Low temperature, rapid and controllable growth of highly crystalline ZnO nanostructure via a diluent hydrolytic process and its application on transparent super-wetting film

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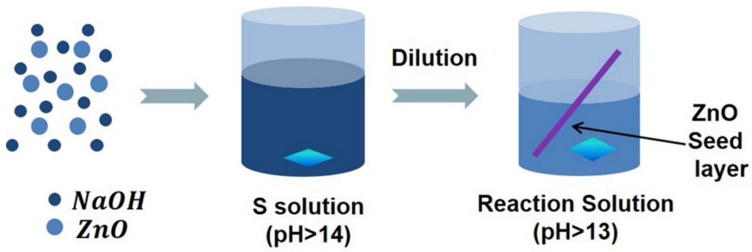

Fig. S1 Reaction diagram using a diluent hydrolysis approach.

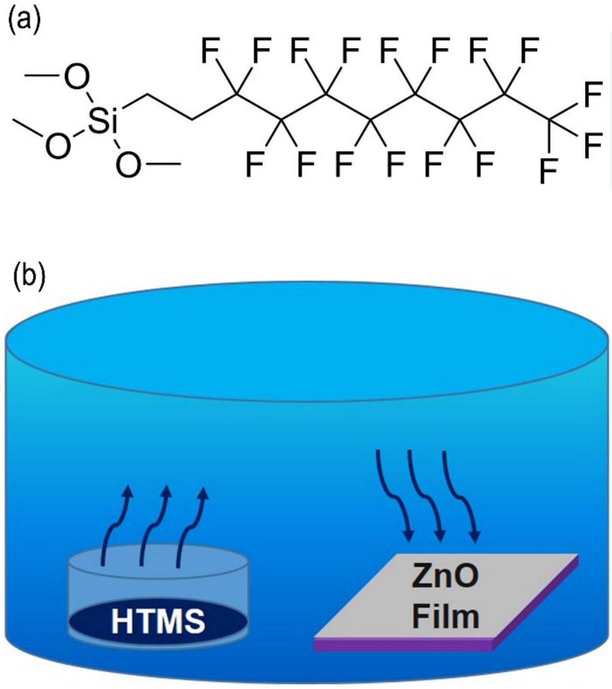

Fig. S2 Low surface modification of ZnO film by HTMS. (a) The molecular structure of HTMS; and (b) the modification process.

Table S1 The effect of temperature on the growth of nanospikes.

Temperature (°C)	35	45	55	65	75	90
Reaction duration (min)	20	20	15	12	8	5
Density (number per μm^2)	0	63	59	55	50	unsure

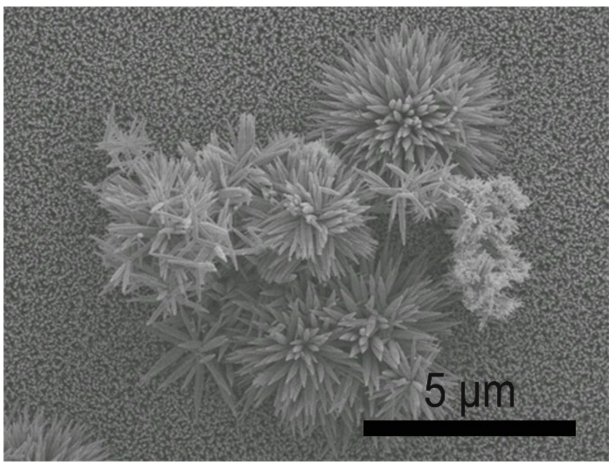

Fig. S3 The result of microflowers local depositing on the top of nanospike arrays.

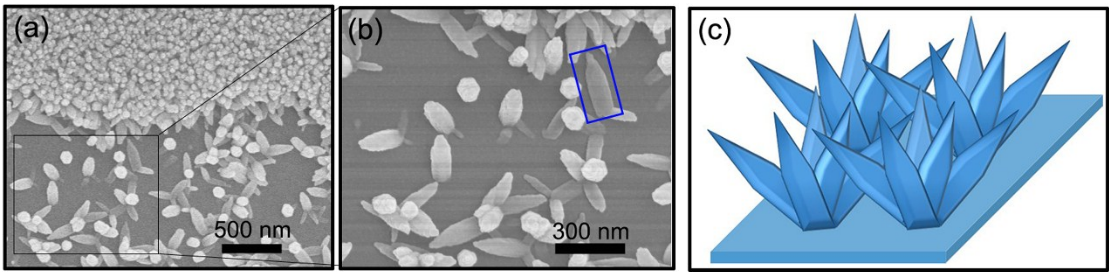

Fig. S4 The result of ZnO growth on glass substrate, with 20 dilution ratio in 60 ℃ environment. (a) Low magnification SEM image; (b) low magnification SEM image; and (c) schematic diagram of ZnO cluster composed of nanospikes.

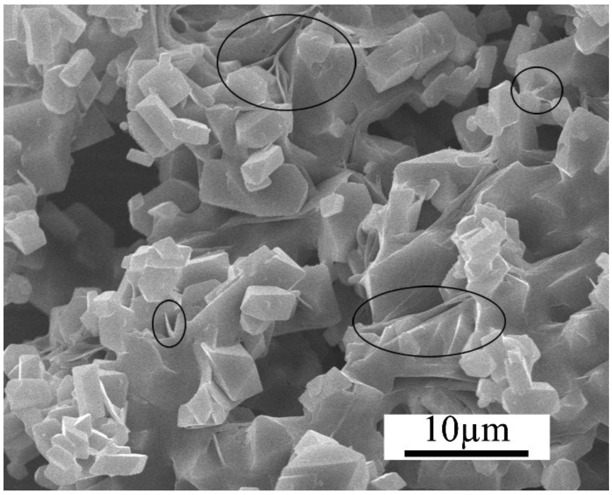

Fig. S5 The result of ZnO growth on glass substrate, with 20 dilution ratio in room temperature environment.

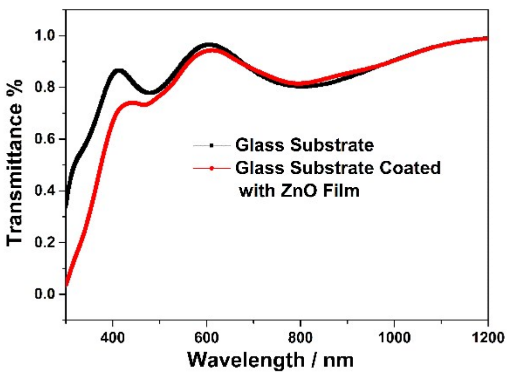

Fig. S6 Simulated result of transmittance using finite difference time domain method.

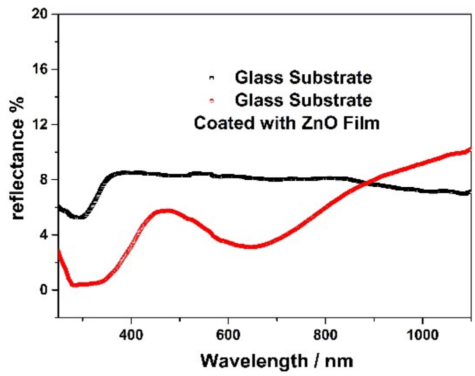

Fig. S7 The reflectance result of the glass substrate and ZnO nanospikes coated glass.

Table S2 The average transmittance and haze results in the visible band.

Sample	Transmittance / %	Haze / %
Glass	90.8	0.18
ZnO film-Glass	88.8	13.56

Effective Refractive Index n_{eff}

The effective refractive index (n_{eff}) is calculated using effective medium theory. For our model in **Fig. S5**, 2-dimensional Bruggeman equation [1] for two material mixtures is shown in ***equation 1***:

$$F\left(\frac{n_{eff}-n_1}{n_{eff}+n_1}\right)+\left(1-F\right)\left(\frac{n_{eff}-n_0}{n_{eff}+n_0}\right)=0 \qquad (1)$$

where F (fill factor) is the area ratio of ZnO in a slice, and n_1 and n_0 are the refractive indexes of ZnO crystal and air, respectively. For the hexagonal wurtzite ZnO nanospike structure, where F increases gradually downward through the structure (Seen in **Fig. S5a**), and incident light will be reflected at each slice with a phase determined by the distance traveled through the structure. The n_{eff} can be modulated by manipulation of the fill factor, as shown in ***equation 2***:

$$F = \frac{A_{ZnO}}{A_{unit}} = \frac{2\times\frac{3\sqrt{3}}{2}r_i^2}{3r\times 3\sqrt{3}r} = \frac{\left(h_i \tan\frac{\theta}{2}\right)^2}{3r^2} \qquad (2)$$

Among which,

$$\tan\frac{\theta}{2} = \frac{25\text{nm}}{600nm} = \frac{1}{24}$$

$$F = \begin{cases} 0, \left(h_i = 0 - 600nm\right) \\ \frac{1}{12} - \frac{1}{3}, \left(h_i = 600 - 1200nm\right) \\ \frac{1}{3}, \left(h_i = 1200 - 2100nm\right) \end{cases}$$

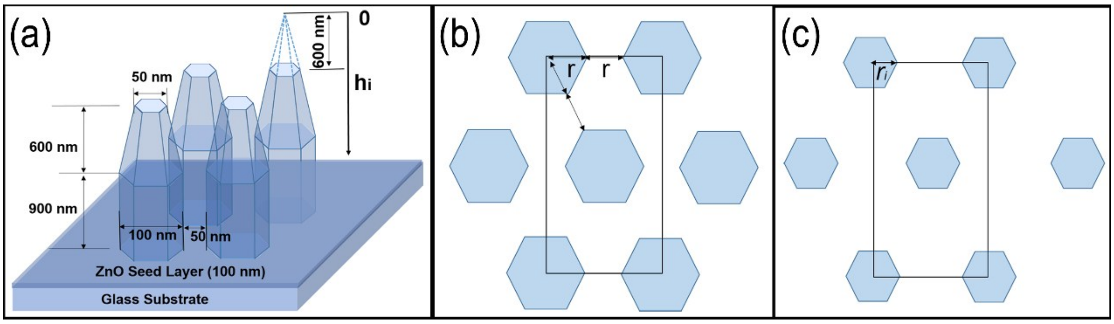

Fig. S8 Correlation model parameters for effective refractive index simulation. (a) The size parameters and coordinate axis; (b) the radius and area of unit cell; and (c) the radius and area of the slice cross section at the height of h_i.

where A_{unit} is the area of unit cell as shown in **Fig. S5b** in a hexagon, and A_{ZnO} is the area of ZnO material at a certain slice in **Fig. S5c,** r and r_i are the radius of ZnO nanospikes at the height of 1200 nm and h_i, respectively.

Substituting $n_1 = 2, n_0 = 1$ to equation (1),

$$n_{eff} = \frac{2F - 1 + \sqrt{(1-2F)^2 + 8}}{2} \qquad (3)$$

In addition, $n_{glass} = 1.51$, $n_{ZnO(monocristal)} = 2$, $n_{ZnO(seed)} = 1.95$ [2]

The transmittance simulation of glass coated with ZnO nanospikes was performed using finite difference time domain method. Perfectly matched layers (PML) and periodic boundary conditions (**Fig. S5b-c**) were used in the perpendicular and horizontal directions. A plane wave source ranging from 300 to 1200 nm was used to illuminate these textures in **Fig. S5a** at the normal incidence. A 2D z-normal frequency-domain field (DFT) power monitor was placed below the glass in **Fig. S5a** to obtain the transmission spectrum.

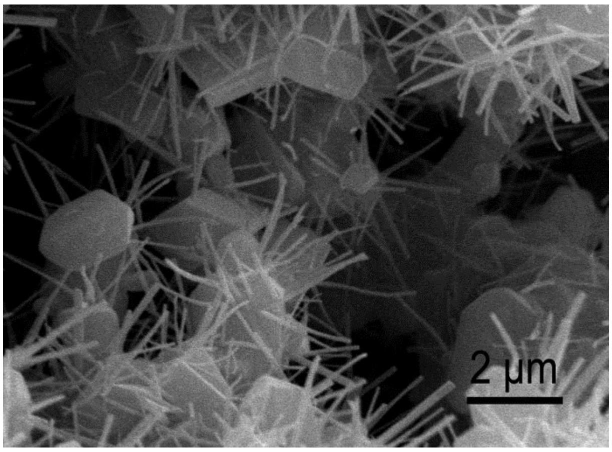

Fig. S9 The result of ZnO growth in 20 dilution ratio diluent, in room temperature environment for 15 min.

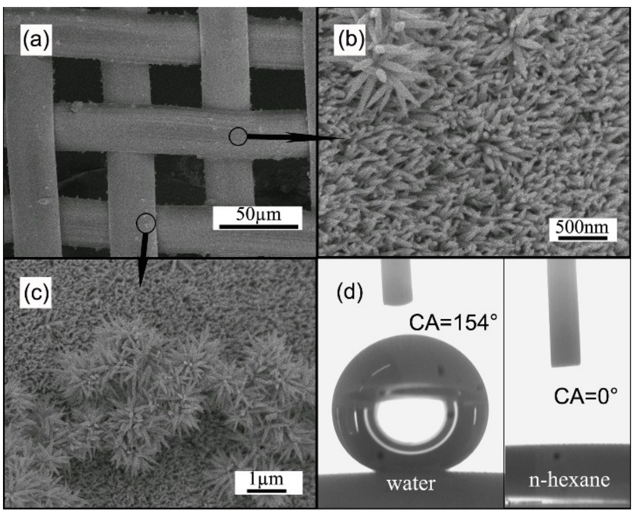

Fig. S10 The surface morphology and the wettability on copper grid using saturated solution diluent hydrothermal reaction method. (a) The low magnification of the grid; (b) and (c) the ZnO nanorods and microclusters growing on the stainless steel wire; and (d) the wettability of water and n-hexane on the surface modified by HTMS.

References

1 B. Jin, J. He, L. Yao, Y. Zhang and J. Li, *ACS Applied Materials & Interfaces*, 2017, **9**, 17466-17475.

2 C. Besleaga, G. E. Stan, A. C. Galca, L. Ion and S. Antohe, *Applied Surface Science*, 2012, **258**, 8819-8824.