Supporting information

Intrinsic Hydrophobic Cairn-like Multilayer Films for Anti-Bacterial Effect with Enhanced Durability

Hyejoong Jeong[a], *Jiwoong Heo*[a], *Boram Son*[b], *Daheui Choi*[a], *Tai hyun Park*[b], *Minwook Chang*[c] *and Jinkee Hong*[a,]*

[a] School of Chemical Engineering and Material Science, Chung-Ang University, 84 Heukseok-ro, Dongjak-gu, Seoul 06974, Republic of Korea

[b] School of Chemical and Biological Engineering, Seoul National University, 1 Gwanak-ro , Gwanak-gu, Seoul 08826, Republic of Korea,

Advanced Institutes of Convergence Technology, 145 Gwanggyo-ro, Yeongtong-gu, Suwon-si, Gyeonggi-do 16229, Republic of Korea

[c] Department of Ophthalmology, Dongguk University Ilsan hospital, 27 Dongguk-ro, Ilsandong-gu, Goyang-si, Gyeonggi-do 10326, Republic of Korea

* E-MAIL: jkhong@cau.ac.kr

Supporting Information Figure S1

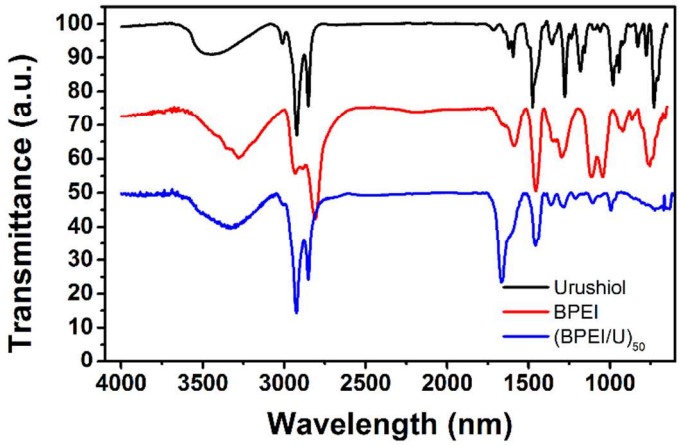

Figure S1. FT-IR spectra of urushiol (black line), BPEI (red line) and $(BPEI/U)_{50}$ film (Blue line).

We analyzed intact materials (urushiol, BPEI) by ATR mode of FT-IR and $(BPEI/U)_{50}$ prepared onto wafer by FT-IR. Phenolic hydroxyl group of urushiol is indicated broad peak at 3450 cm^{-1} and amine groups of BPEI is presented peak at 3280 cm^{-1}. In the spectrum of $(BPEI/U)_{50}$ film, the broad peak shifted to lower wavenumber at 3330 cm^{-1} due to the reduction of OH vibrational frequency. Generally, formation of intermolecular hydrogen bonding induces increase of IR adsorption intensity and decrease of OH vibrational frequency[1]. In this result, we determined that urushol and BPEI are interacted with hydrogen bonding.

Supporting Information Figure S2

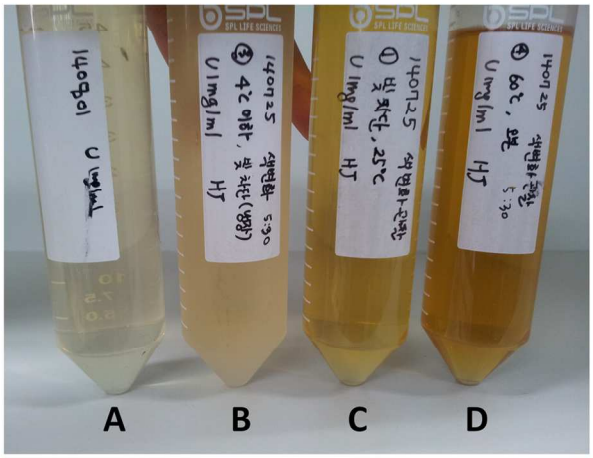

Figure S2. Color change of as-prepared urushiol solutions. (A) shortly after preparation, (B, C, D) elapsed 7 days from preparation; (B) stored in the refrigerator(dark, 4℃), (C) stored in the dark, (D) stored in the oven(dark, 60℃)

Self-oxidation of urushiol changed solution's color to deep yellow and the promotive factor is temperature. It could be induced mild polymerization of urushiol.

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Supporting Information Figure S3

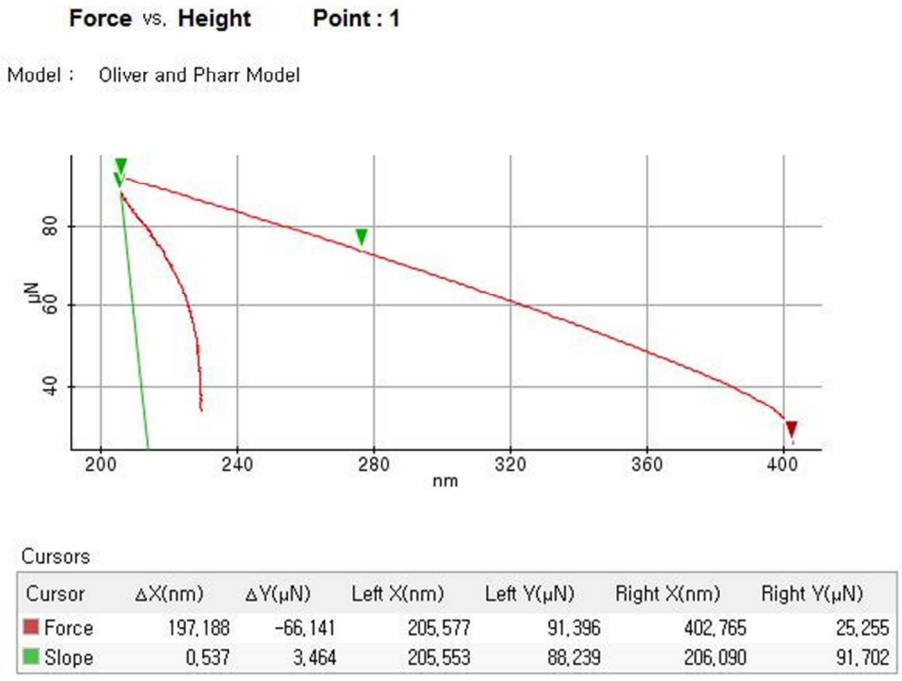

Figure S3. Hardness and Young's modulus measured by the AFM in nanoindentation mode, and calculated by the XEI software (Park Systems, Inc.).

The hardness (H) was measured with a Berkovich-type diamond tip and obtained from equation (1) as shown below.

$$\mathrm{H} = \frac{P_{max}}{A_r} \qquad (1)$$

P_{max} is the maximum load and Ar is the indentation area. In the case of a perfect Berkovich indentor, Ar is $24.5h^2$ where h is the penetration depth. Hardness is inversely proportional to the square of penetration depth. Young's modulus was calculated by XEI software (Park Systems) based on the Oliver-Pharr nonlinear curve fit method[2].

Supporting Information Figure S4

$(BPEI/U)_{5.5}$ multilayer films are approximately 100 nm in thickness, and their outermost layer is BPEI in order to enhance the biocompatibility of the film. Figure S2 shows the average cell viability after 24 hours cultivation; the $(BPEI/U)_{5.5}$ multilayer films had a positive effect on the cells and presented higher cell viability in comparison with the control (156.9%). The urushiol that we used for this study had a low concentration (1 mg/mL); moreover, an even smaller amount was incorporated into the multilayer thin films. From the QCM results in figure 2B, it can be seen that the urushiol mass content was approximately 1.98 μg per layer(Diameter of the electrode was 13.4 mm) and 10 μg was incorporated in the 5 layers. BPEI was incorporated at 1.58 μg per layer, and the outermost layer was capable of helping the growth of cells. Thus, we demonstrated that the nanoscale urushiol thin films have no cytotoxicity effect and are safe for biological applications. Urushiol is known to be slightly toxic, and can cause allergic skin reactions, but the toxicity can be removed through simple methods such as oxidation, UV irradiation and annealing. However, in this study, we did not need to use any special method to remove the toxicity. Urushiol based thin film prepared in this report shown acceptable biocompatibility for biological applications.

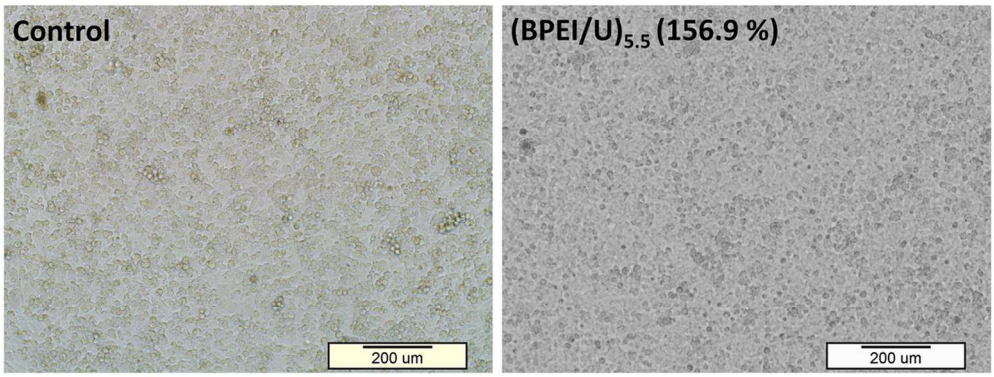

Figure S4. Morphology of the cultured HeLa cells on $(BPEI/U)_{5.5}$ multilayer films on the glass substrate, compared to those on a control sample, which was bare glass cleaned by the RCA treatment

(negative control). The cell viability was tested for 24h, and repeated four times. Control cells were compared with the cells cultured on the $(BPEI/U)_{5.5}$ multilayer films.

(1) Mitsuzuka, A.; Fujii, A.; Ebata, T.; Mikami, N., Infrared Spectroscopy of Intramolecular Hydrogen-Bonded OH Stretching Vibrations in Jet-Cooled Methyl Salicylate and Its Clusters. *J. Phys. Chem. A* **1998**, 102, 9779-9784.

(2) Oliver, W. C.; Pharr, G. M., Measurement of Hardness and Elastic Modulus by Instrumented Indentation: Advances in Understanding and Refinements to Methodology. *J. Mater. Res.* **2004**, 19, 3-20.