700F field emission scanning electron microscope operated at 10 kV. The cathodoluminescence (CL) spectra were carried out on a JEOL-JSM-6500 scanning electron microscope equipped with Gatan-Mono-CL3 operating at 15 kV. The monochromatic CL image was monitored at the wavelength of 380 nm.

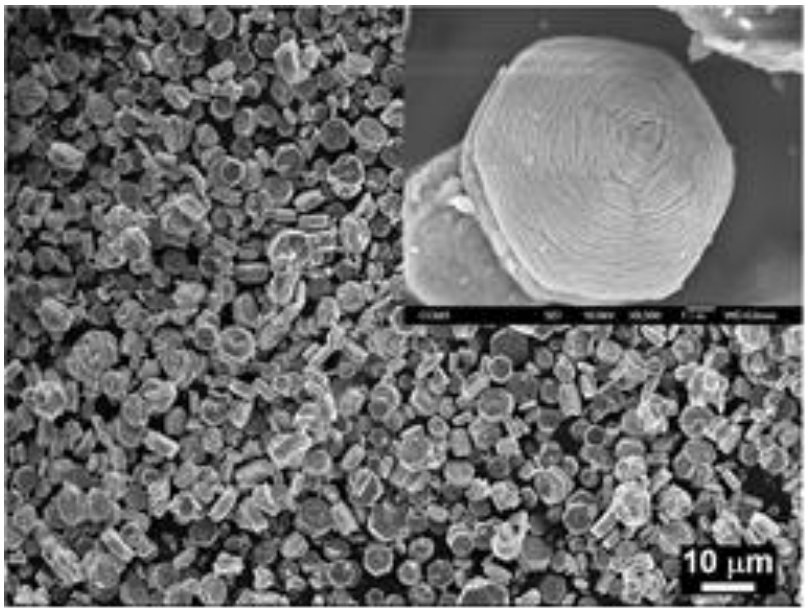

Figure S1. ZnO crystals prepared in a solution in hydrothermal condition with gelatin as additive.

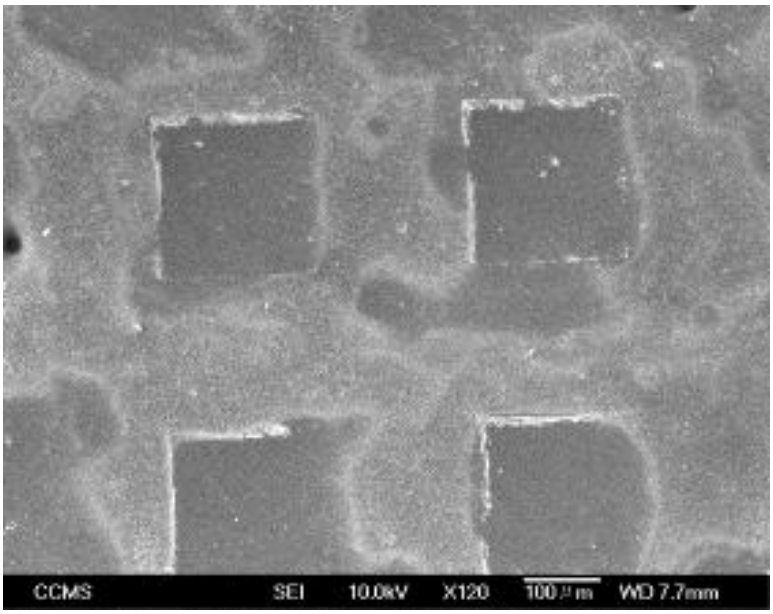

Figure S2. ZnO crystals grown on the substrate with the patterned squares of 200μm x 200μm in the presence of 10g/L gelatin. The HMT was replaced by urea.

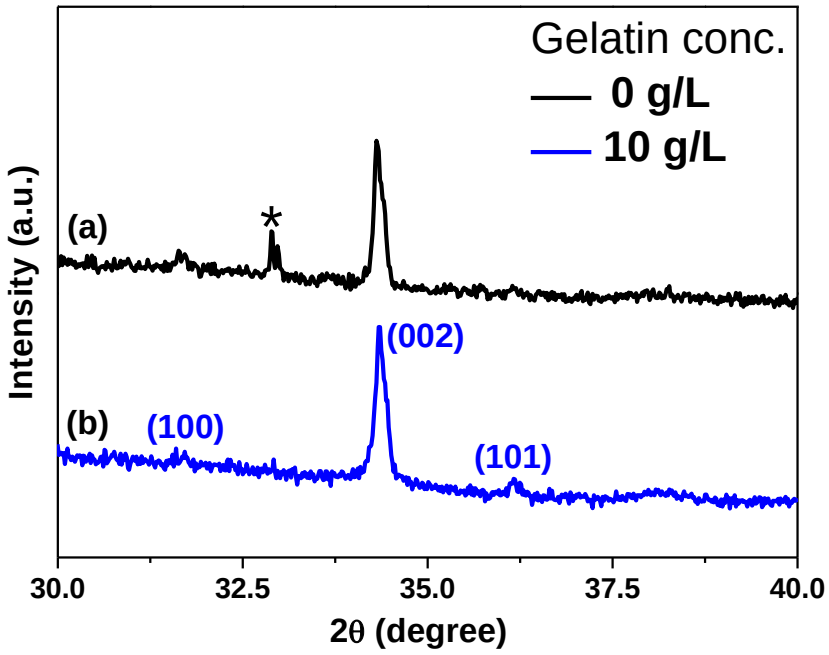

Figure S3. XRD data of the patterned ZnO crystals with the presence of (a) 0g/L gelatin and (b) 10g/L gelatin, respectively. * denotes the signal from the substrate.

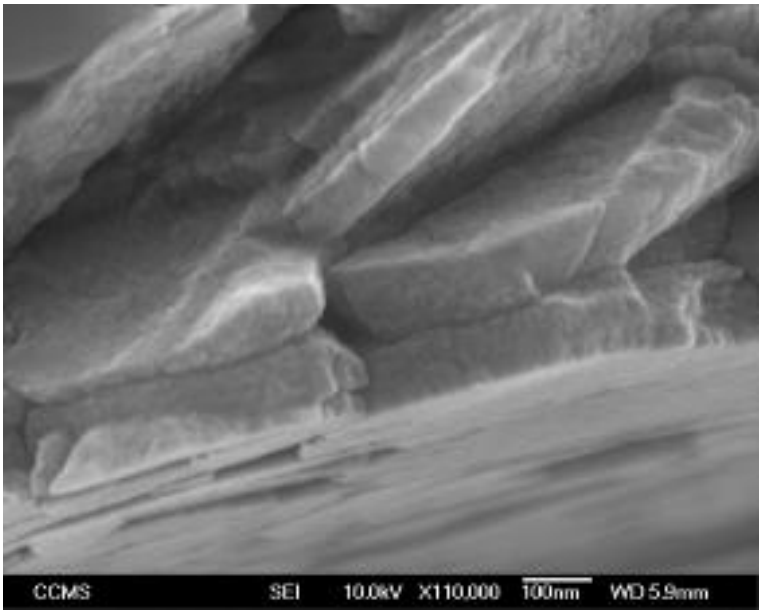

Figure S4. Cross sectional view of the ZnO crystals deposited on the substrate with the patterned squares of 200μm x 200μm in the presence of 10g/L gelatin. The as-deposited sample was peeled off from the substrate for SEM measurement.

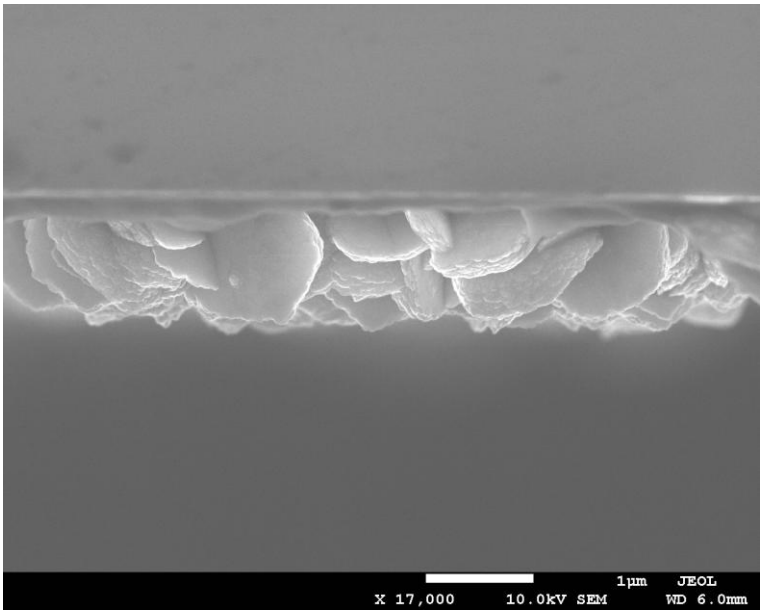

Figure S5. Cross sectional view of the ZnO crystals deposited on the substrate with the patterned squares of 200μm x 200μm in the presence of 5g/L gelatin and one-third of Zn precursor.

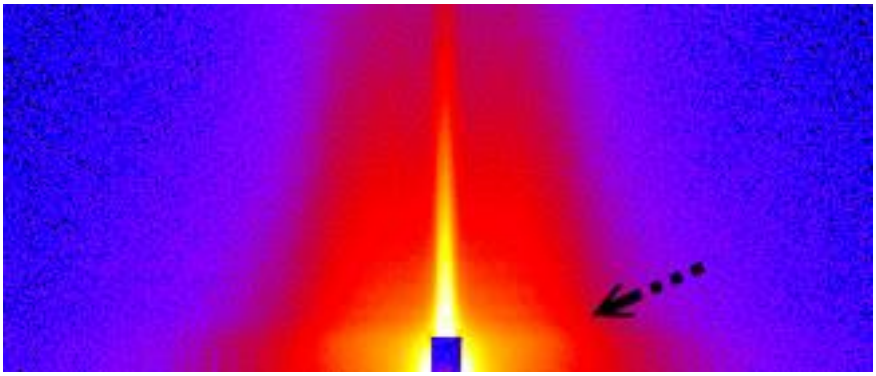

Figure S6. The orientation of Fig. S5 was investigated by grazing incidence small-angle X-ray scattering (GISAXS). The 2D GISAXS ring pattern (as arrow indication) represents a faulty ordered structure with ZnO mesocrystals randomly distributed while perpendicular to the substrate. The faint scattering ring corresponds to a periodical structure of ~ 20 nm which agrees roughly with stacked tnanoplates observed under SEM(~ 24 nm).