

Supplementary information for

Fast Fabrication of Self-Cleaning Coating Constructed with Scallion-Like ZnO Using Perfect Colloidal Monolayer Enabled by Predictive Self- Assembly Method

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1. EXPERIMENTAL SECTION

(1) Chemicals and materials. All of the reagents, such as styrene ($\geq 99.0\text{wt}\%$), sodium hydroxide ($\geq 96.0\text{wt}\%$), sodium dodecyl sulfate (CP grade), potassium peroxydisulfate ($\geq 99.5\text{wt}\%$), ethylene glycol ($\geq 99.0\text{wt}\%$), ethanol ($\geq 99.5\text{wt}\%$) and zinc nitrate hexahydrate ($\geq 99.0\text{ wt }\%$), were used directly without any further purification, which were purchased from Sinopharm Chemical Reagent Co., Ltd. (SCRC, (Shanghai, China)). Heptadecafluorodecyltrimethoxysilane ($\text{C}_{13}\text{F}_{17}\text{H}_{13}\text{O}_3\text{Si}$, HTMS) was bought from Dow Corning Co. (USA). The resistivity of the deionized water (DI water) is $18.25\text{ (M}\Omega\cdot\text{cm)}$. Silicon wafer with the size of $1.5\text{cm}\times 1.5\text{cm}$ and another two-inch wafer were cleaned according to the RCA procedure¹ and subsequently cleaned in Piranha solution ($70\%\text{H}_2\text{SO}_4+30\%\text{H}_2\text{O}_2$) for 12h, followed by triple rinsing in DI water.

(2) Preparation of colloidal dispersions. Monodisperse PS spheres are synthesized according to our previous report². The obtained polystyrene spheres were cleaned using successive centrifugation and ultrasonic cleaning in ethanol system three times. Prior to use,

the purified polystyrene spheres were re-dispersed in miscible liquid of ethanol and glycol, and the final volume fraction was set to about 20% and 40%.

(3) Spin-coating of PS spheres latex and thermal treatment. Certain volume of above colloidal latex was deposited on wafer substrate. The wafer was spin-coated at 550 rpm on a commercial spin coater (CAS, KW-4A) for 9 seconds to spread the PS latex and then the wafer was then quickly accelerated to 3500 rpm for 30 seconds. For some samples, six-arm diffraction star were formed in about 15 seconds. After spin-coating, the substrates were transferred to an electric thermostatic drying oven with a quartz window for special time. The sample was dried from edge to center gradually and a variety of colors emerged in the end.

(4) Synthesis of ZnO nanostructures. To deposit a uniform coating of ZnO nanoparticles as nucleation seeds, a **10 nm ZnO** seed layer was first deposited on the Si (100) substrates (with and without colloidal monolayer) by the RF Magnetron Sputtering method. For the sample with colloidal monolayer, they were soaked in methylbenzene for **24 h**, and then ultrasonic cleaning in water system to remove the PS spheres. Both samples with and without colloidal monolayer annealed in air for **20 min at 325 °C**. A Teflon bottle was filled 50 mL of aqueous solution containing 2.5 mM of both $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and HMT. And then the silicon substrate with the ZnO seeds was placed vertically in a capped Teflon bottle. The reaction was performed for 12 hours at 95 °C.

(5) HTMS modification. For self-cleaning research, the samples with ZnO nanostructures and a bottle of 1 mL HTMS solution (2.9 vol%, the solvent was methylbenzene) were sealed in a glass container. Hereafter, they are placed in an oven at 80°C for 4 h to reduce the surface energy.

(6) Sample Characterizations. The structure and morphology of the resultant colloidal crystal were examined by field emission scanning electron microscopy (SEM, JSM-6700F) operating at 5KV. The the crystallinity of the ZnO is also analyzed using high resolution transmission electron microscopy (HRTEM) JEOL 2000FX with an acceleration voltage of 200kV. The X-ray diffraction data were collected on a X'Pert diffractometer with Cu K α radiation. Photoluminescence (PL) spectra of ZnO nanostructures were measured using a fluorescence spectrophotometer (JYfluorolog-3-Tou), which were recorded at room temperature. Contact angle measurements were performed with a the CAST 2.0 contact angle analysis system (Solon Information Technology Co. Ltd., Shanghai, China) equipped with a CCD camera for image capture in ambient atmosphere. The volume of the water droplets used for the static CA and SA measurements was 4 mL.

2. The reason for only considering that every particle only interacting with its nearest nucleus

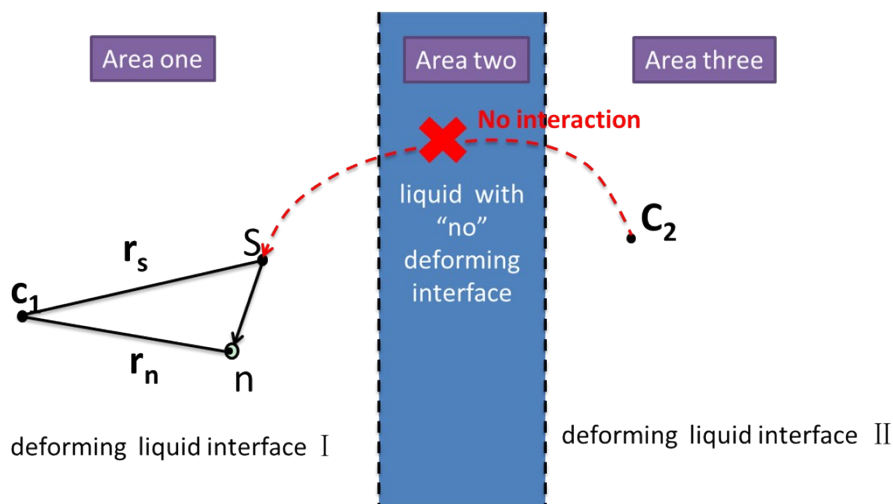


Figure S1. Schematic diagram for illustrating every particle only interacting with its nearest nucleus. S denotes the probe particle; C_1 denotes the first neighbor nucleus of the probe particle S; C_2 denotes the second neighbors nucleus of the probe particle S; r_s denotes the distance between C_1 and S; r_n denotes the distance between C_1 and n.

In the colloidal spheres system, interaction truncated at the first neighbors is allowed because the capillary interaction exists only in the deforming liquid interface³. There is “no deforming liquid” interface between two neighbor nucleuses (the liquid film is “high”), and hence the probe particle S in area one wouldn’t suffer the interaction of the second neighbor nucleus area of the probe particle S in area two. And thus there is no contribution to $U(r)$ at the other nucleuses area, namely, the capillary interaction is limited to the deforming liquid interface.

3. The total energy of the system varying with the evolution steps of the Monte Carlo simulation

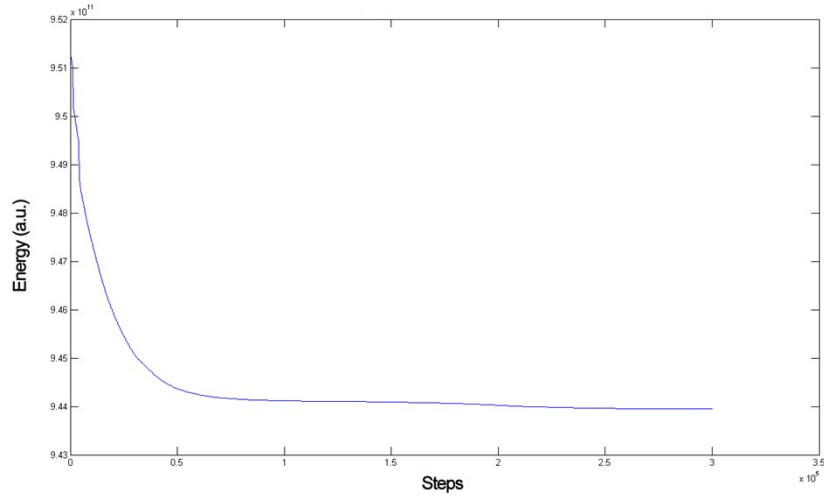


Figure S2. Monte Carlo simulation pattern with the self-assembly condition of: $T=30^\circ\text{C}$, $VF=20\%$.

4. Detail process of proof for satisfying detailed balance when Equation (4) and (5) being employed

The Hamiltonian of our self-assembly system could be written as:

$$H(x, s) = U_j - U_s = Q \sum_j \ln(r_j) - Q \sum_s \ln(r_s) = A e^{\frac{-\Delta}{T}} e^{-\frac{s}{\tau_0(1-\frac{T}{T_c})}} \left[\sum_j \ln(r_j) - \sum_s \ln(r_s) \right]$$

Considering that s is the number of accepted steps and it corresponds to evaporation time of

the real system, we have

$$s \propto t$$

$$\therefore H(x,t) = U_j - U_s = Q \sum_j \ln(r_j) - Q \sum_s \ln(r_s) = A e^{-\frac{A}{T}} e^{-\frac{t}{\tau_0(1-\frac{T}{T_c})}} [\sum_j \ln(r_j) - \sum_s \ln(r_s)] \propto M(x)N(t)$$

$$\therefore w(x,t) \propto \exp[-H(x,t) / kT] \propto \exp[-M(x)N(t)] = \exp[-M(x)] \exp[N(t)]$$

From Master equation, we know

$$\frac{\partial P(x,t)}{\partial t} = \exp[N(t)] [\Sigma w(x \rightarrow x') p(x,t) - \Sigma w(x' \rightarrow x) p(x',t)]$$

Considering that the self-assembly is an equilibrium system, we have

$$\frac{\partial P(x,t)}{\partial t} = 0$$

$$\text{Thus, } \Sigma w(x \rightarrow x') p(x,t) - \Sigma w(x' \rightarrow x) p(x',t) = 0$$

After the system reach the final state, $P(x,t)$ has nothing to do with t.

$$\therefore \frac{p(x)}{p(x')} = \frac{w(x' \rightarrow x)}{p(x \rightarrow x')}$$

Consequently, the detailed balance could be satisfied.

From above analysis, we can see that bias the steps via Equation (4) and (5) is required by drive forces of capillary. However, employ the usual Metropolis acceptance criterion, Equation (6) still work.

5. SEM images of the colloidal crystal prepared under optimum condition

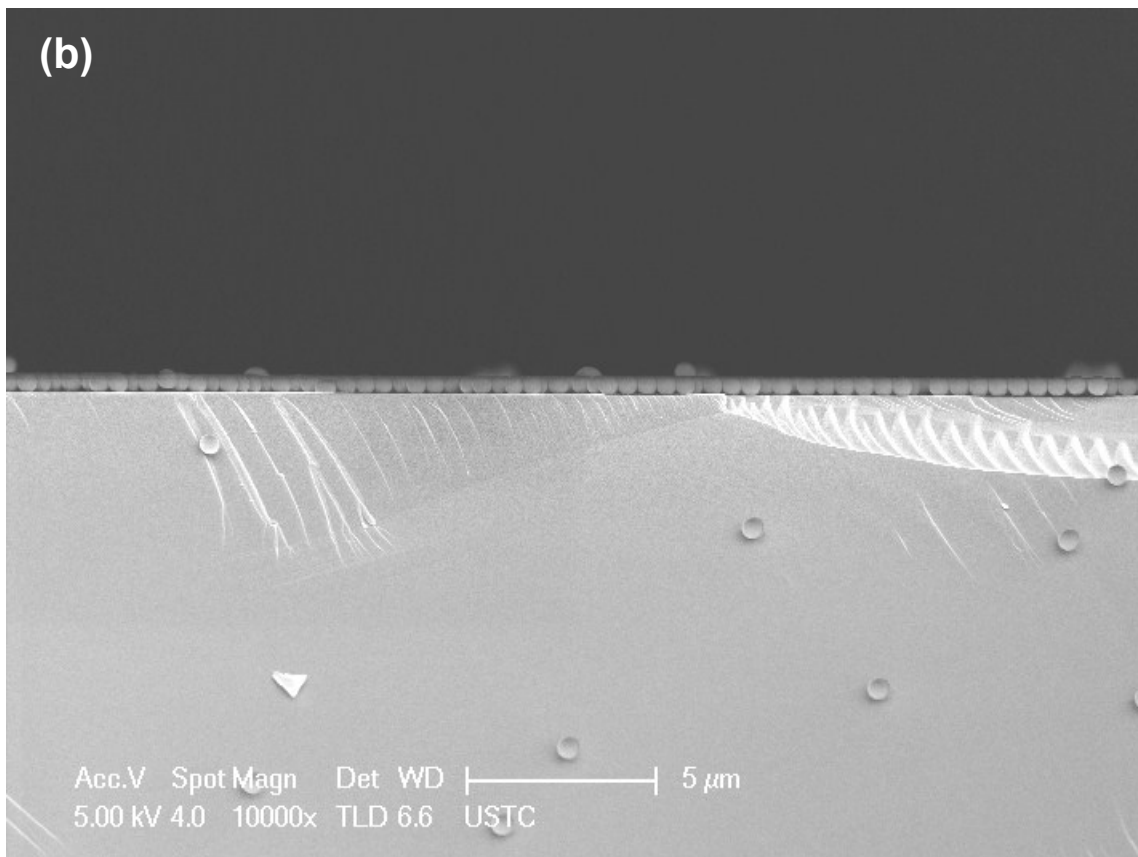
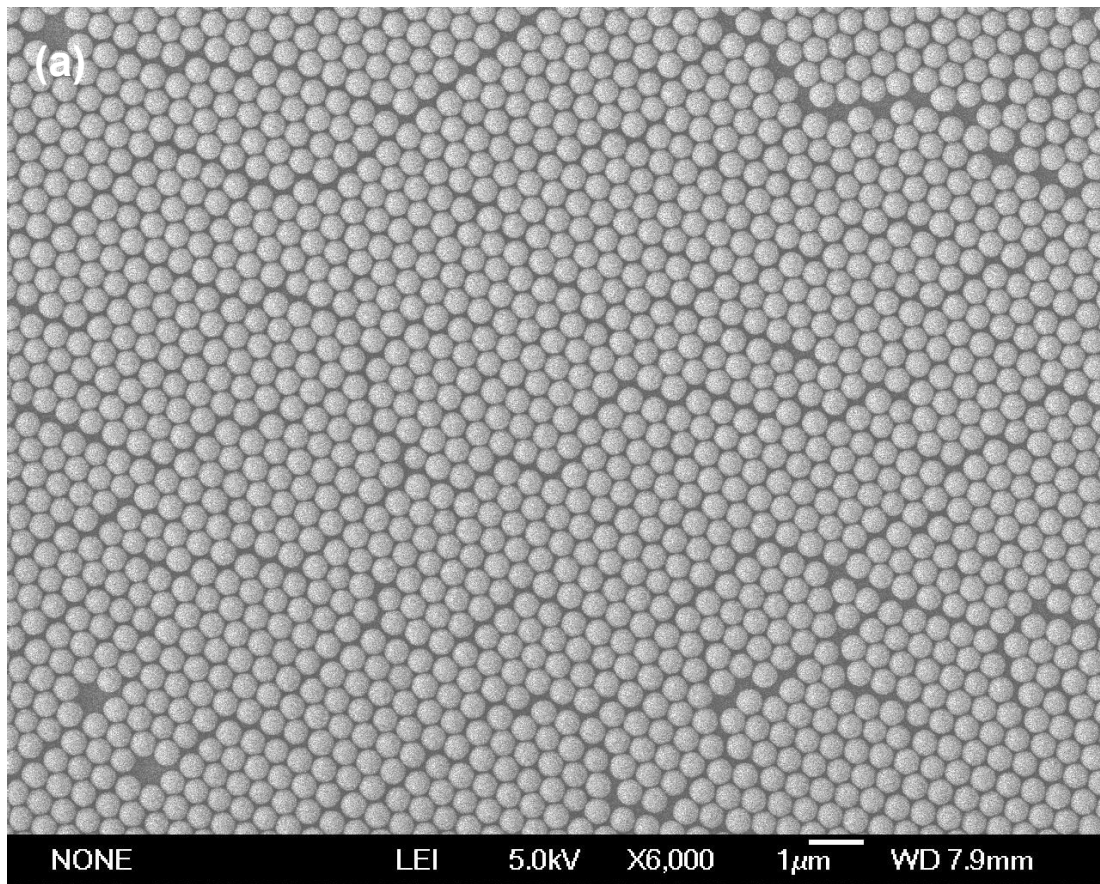


Figure S3. SEM images of the wafer-scale monolayer close-packed PS spheres prepared in condition of 40% volume fraction and 45 °C self-assembly temperature. (a) low magnification, top-view; (b) high magnification, top-view; (c) high magnification, side-view.

6. Details of quantitative assessment for the crystallinity of colloidal monolayer

We employed the well-established method, namely two-dimensional Discrete Fourier Transform (DFT), to quantitatively evaluate the degree of crystallinity of the colloidal monolayer^{2, 4}. For a perfect lattice, the sharp bright spots can be approximated by an array of delta functions, $p(x)$, composed of m elements separated in space by an interval T ,

$$p(x) = \sum_{m=-\infty}^{\infty} \delta(x - mT)$$

The corresponding Fourier Transform (FT) harmonics are all of the same magnitudes described by:

$$p(f) = \frac{1}{T} \sum_{n=-\infty}^{\infty} \delta(f - nf_0)$$

where $f_0=1/T$. In contrast, the magnitude of a harmonic in a disordered lattice decreases with the harmonic index. Therefore, the ratio of the harmonic magnitudes quantifies the identity and the spatial resolution of the lattice points in the pattern. The uniformity of the lattice spacing across the image corresponds to the magnitude of the first harmonic. The apparently lower decrease rate of harmonic magnitudes points to a lower concentration of lattice defects.

The SEM images were captured with the same magnification, brightness, and contrast along the direction normal to the film. We carried out a statistical analysis on them. Each sample is examined based on a series of SEM images taken from 18 equidistant positions at 1mm separation across the sample. Figure S4 illustrates the process of the quantitative assessment of the ordering of the colloidal crystal.

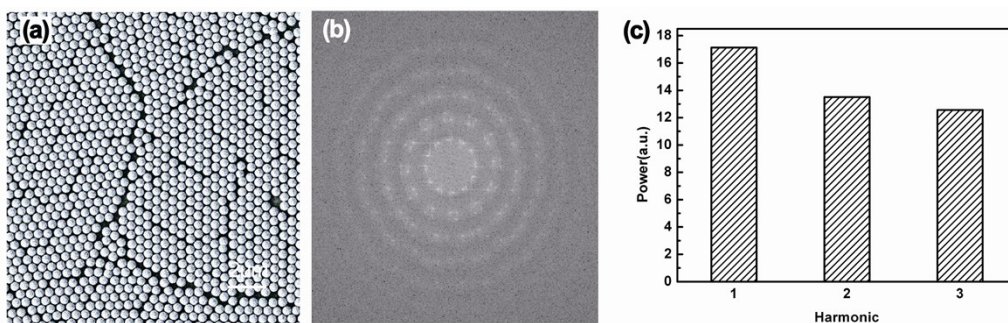


Figure S4. Process of the quantitative assessment the ordering of spheres in the growth plane: (a) typical scanning electron micrographs of colloidal crystal treated at the temperature of 35°C; (b) FT patterns of the SEM images in panel (a). The panel (c) shows the magnitude of the first three harmonics in the FT patterns shown in panel (b).

The colloidal crystal shown in Figure S4 (a) is obtained under the condition of VF=20% and the self-assembly temperature, final spin-coating speed and time being 35°C, 3500 rpm and 30 seconds, respectively. Figure S4 (b) shows the corresponding FT pattern. The bright spots are dim and not very regular, which results from the loose packing and multilayer of arrays obtained at low temperature. In addition, diffuse rings appear due to azimuth misalignment of the lattices in colloidal crystal. The magnitudes of the first three harmonics (M_1 , M_2 and M_3) in the FT pattern are shown in Figure S4 (c) and they are 17.13, 13.51 and 12.56, respectively.

7. The illustration for the conclusion of “The no marked XRD peak located at 33° is caused by harmonic of X-ray rather than the silicon (200)”

In order to understand our conclusion of “XRD peak located at 33° is caused by harmonic of X-ray”, we will describe more information about harmonic of XRD. As commonly known, monochromator of graphite is widely used to obtain monochromatic light. But the harmonic still exists because of the limitation of monochromator’s working principle. And the wavelength of the harmonic of X-ray is half of predetermined wavelength of X-ray. Consequently, for a special crystal plane (hkl) with the interplanar spacing d , there will be

two wavelength to satisfy the Bragg diffraction formula, namely $2d\sin\theta = n\lambda$, resulting to two diffraction peaks. What we should mention here is the peak caused by harmonic of X-ray will usually appear when the sample is single crystal or single crystal films.

Two conditions must be satisfied to confirm a diffraction peak as the peak caused by harmonic of X-ray: (1) There is a strong diffraction peak; (2) The interplanar spacing d corresponding to main peak (namely the strong diffraction peak mentioned in (1); such as Si (400) for our sample), $1/2$ object wavelength of X-ray ($1.54187 \text{ \AA}$ is the wavelength of X-ray we used) and the position of diffraction peak must satisfy the Bragg diffraction formula. In our case, these two conditions are satisfied (For our sample, $2 \times (1.357 \text{ \AA}) \times \sin(16.5^\circ) = 1 \times (1/2 \times 1.54187 \text{ \AA})$). Consequently, the no marked XRD peak located at 33° is caused by harmonic of X-ray. In addition, the silicon (200) at 33° is a forbidden reflection that shows no detectable intensity according to theory of XRD, which can also refer to JCPDF-89-5012.

8. XRD pattern of monocrystal silicon

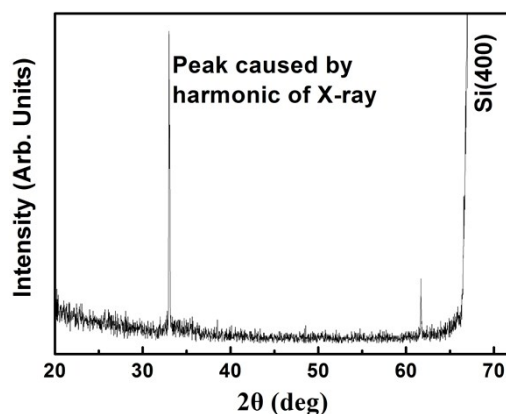


Figure S5. XRD pattern of monocrystal silicon

Figure S5 shows that the XRD peak located at 33° and a strong peak at 69° both appear, which indicates the peak located at 33° is attributed to the harmonic of X-ray.

References:

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