Electronic Supplementary Information for

Inkjet printing for direct micropatterning of superhydrophobic surface: toward biomimetic fog harvesting surfaces

Lianbin Zhang,[a] Jinbo Wu,[a] Mohamed Nejib Hedhili,[b] Xiulin Yang[a] and Peng Wang*[a]

a Biological and Environmental Sciences and Engineering Division, Water Desalination and Reuse Center, King Abdullah University of Science and Technology, Thuwal 23955-6900, Saudi Arabia.

E-mail: peng.wang@kaust.edu.sa

b Imaging and Characterization Laboratory, King Abdullah University of Science and Technology, Thuwal 23955-6900, Saudi Arabia.

This file includes Experimental details, Supplementary Fig. S1-S5, and Supplementary reference.

Experimental details:

Superhydrophobic surface preparation on Cu foil substrate. The superhydrophobic surface on Cu foil was obtained by a reported literature method with slight modification.[1] Briefly, the Cu foils were first immersed in a 4 M HCl aqueous solution for 5 seconds to remove surface oxide layer and then washed with copious of ethanol and DI water. Next, the copper foils were incubated in an aqueous solution of 2.5 M NaOH and 0.1 M $(NH_4)_2S_2O_8$ at 4 ˚C for 60 min. Then the blue copper foils were thoroughly washed with water and dried at 180 °C for 2 h to change $Cu(OH)_2$ into stable CuO by completing the dehydration reaction. Finally, the black copper foils were coated with POTS by chemical vapor deposition to obtain superhydrophobic surfaces.

Partial modification of the superhydrophobic substrate by polydopamine. A slide of the as-prepared superhydrophobic glass substrate was partially immersed in a freshly prepared solution of dopamine (5.0 mg mL^{-1}) in tris buffer solution (10 mM, pH 8.5), ethanol, and ethylene glycol at a ratio of 1:1:1 (v:v:v) and then kept in a sealed chamber at 50 ˚C for 36 hours to allow dopamine to polymerize. After polymerization, the substrate was taken out and washed with copious ethanol and dried with nitrogen flow for the following characterizations.

Preparation of rhodamine B labeled PS microspheres. 0.5 mL of PS microsphere suspension (2.5 wt%) was added to 1.0 mL of PEI solution (1.0 mg mL^{-1}) and the mixture was incubated under slight shaking for 1 hour. Afterwards the PS microspheres were separated by centrifugation and washed three times with 1.5 mL of water. The PEI modified PS microspheres were then dispersed well in 1.5 mL of water and 0.5 mL of the above PEI modified PS microsphere dispersion was then taken and mixed with 0.5 mL of water before adding 50 μL of rhodamine B isothiocyanate methanol solution (2 mg mL^{-1}). After incubation for 48 h with slight shaking and subsequent washing with water, the fluorescent rhodamine B labeled PS microspheres were obtained. The fluorescent PS microspheres were finally dispersed in water to a concentration of 2.0 mg mL^{-1}.

Immobilization of rhodamine B on the patterned superhydrophobic surface. The patterned superhydrophobic substrate was immersed in an aqueous solution of rhodamine B (10 μM) for 30 min before being taken out and was then dried with nitrogen flow. Rhodamine B was selectively immobilized on the hydrophilic polydopamine area on the superhydrophobic surface.

Immobilization of rhodamine B labeled PS microspheres on the patterned superhydrophobic surface. Droplets of the aqueous suspension of the PS microspheres with fluorescent label were placed on the superhydrophobic substrate with the superhydrophilic polydopamine patterns. After sitting on the surface for several minutes, the droplets were removed from the surface by using a micropipette. The PS microspheres in the aqueous suspension were absorbed selectively on the hydrophilic patterns.

Supplementary Figures:

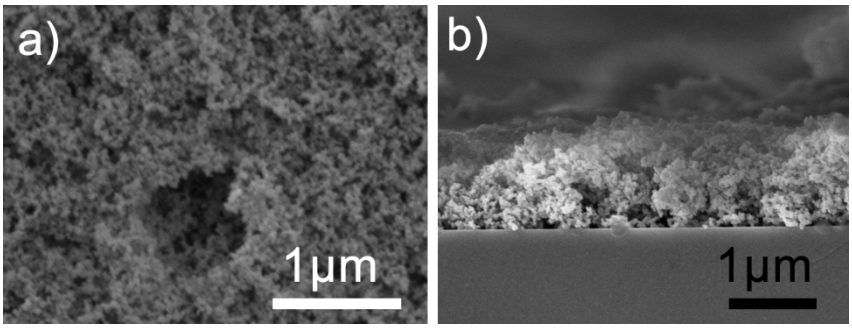

Fig. S1.SEM images of the as-prepared superhydrophobic surface on the glass slide substrate. (a) Top view. (b) cross-sectional view. Due to the deposition of the silica nanoparticle on the surface, a rough surface with highly porous surface structure was obtained on the glass slide substrate. The thickness of the silica-nanoparticles coating was ca. 1.5 μm.

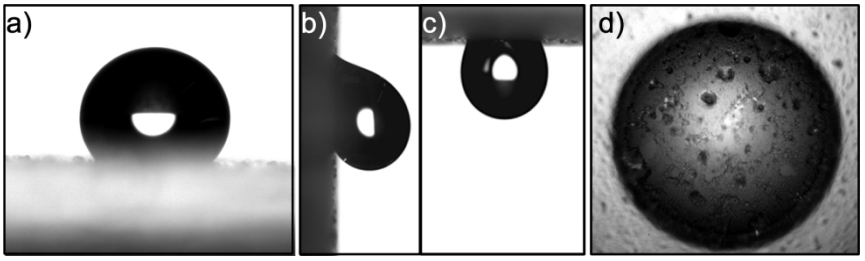

Fig. S2. Shapes of the dopamine solution (5 mg mL^{-1}) droplets prepared by the tri-solvent system (tris buffer solution, ethanol, and ethylene glycol at a ratio of 1:1:1(v:v:v)) on the superhydrophobic surfaces with different tilting angles: (a) tilting angle of 0˚(contact angle was around 128˚), (b) tilting angle of 90˚, and (c) tilting angle of 180˚. (d) Top-view optical image of the interface between the dopamine droplet and the superhydrophobic surface.

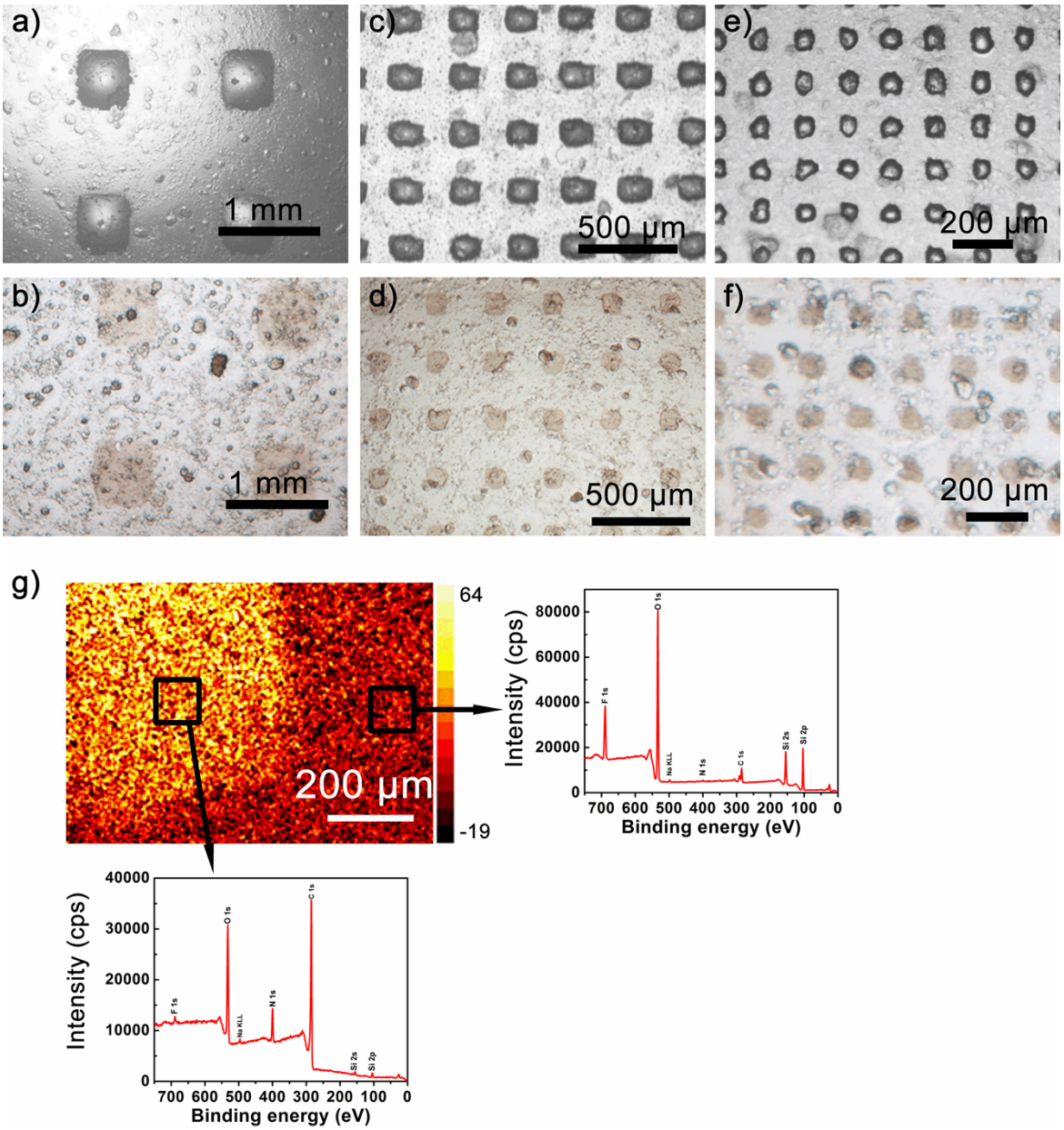

Fig. S3. Optical microscopic photographs of the as-printed dopamine droplet on the superhydrophobic surface: (a) 500 µm pattern, (c) 100 µm pattern, and (e) 50 µm pattern. Optical microscopic photographs of the formed polydopamine patterns on the surface after oxidative polymerization: (b) 500 µm pattern, (d) 100 µm pattern, and (f) 50 µm pattern. (g) Nitrogen mapping of the polydopamine micropattern (500 µm pattern) on the superhydrophobic surface. The XPS image was corrected for inelastic background. The image shows clearly the polydopamine pattern according to the presence of nitrogen signal. Survey spectra with small spot analysis were recorded in two selected area (110 µm×110 µm) of polydopamine modified area and unmodified area. For the unmodified area, Si, C, O, and F elements were observed associated to the superhydrophobic substrate. For polydopamine coated area, additional nitrogen element was observed accompanied with a decrease of F and Si signals.

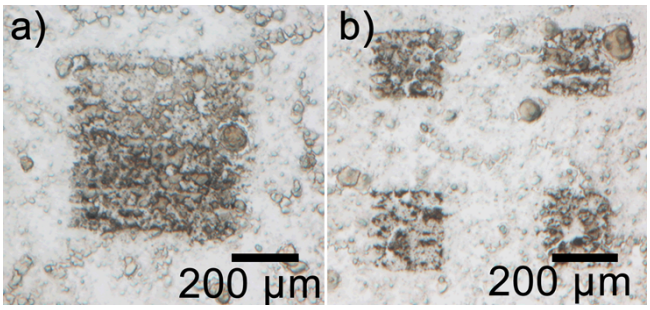

Fig. S4. Optical microscopic photographs of the as-printed dopamine solution (5 mg mL^{-1}) patterns by using tris buffer (10 mM, pH 8.5) and ethanol (1:1, v:v) as the solvents, in the absence of ethylene glycol. (a) 500-μm pattern. (b) 200-μm pattern. Due to the relatively high vapor pressure of water and ethanol, and the small volume of the printed droplets, the droplets evaporated quickly, leaving behind only the solutes on the printed area. The dopamine under this condition could not polymerize well under otherwise the same conditions, and could be easily washed off by water. This result demonstrates the importance of ethylene glycol for the inkjet printing of dopamine solution to obtain superhydrophilic polydopamine patterns.

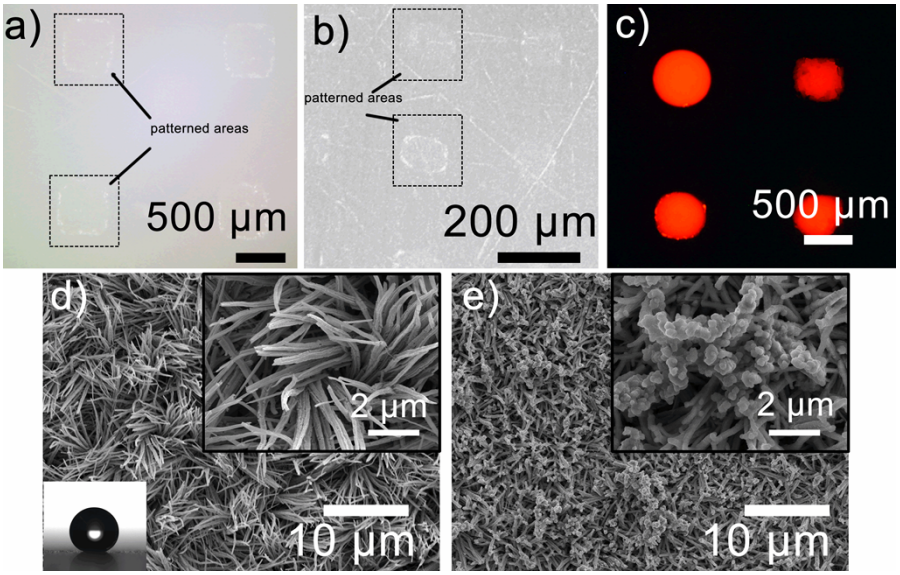

Fig. S5. Optical microscopic photographs of the formed polydopamine patterns on the superhydrophobic Cu substrate by using the same inkjet printing method. (a) 500 μm pattern, (b) 100 μm pattern. For a facilitated observation, some of the polydopamine patterns are outlined. (c) Fluorescent microscopic image of aqueous rhodamine B droplets on the polydopamine patterned superhydrophobic Cu surface (500 μm pattern). It could be found that significant red fluorescence was clearly visible only in the polydopamine patterned area, which confirms that the water droplets, labeled with rhodamine B, attached only on the hydrophilic areas, confirming the successful patterning of the superhydrophobic surface. SEM images of the superhydrophobic Cu surface (d) and the formed polydopamine pattern on the superhydrohobic Cu surface. Insests in (d) and (e) are the magnified view of the surfaces. The superhydrophobic Cu surface consisted of densely distributed CuO nanorods with their length and diameter being 2-4 μm and 200-500 nm, respectively. These nanorod structures on the surface together with the low surface energy of POTS coating on the surface contributed to the superhydrophobic property of the Cu surface. The inset of (d) showed the shape of a water droplet on the superhydrophobic Cu surface with a contact angle of ~157˚. After the polydopamine modification by the inkjet printing method, an increase of the nanorods diameter was observed, which is due to the polydopamine coating formation. Furthermore,

polydopamine nanoparticles with the sizes of ~100-200 nm could also be found at the surfaces. After the polydopamine coating, a superhydrophilic property was resulted at the modified area.

Supplementary reference:

1. J. Feng, Z. Q. Qin and S. H. Yao, *Langmuir*, 2012, **28**, 6067-6075.