Electronic Supplementary Information (ESI) for Soft Matter.

Wetting Behavior on Hexagonally Closed-packed Polystyrene Bead Arrays with Different Topographies

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Experimental deails

Chemicals. Styrene (≥ 99%), 2,2'-azobis(2-methylpropionitrile) (AIBN) and polyethyleneimine (branched) (PEI) were purchsed from Sigam-Aldrich. Polyvinylpyrrolidone (K 30, average Mw 40,000) (PVP K 30) was purchased form Fluka. Silicone elastomer base and silicone elastomer curing agent (SYLGARD® 184) were purchased from Dow-Corning. Ethyl alcohol (99.9%), sulfuric acid and hydrogen peroxide were purchased from Duksan.

Synthesis of the polystyrene beads. To make the polystyrene (PS) beads as building blocks, styrene, PVP K 30 and AIBN was used as monomer source, capping material and initiator, respectively. First, the PVP K 30 was dissolved in ethanol in three-necked round-bottom flask under argon atmosphere with stirring, then, the reaction temperature was elevated until 70 ^{o}C in which AIBN could decompose. After arrival of the reaction temperature, styrene solution containing AIBN (15.9 mM) was injected to the flask using the syringe and the injection rate was constant. Following injection, polymerization reaction was maintained for over 24 h. The PS beads were obtained by centrifugation and washed to remove residual styrene and PVP K 30 several times. The PS beads were dried at the room temperature. Here, PS beads with various sizes were synthesized by controlling the injection rate of the source, the concentration of the initiator (AIBN), and the concentration of the capping material (PVP K 30).

Preparation of the patterned Si substrates. The patterned Si wafer with hexagonal arrays with silicon pillar was fabricated by KrF stepping method. At first, a bottom anti-reflection (BAR) layer was spin-coated with the thickness of 58 nm on a 6 inch Si(100) wafer. And then, a positive photoresists (PR) was spin-coated onto the BARC/Si wafer. The PR/BAR/Si wafer and a photomask was placed and the set up was exposed to the KrF UV light (248 nm) with the non-contact and step, repeatedly. The desired pattern sizes of hole and pitch in the photomask are 3.4 μm/4.8 μm, 8.5 μm/12 μm, 14.2 μm/20 μm, and 20 μm/28 μm which

are four times larger than the desired image sizes on the wafer (4×). After the KrF stepper, the patterned Si wafer was obtained with the pattern sizes of hole/pitch which are 0.80 μm/1 μm, 2.125 μm/3 μm, 3.55 μm/5 μm, and 5 μm/7 μm. We can employ the 1 μm, 3 μm, 5 μm, and 7 μm of PS beads. The irradiated PR/BAR/Si wafer was developed on a AZ 300 MIF developer. Deep etching of the PR-free Si areas was carried out by ion coupled plasma (ICP) using Ar-based SF_6. The depths of etching were varied from 700 nm to 2 μm. The remaining BARC and PR layers after etching were removed by a PR asher. The patterned Si wafer was diced into 1.5 cm × 1.5 cm.

Template-assisted manual assembly of the polystyrene beads. The patterned Si substrates were immersed in a piranha solution (a 3: 1 mixture of sulfuric acid and hydrogen peroxide) and washed with deionized (DI) water. On the patterned Si substrates, the poly (dimethylsiloxane) (PDMS) solution which was a 10: 1 mixture of silicone elastomer base and curing agent was poured and maintained in the 70 ^{o}C for few hours. When the PDMS substrate was prepared as a template, a small amount of the PS beads powder was placed on the template and this powder was rubbed using PDMS slab with uniform direction repeatedly. After rubbing process, the randomly aggregated upper layers of PS beads were removed from the bottom monolayer with hexagonally close-packing (HCP) by using a fresh sticky PDMS slab for a few seconds on top of the PS beads array and subsequently removing the PDMS slab. Finally, this monolayer of the HCP PS beads on the PDMS substrate was transferred to the PEI coated glass substrate, which were coated by spin coating. The PEI coated glass substrate was kept at 70 ^{o}C during the transfer process.

Contact Angle Measurement. The hydrophobic wetting characteristics of a flat PS film and the PS bead arrays with different beads sizes over the range of 1-7 μm were measured using a contact angle measurement apparatus (DSA 100), using a 3μl water droplet.

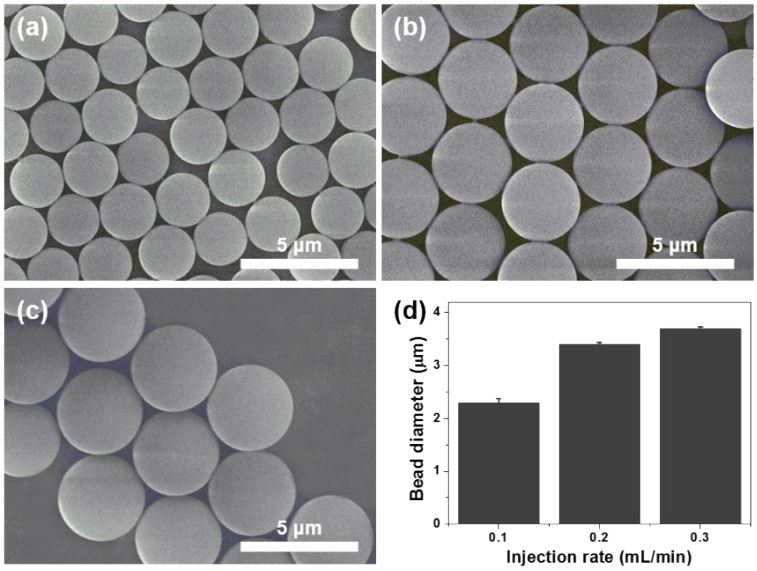

Fig. S1. SEM images of the PS beads synthesized under different injection rate of the styrene solution containing AIBN: (a) 0.1, (b) 0.2, and (c) 0.3 mL/min at the polymerization temperature of 70 °C. (d) The histogram of each average diameter and standard deviation of synthesized PS beads. According to an increase of the injection rate, the size of the PS beads became larger from 2.3, to 3.4, and then to 3.7 μm, respectively; the standard deviations for each particle size were 3.4%, 1.1%, and 0.8%, respectively. The scale bars are 5 μm.

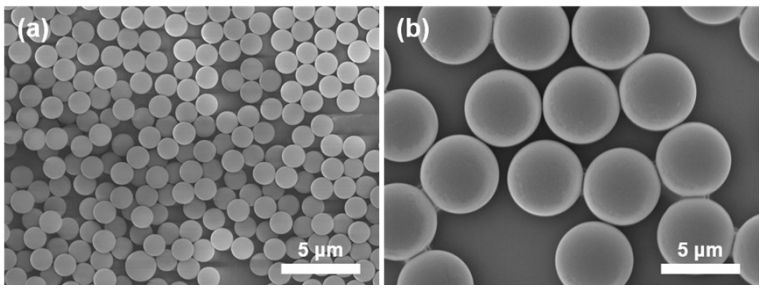

Fig. S2. SEM images of the PS beads synthesized under the decreased concentration of (a) the AIBN (5.5 mM) or (b) PVP K 30 (0.17 mM) with 70 °C reaction temperature and 0.3 mL/min injection rate. The average diameter of the synthesized PS beads were (a) 1.4 and (b) 4.8 μm, respectively. The scale bars are 5 μm.

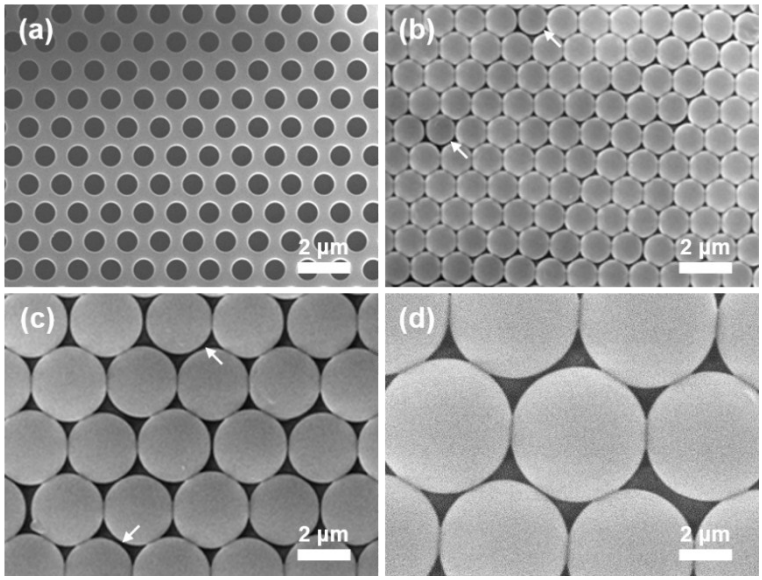

Fig. S3. SEM images of (a) the PDMS template with 1 μm of pitch size and the hexagonally close-packed PS bead arrays with different sizes; (b) 1, (c) 3, and (d) 5 μm, respectively. The arrows indicated unequal PS beads, with diameters larger or smaller than the average diameter of the population, disrupt the close packing of the PS beads and induce defects in the PS bead array. The scale bars are 2 μm.

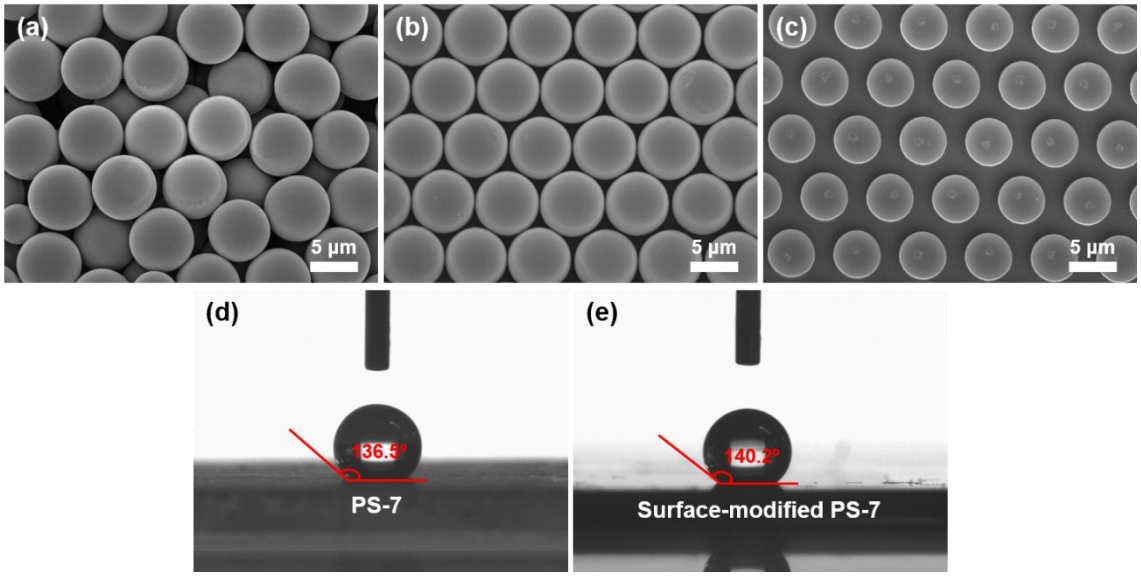

Fig. S4. SEM images of (a) 7 μm of PS beads and (b) the hexagonally close-packed PS-7 beads array. (c) SEM image (top-view) of the surface-modified PS-7 beads array by a thermal imprinting method above T_g (150 °C) of PS during the transfer process. The scale bars are 5 μm. CA measurements on (d) PS-7 and (e) surface-modified PS-7 substrates.

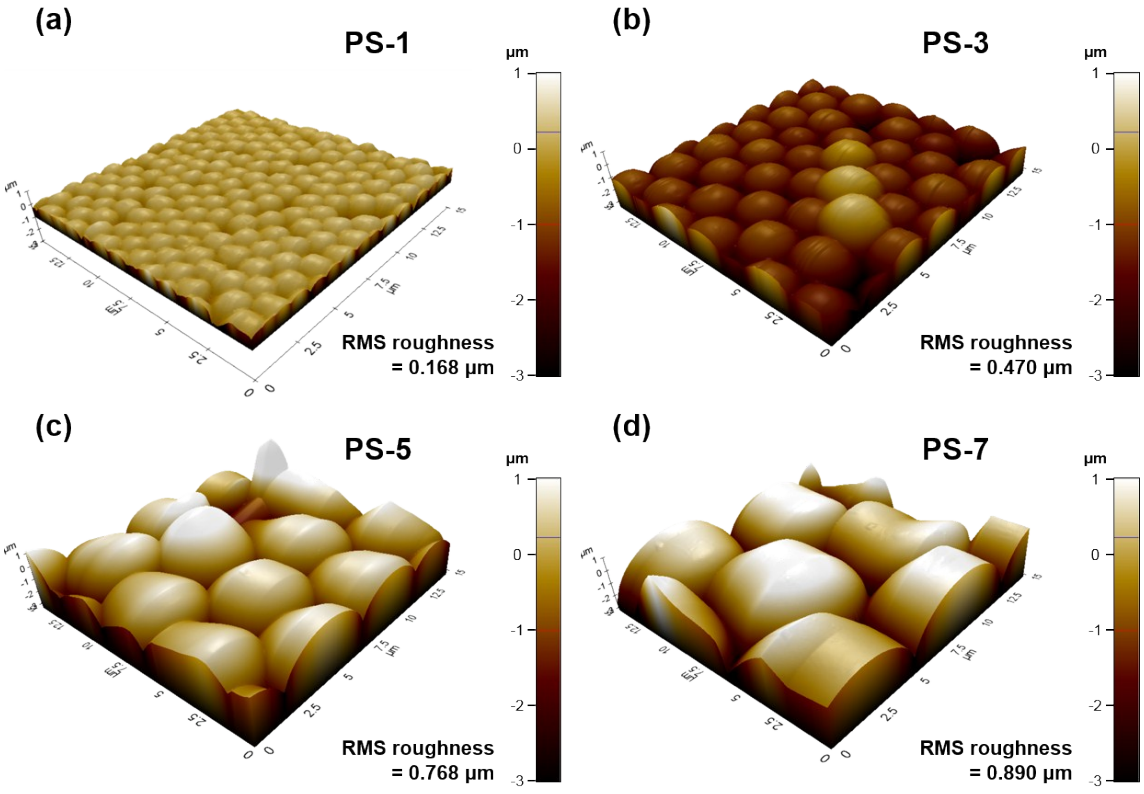

Fig. S5. Three-dimensional AFM images and RMS roughness values of the hexagonally close-packed PS bead arrays with different sizes; (a) 1, (b) 3, (c) 5, and (d) 7 μm, respectively. The scan area and the z-axis scale of (a–d) images are 15 μm × 15 μm and 1 μm to -3 μm, respectively.