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Supplementary Information

# Bioinspired Silicon Hollow-Tip Arrays for High Performance Broadband Anti-Reflective and Water-Repellent Coatings

Yunfeng Li, Junhu Zhang, Shoujun Zhu, Heping Dong, Zhanhua Wang, Zhiqiang Sun, Jinrui Guo, and Bai Yang *

## Experimental Section

***Materials:*** Polystyrene (PS) microspheres were prepared by dispersion polymerization as mentioned in reference.[1] The PS microspheres used in our work were 792 nm in diameter. The silicon wafers (100) were cut into 20 mm×20 mm pieces, were soaked in the mixture of 98% $H_2SO_4$/30% $H_2O_2$ (volumetric ratio 7:3) for 20 min under boiling (caution: strong oxide), and then were rinsed with deionized water several times, at last were dried with $N_2$ stream. All the chemical reagents in our work were used as received.

***Non Close-packed PS Colloidal Crystals Fabricated by Reactive Ion Etching (RIE):*** The monolayer PS microspheres were prepared by interface method.[2] In brief, 0.2 ml PS microsphere dispersion in absolute ethanol was dropped on the surface of the water in the 8 cm in diameter glass tank, and then the monolayer microspheres were lift up onto the silicon wafer, the 2D colloidal crystals were obtained when the slides become dry. The oxygen reactive ion etching was performed on a Plasmalab Oxford 80 plus (ICP 65) system (Oxford Instrument Co., UK). To prepare the non close-packed 2D colloidal crystals, oxygen RIE operating at 10 mTorr pressure, 50 SCCM flow rate, and RF power of 30 W and ICP power of 300 W were carried out for 75 s. The non close-packed 2D colloidal crystals were heated in oven at 120 □ for 10 min to enhance the stability of the colloidal crystals.

***Silicon Post Arrays Fabricated by Silver Catalytic Wet Etching:*** The silicon post arrays were fabricated similar to the reference. Before wet etching, a thin silver film (ca. 40 nm) was

thermal deposition on the non close-packed 2D colloidal crystals as catalyst. For solution etching process, an etching mixture consisted of deionized water, HF, and $H_2O_2$ was used at the room temperature. The concentrations of HF and $H_2O_2$ were 4.6 M and 0.44 M, respectively. The duration was from 6 min to 16 min, depending on the length of the silicon posts. After etching, the substrates were calcined at 500 □ for 1 h to remove the polymer, and then the silver film was removed using aqua regia (volumetric ratio 3:1, $HCl/HNO_3$). At last the substrates were rinsed using deionized water several times to remove the residual acid, the silicon post arrays were obtained when the substrates were dried by $N_2$ stream.

***Silicon Hollow-tip Arrays Fabricated by Reactive Ion Etching:*** The silicon hollow-tip arrays were fabricated by a short time RIE process using a Plasmalab Oxford 80 plus (ICP 65) system (Oxford Instrument Co., UK). The flow gases in the RIE process were 30 SCCM $CHF_3$ and 4.0 SCCM $SF_6$, a pressure of 5 mTorr, and applied RF power and ICP power were 100 W and 500 W, respectively. Different duration RIE processes were performed relative to different length of silicon posts. The duration was from 90 s to 180 s.

***Surface Modification and CA Measurement:*** First, the silicon hollow-tip arrays were performed in the oxygen plasma to make the surface of tip arrays hydrophilic, and then put in the sealed jar with a little amount of trichloro (1H, 1H, 2H, 2H-perfluorooctyl) silane (Aldrich) at 60 □ for 6 h. The water CA is measured using a KRUSS DSA 10 MK2 contact angle goniometer. Each reported contact angle is the average of five measurements. The static contact angle was read by injecting a 5 μL water liquid, and the sliding angle was obtained from a drop of 9 μL.

***Characterization:*** SEM micrographs were taken with a JEOL FESEM 6700F electron microscope with primary electron energy of 3 kV. The samples were sputtered with a thin layer of Pt prior to imaging. TEM measurements were performed with a JEOL-2010 electron microscope operated at an acceleration voltage of 200 kV. A Shimadu 3600 UV-VIS-NIR spectrophotometer with standard mirror optics was used to measure the specular reflectance in

the 250–2500 nm range at the incidence angle of 5 degree. A Lambda 950 UV-VIS-NIR spectrophotometer attached with an integrating sphere was used for reflectance measurement in the 250–1000 nm range at the incidence angle of 8 degree. A Thermo Nicolet 6700-Fourier transform infrared (FTIR) spectroscope was used for the mid-IR region (4000 $cm^{-1}$- 650 $cm^{-1}$) at normal incidence. The photographic images of the silicon wafer and the silicon hollow-tip arrays were taken when they were placed near paper with some words in it.

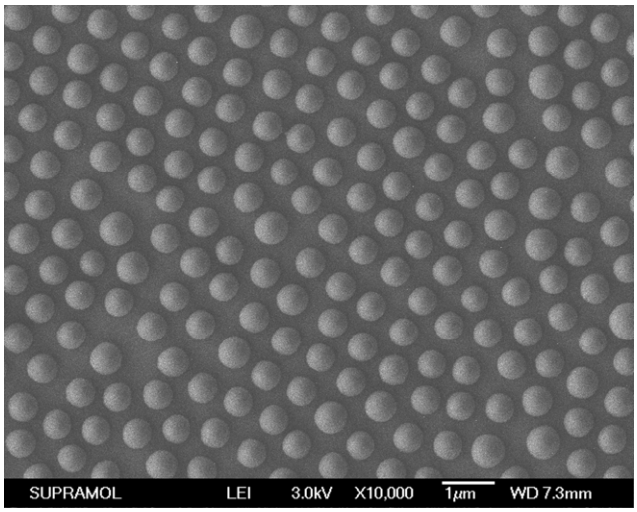


**Fig. S1.** Non close-packed PS colloidal crystals fabricated by RIE.

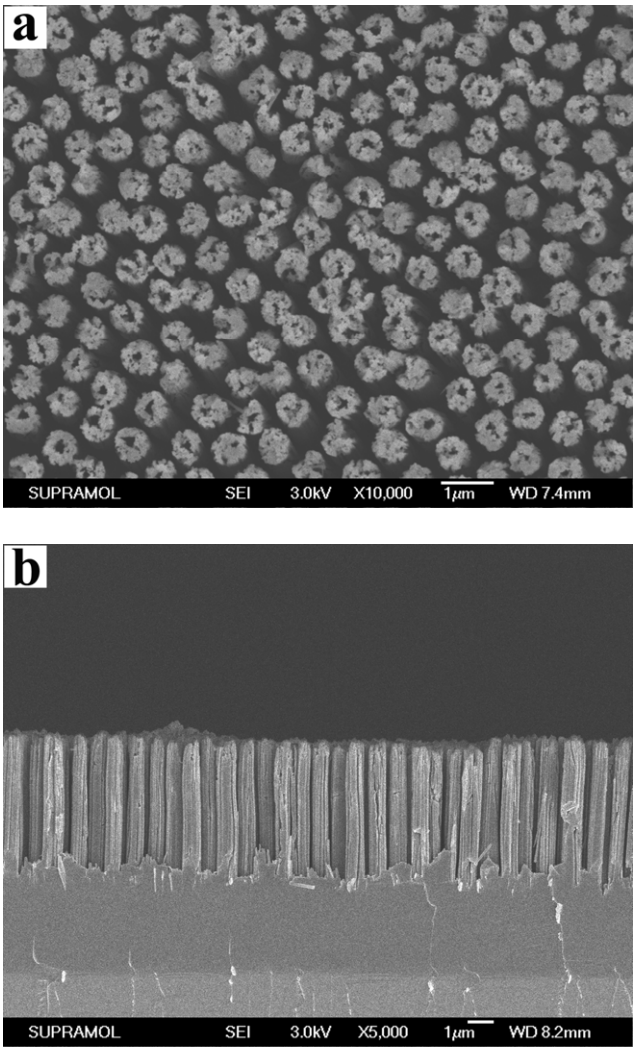


**Fig. S2.** SEM images of silicon post arrays. a) Top view. b) Cross-sectional view.

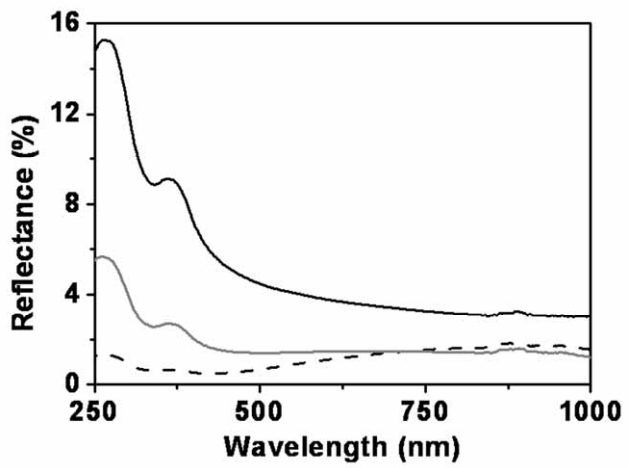


**Fig. S3.** Comparison of the hemispherical reflectance as a function of wavelength for hollow-tip arrays of 2.1 μm (black solid line), 3.4 μm (grey solid line) and 7.1 μm (black dash line) in length in the 250–1000 nm range.

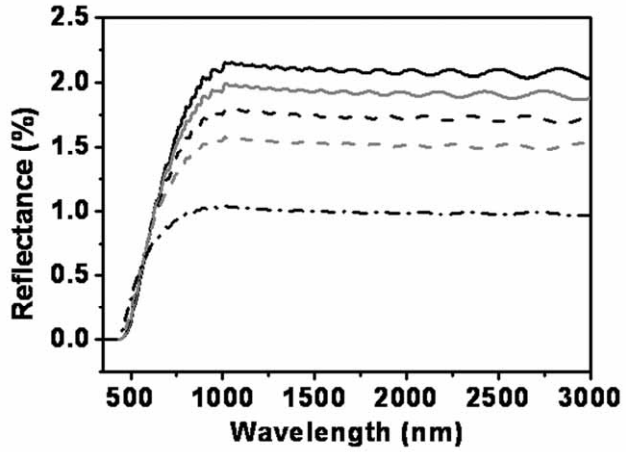


**Fig. S4.** The simulated specular reflectance of the hollow-tip arrays (7.1 μm in height) with porosity 0 (black line), 10% (grey line), 20% (black dash line), 30% (grey dash line), and 50% (black dash dot line) in the 350–3000 nm range.

**Notes and references**

1 J. H. Zhang, Z. Chen, Z. L. Wang, W. Y. Zhang, N. B. Ming, *Mater. Lett.* 2003, **57**, 4466.

2 S. M. Yang, S. G. Jang, D. G. Choi, S. Kim, H. K. Yu, *Small* 2006, **2**, 458.