# **Electronic Supplementary Information**

# Effect of Lithographically Designed Structures on the Caffeine Sensing Properties of Surface Imprinted Films

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### **EXPERIMENTAL**

### Concave hemisphere-patterned poly(dimethylsiloxane) (PDMS) molds

Highly packed 2-D polystyrene (PS) colloidal arrays ( $d_{PS} = 750$  nm, 2.5 wt% (w/v), Alfa Aesar Co., slightly negatively charged) were fabricated using a previously reported floating/transfer method.<sup>1</sup> After drying for one day, the array was used as a master mold. For the preparation of the PDMS replica, the silicone elastomer and curing agent (10:1 wt. ratio, Sylgard 184, Dow Corning Co.) were vigorously mixed in a beaker. Air bubbles were removed by degassing under vacuum, and the mixture was carefully poured in the PS colloid-arrayed mold placed in a plastic Petri dish. After thermal curing at 60 °C for 2–3 h, a PDMS replica with a concave hemispherical structure was obtained. The sample was then cut to a specific size (2 × 2 cm<sup>2</sup>), rinsed with toluene to remove residual PS colloids, and finally stored in a clean Petri dish.

## Convex hemisphere-patterned PDMS molds

For convex hemispherical patterns, the same PS colloidal array on a planar PDMS was used. SU-8 50 negative photoresist (10  $\mu$ L) (MicroChem Corp.) was carefully spin-coated on the array at a speed of 4000 rpm for 60 s; the thickness of the SU-8 film was then controlled by weight pressure ( $\approx$  90 Pa), before being continuously photo-cured for 10 min using a UV lamp ( $\lambda$  = 370 nm and 36 W, the distance from the substrate: 3 cm) (DR-301C, DR/Bemi). After demolding and rinsing with toluene to remove the PS colloids, the concave hemispherical SU-8 pattern was dried at 60 °C for 2 h and used as a secondary master mold (Fig. S1). Then, the PDMS replica with a convex hemispherical structure was replicated using the same procedure described above.

#### Preparation of the molecularly imprinted polymer (MIP) solutions

For the fabrication of the MIP films, methacrylic acid (MAA, Daejung Chemicals & Metals Co.), ethylene glycol dimethacrylate (EGDMA, Sigma-Aldrich Co.), caffeine (Alfa Aesar Co.), and 2,2'azobis(2-methylpropionitrile) (AIBN, Daejung Chemicals & Metals Co.) were used as functional monomer, cross-linker, template molecule, and photo-initiator, respectively. Various MIP precursor solutions containing caffeine, MAA, and EGDMA were prepared in dimethylformamide (DMF, Tokyo Chemical Industry Co.) (Fig. S2(a)). All the solutions (placed in vials) were sonicated for 30 min, and purged with N<sub>2</sub> for 5 min after adding the AIBN. Then, the solutions were irradiated with UV light ( $\lambda$ = 370 nm, 36 W) for 30 s to increase their viscosity. The non-imprinted polymer (NIP) precursor solutions (no caffeine) were prepared using the same procedure. To investigate the sensing properties, various aqueous solutions (ultra-pure water, 18 M $\Omega$ ·cm) containing caffeine were prepared, and analogous chemicals such as xanthine, theophylline, and theobromine (Sigma-Aldrich Co.) were used to investigate the selectivity of both MIP and NIP films.

#### Concave and convex hemisphere-patterned MIP (cch- and cvh-MIP) films

The fabrication of all poly(MAA-co-EGDMA) MIP sensors was performed using a previously reported method.<sup>2</sup> For both MIP films, an optimized DMF solution (100  $\mu$ L) containing 0.0625 g of caffeine, 0.54 g of MAA, 5.64 g of EGDMA, and 0.072 g of AIBN, was prepared. The fabrication process of the two imprinted films was as follows: 5  $\mu$ L of an imprinting solution was carefully dropped on the structured PDMS molds, and a 9 MHz Au-coated AT-cut quartz crystal (active Au area: 0.196 cm<sup>2</sup>) was carefully placed on it under low pressure, to maintain a well-distributed physical contact between the PDMS and the substrate. Simultaneously, UV-initiated polymerization was carried out for ~7–8 min. After demolding, all the MIP films were dried at 60 °C for 2–3 h to remove residual solvent and complete the polymerization.

#### **Characteristics**

For a quantitative analysis of the caffeine rebinding process, the resonant frequency shift during caffeine sensing was monitored *in situ* under various conditions (including different caffeine concentrations, two structured MIP films, and analogous chemicals) using a quartz crystal analyzer (QCA 922 analytical instrument, Seiko EG&G Co.). Field-emission scanning electron microscopy (FE-SEM, S-4800, Hitachi, Ltd) was used to investigate the surface topography of the SU-8 replicas and two structured MIP films. In addition, a non-contact mode of atomic-force microscopy (AFM, NX20, Park Systems) was used to measure the dimensions of the *cch*- and *cvh*-MIP films. Fourier transform infrared spectroscopy (FT-IR-4100) with attenuated total reflectance (PRO450-S, Jasco), and X-ray

photoelectron spectroscopy (Quantera SXM, ULVAC-PHI) with an Al-K $\alpha$  X-ray source (15 kV, 25 W, depth profiling, 2 kV) were used to monitor the removal of imprinted caffeine molecules from the *cch*- and *cvh*-MIP films.



Fig. S1. Fabrication process of the *cch*-PDMS mold using colloidal lithography.



**Fig. S2**. (a) Summary of various MIP precursor solutions for the poly(MAA-*co*-EGDMA) films containing caffeine molecules, (b) photograph of the corresponding spin-coated films and solutions, (c) SEM images of the *cvh*-MIP films prepared using PDMS molds with concave hemispherical patterns and different MIP solutions, and (d) resonant frequency shift as a function of time for the *cvh*-MIP films during a sensing period of 60 min. Increasing concentration (C-5 > 70 mg) causes the aggregation of caffeine in the solution, resulting in a relatively lower frequency shift compared to C-4. In addition, regardless of the concentration variation of the precursor mixture, the geometry (diameter and height) of the *cvh*-MIP films was almost identical.



Fig. S3. AFM images and line profilometries for the (a) cvh- and (b) cch-MIP films.



**Fig. S4**. FT-IR spectra for the non-imprinted (NIP), caffeine-imprinted MIP, and caffeine-extracted MIP films. The imprinted planar MIP (or NIP) film was fabricated using a MIP precursor solution containing 0.0242 g of caffeine, 0.09 g of MAA, 1 g of EGDMA, and 0.041 g of AIBN in 1 mL of DMF.



**Fig. S5**. XPS spectra for the (a) caffeine-imprinted MIP, and (b, c) caffeine-extracted MIP films (*cvh*-MIP film) (3 and 10 h of extraction, respectively).



**Fig. S6**. Sensor response for the surface-imprinted *cch*- and *cvh*-MIP films fabricated using a 100  $\mu$ L DMF solution containing 0.0625 g of caffeine, 0.54 g of MAA, 5.64 g of EGDMA, and 0.072 g of AIBN: resistance variation as a function of time for a 1 mg mL<sup>-1</sup> aqueous solution of caffeine during the caffeine rebinding process.



**Fig. S7**. Resonant frequency shift as a function of time for the *cch*- and *cvh*-MIP (or NIP) films with various caffeine concentrations ( $10^{-6}$ –1 mg mL<sup>-1</sup> in H<sub>2</sub>O). The surface-imprinted *cch*- and *cvh*-MIP (or NIP) films were fabricated using a 100 µL DMF solution containing 0.54 g of MAA, 5.64 g of EGDMA, 0.072 g of AIBN, and 0.0625 g of caffeine (or no caffeine).



**Fig. S8**. Resonant frequency shift as a function of time for sensing of various target molecules (individual caffeine, theobromine, theophylline, and xanthine solutions; mixture of three analogues (theobromine, theophylline, and xanthine), and mixture of all chemicals (caffeine, theobromine, theophylline, and xanthine) for the surface-imprinted *cch*-MIP and *cvh*-MIP films.

<sup>&</sup>lt;sup>1</sup> (a) J. M. Kim, U. –H. Lee, S. –M. Chang and J. Y. Park, *Sens. Actuators B*, 2014, **200**, 25; (b) J. M. Kim, J. C. Yang and J. Y. Park, *Sens. Actuators B*, 2015, **206**, 50.

<sup>&</sup>lt;sup>2</sup> (a) J. C. Yang, H. –K. Shin, S. W. Hong and J. Y. Park, *Sens. Actuators B*, 2015, **216**, 476; (b) J. C. Yang and J. Y. Park, *ACS Appl. Mater. Interfaces*, 2016, **8**, 7381.