Electronic Supplementary Information (ESI)

Facile synthesis of self-aligned gold nanoparticles by crack templated reduction lithography

Min-Cheol Lim,[a] Sae-Hyung Kim,[b] Kisang Park,[ab] Young-Rok Kim,[c] Jae-Ho Kim,[b] Gyeongsik Ok[a] and Sung-Wook Choi*[a]

[a] *Food Safety Research Group, Korea Food Research Institute, Sungnam 13539, Korea*

[b] *Department of Molecular Science and Technology, Ajou University, Suwon 16499, Korea*

[c] *Graduate School of Biotechnology & Department of Food Science and Biotechnology, Kyung Hee University, Yongin 17104, Korea*

* Corresponding author. Tel:+82-31-780-9327

Fax:+82-31-709-9876 E-mail address: *swchoi@kfri.re.kr*

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Materials:

The gold precursor, $HAuCl_4$, was purchased from Sigma-Aldrich (St. Louis, MO, USA). Polydimethoxysiloxane (PDMS, Sylgard 184) including monomer and curing agent with a molecular weight of ~60,000 was purchased from Dow Corning (Midland, MI, USA). All reagent solutions were prepared with doubly distilled water filtered through a 0.2 μm cellulose acetate membrane filter (Whatman, Dassel, Germany).

Fabrication of crack patterns on PDMS substrate:

A mixed solution (20 mL) of the PDMS monomer and curing agent (5:1 (w/w)) was degassed for 30 min in a vacuum desiccator and poured into a petri dish (9.5 cm in diameter). To cure the PDMS, the petri dish and its contents were placed in an oven at 70°C for 6 hr. The PDMS was peeled off and cut for use. A 1.0 cm (W) × 5.0 cm (L) piece of PDMS substrate with a thickness of 3.0 mm was used as the elastomeric substrate in all experiments. A freshly prepared PDMS mixture (5:1 (w/w)) was poured onto the cured PDMS substrate and spread using a glass slide to fabricate the patterned cracks. The contents of curing agent in PDMS mixture was chosen to maximize the formation of gold NPs from the published report earlier.[1] The thickness of the liquid PDMS on the elastomeric substrate was measured by FE-SEM (LEO SUORA 55, GENESIS 2000, Carl Zeiss, Jena, Germany) after curing at 70°C for 6 hr. Prior to forming the crack patterns, elastomeric substrate covered with liquid PDMS was treated with oxygen plasma to form a stiff layer on top of the liquid PDMS. The prepared PDMS substrate was treated with oxygen plasma (50 W) for 2 min under 10 mTorr using a plasma system (CUTE, Femto Science, Seoul, Korea). The generated stiff layer was transferred to a glass substrate, and the thickness was measured by AFM (XE-70, Park Systems, Suwon, Korea). After oxygen plasma, cracks were generated by wrapping the

PDMS substrate around a cylindrical support with a 15 mm diameter and then placed on a glass slide to prevent the generation of additional, undesired cracks.

In situ synthesis of the gold NPs in cracked regions:

To synthesize gold NPs in the cracked regions, the oxygen-plasma-treated and banded PDMS substrate described above was immersed in 50 mL of 10 mM $HAuCl_4$ solution and incubated at room temperature for 6 hr. Then, the substrate was washed with doubly distilled and filtered water and blown dry with nitrogen. The sample was placed in the oven at 70°C for 1 hr to cure the liquid PDMS on the top of the substrate. The prepared samples were then stored in a vacuum desiccator until further investigation.

Characterization:

The crack patterned gold NP arrays were examined with an optical microscope (Eclipse 80i, Nikon, Tokyo, Japan) equipped with a digital camera (DXM 1200F, Nikon, Tokyo, Japan). The synthesized gold NP arrays were examined by SEM (LEO SUORA 55, GENESIS 2000, Carl Zeiss, Jena, Germany) and samples were not sputter coated with a metal layer prior to examination. The morphologies of synthesized gold NP arrays were examined by AFM (XE-70, Park Systems, Suwon, Korea). UV-visible spectra were recorded before and after the *in situ* synthesis of the gold NPs using a V-670 spectrophotometer (Jasco, Tokyo, Japan).

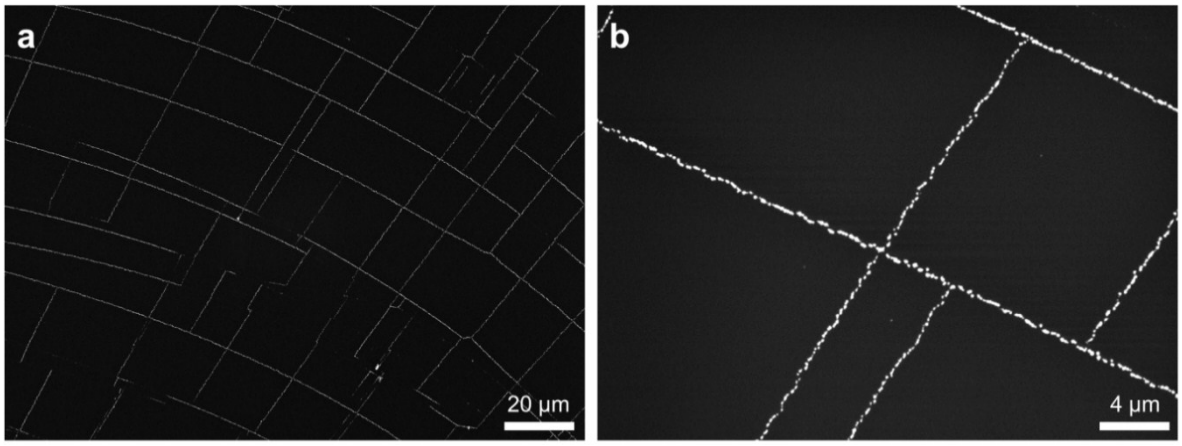

Figure S1. Morphology of the gold NP arrays produced by CTRL without the liquid PDMS layer. (a) SEM image of gold NP arrays on a PDMS substrate. (b) Magnified SEM image of gold NP arrays on a PDMS substrate.

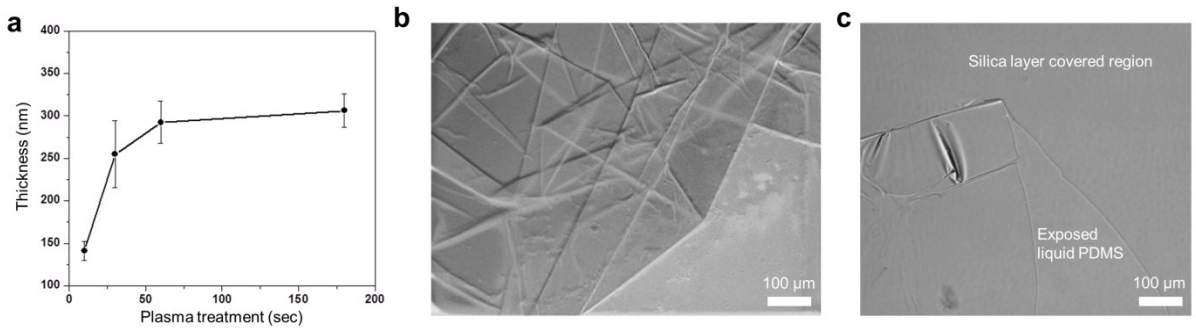

Figure S2. Characterization of produced silica layer by plasma treatment. (a) The thickness of the silica layer produced by oxygen plasma, as measured by AFM after transferring the formed layer onto a flat solid surface. (b) The solidified PDMS layer produced by oxygen plasma treatment and observed by SEM after being transferred onto a glass slide. (c) The liquid PDMS regions exposed by cracking on the thicker liquid PDMS after oxygen plasma and bending.

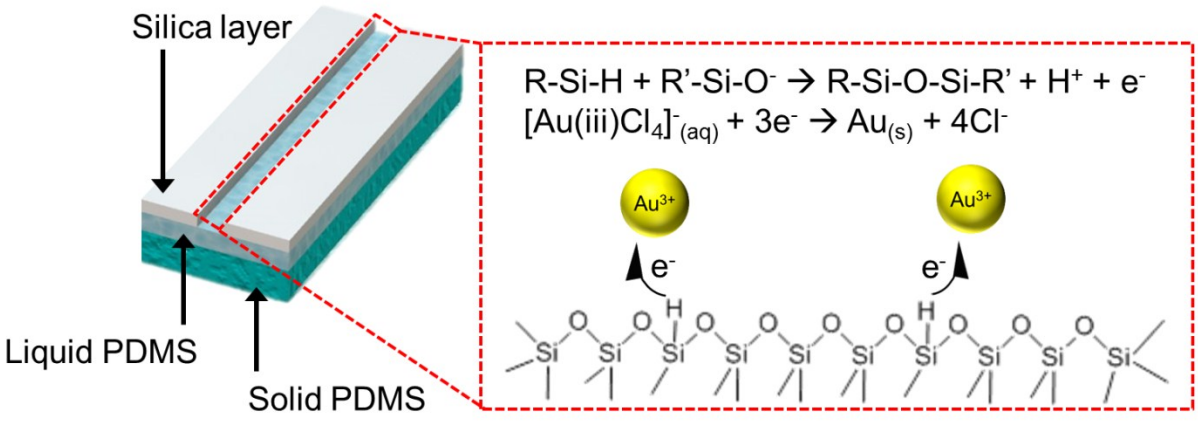

Figure S3. Schematic illustration of gold NP formation mechanism in the crack patterns.

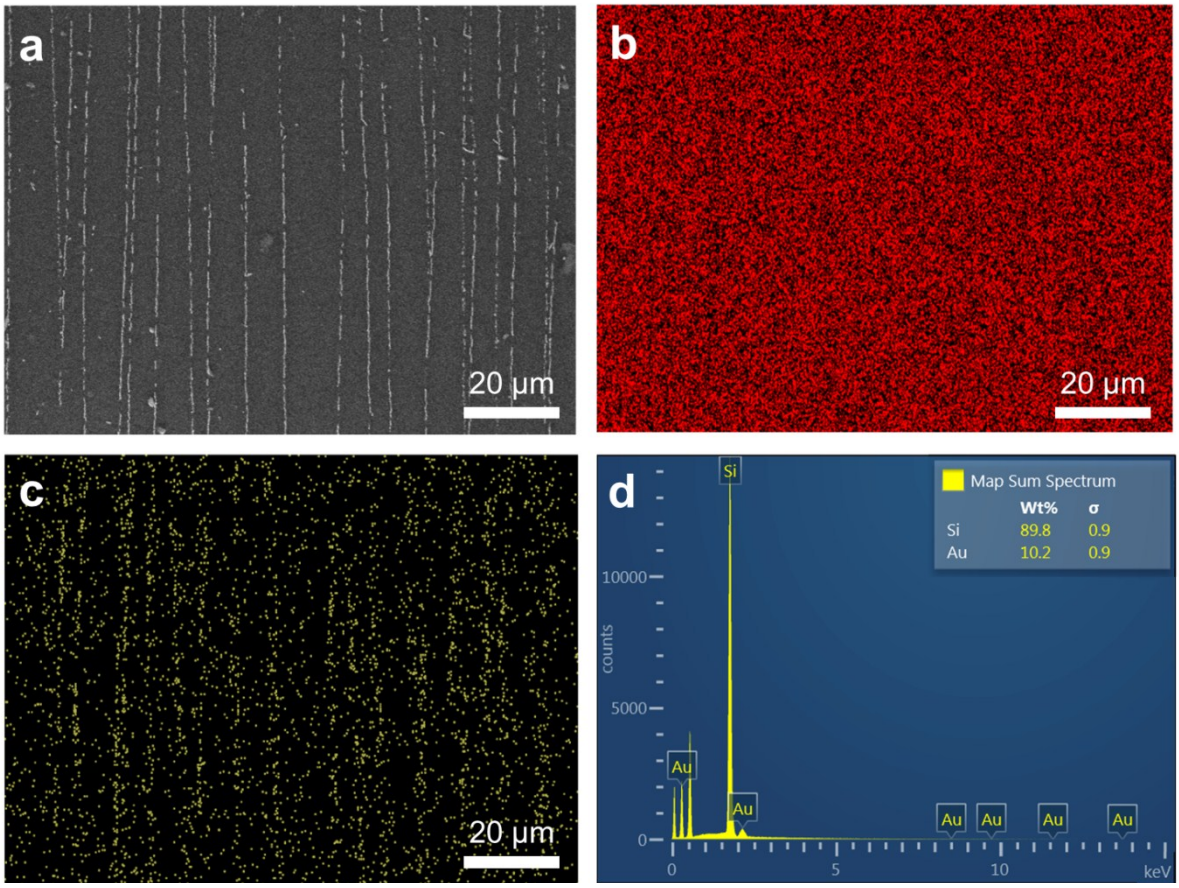

Figure S4. Elemental mapping by SEM-EDS of gold NP arrays prepared on PDMS by SEM-EDS. (a) Electron image of gold NP arrays on PDMS. (b) Si Kα1 mapping of the corresponding electron image. (c) Au M α1 mapping of the corresponding electron image. (d) EDS spectrum of the whole area shown in the electron image.

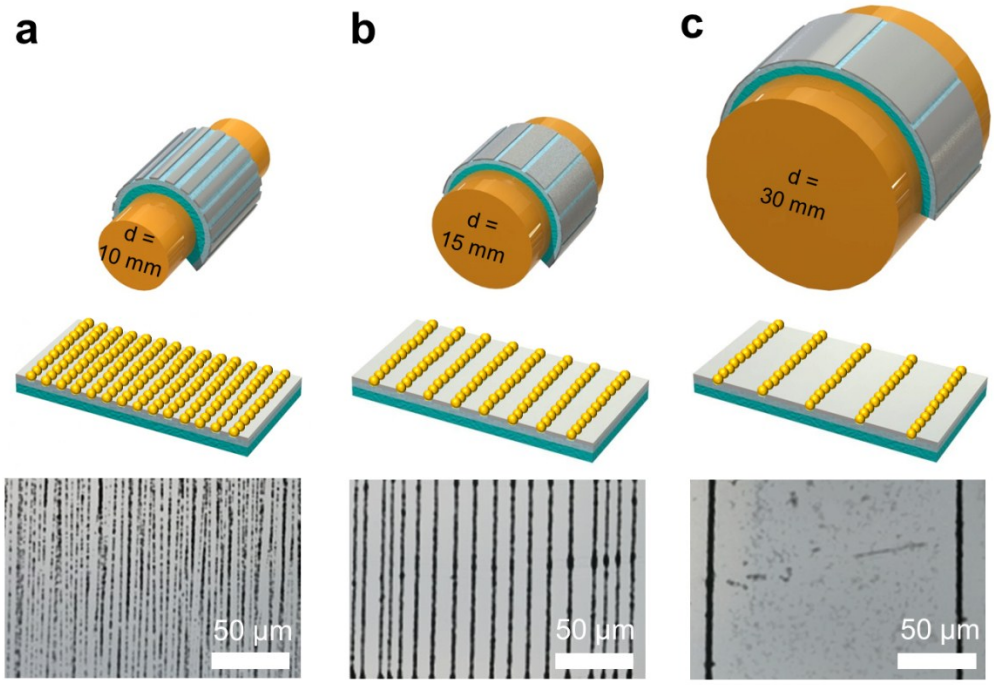

Figure S5. Periodicity of the produced gold NP arrays. Cylindrical supports with diameters of (a) 10 mm, (b) 15 mm and (C) 30 mm were used to bend the oxygen-plasma-treated PDMS substrate.

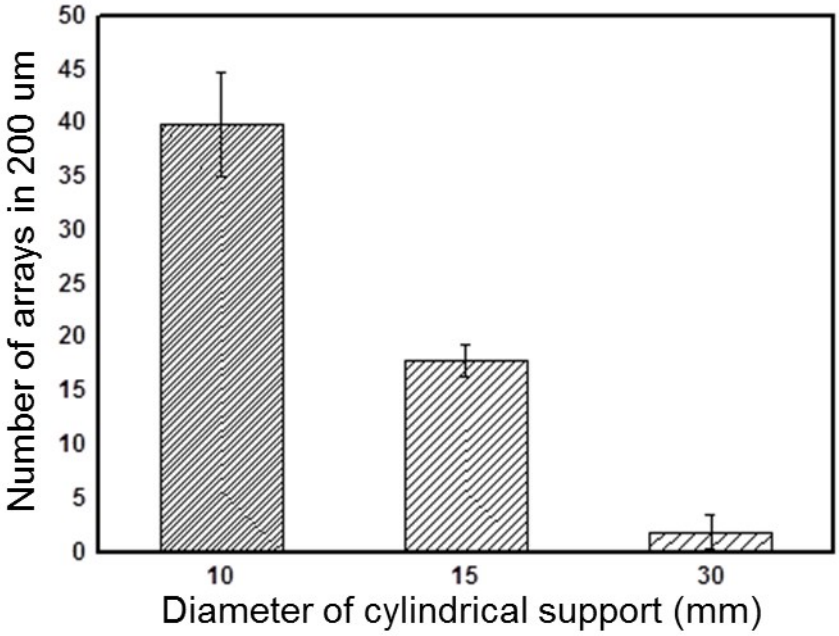

Figure S6. Number of arrays on the PDMS substrate depending on the diameter of used cylindrical support.

References

1. Q. Zhang, J.-J. Xu, Y. Liu and H.-Y. Chen, *Lab on a Chip*, 2008, **8**, 352-357.