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Supporting information for

RIR-MAPLE Deposition of Multifunctional Films Combining Biocidal and Fouling Release Properties

Qian Yu,[a#] Wangyao Ge,[b#] Ayomide Atewologun,[b] Gabriel P. López[acd*]

and Adrienne D. Stiff-Roberts[bd*]

[a] Department of Biomedical Engineering, Duke University, Durham, NC, 27708, USA.

[b] Department of Electrical and Computer Engineering, Duke University, Durham, NC, 27708, USA.

[c] Department of Mechanical Engineering and Materials Science, Duke University, Durham, NC, 27708, USA.

[d] NSF Research Triangle Materials Research Science & Engineering Center, Duke University, Durham, NC, 27708, USA.

# These authors contributed equally.

Email: adrienne.stiffroberts@duke.edu; gabriel.lopez@duke.edu

1. Surface morphology of PNIPAAm films prepared by different methods

The surface morphology of PNIPAAm films prepared by RIR-MAPLE and surface initiated polymerization (SIP) was examined by atomic force microscopy (AFM). As shown in **Figure S1**, PNIPAAm film deposited by RIR-MAPLE exhibits large domain features, which might be due to the aggregation of polymers. In contrast, the PNIPAAm film prepared by SIP is much smoother. The root-mean-squared (RMS) surface roughness values of these two films are 10.7 nm and 0.8 nm, respectively. It is well accepted that surface topography and roughness play a crucial role in liquid spreading on a solid surface.[1] Based on the Wenzel model, for a homogeneous hydrophilic surface

(contact angle less than 90°), increase of surface roughness usually results in decrease of contact angle.[2] Therefore, the increased surface roughness might be the main reason that the water contact angle of PNIPAAm film deposited by RIR-MAPLE is much lower water contact angle compared with that of PNIPAAm film prepared by SIP (~20° *vs.* ~60°).

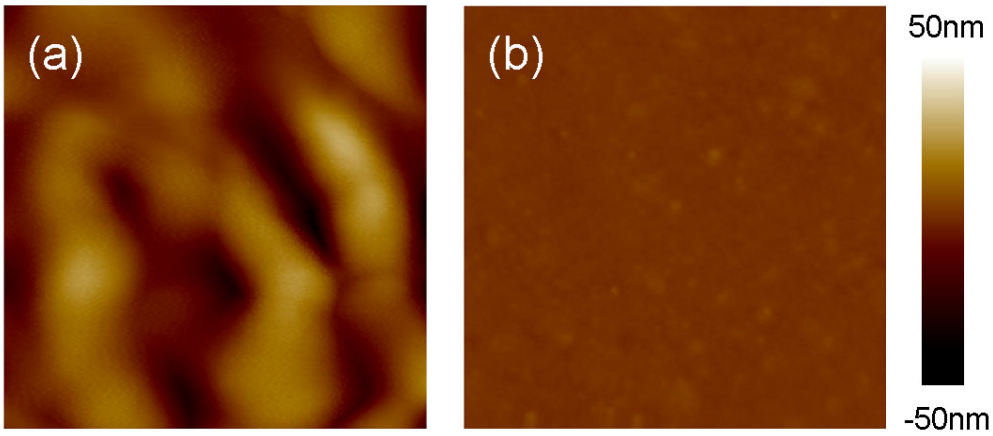

Figure S1. Tapping mode AFM height images obtained in air of PNIPAAm film deposited by RIR-MAPLE (a) and prepared by SIP (b). These two films showed similar thickness of ~ 100 nm. The size of images is 1×1μm.

2. Confirmation of chemical integrity of films deposited by RIR-MAPLE

PNIPAAm and QAS films deposited by RIR-MAPLE and drop-casting were examined by Fourier transform infrared (FTIR) spectroscopy (**Figure S2**). The positions of FTIR absorption peaks were almost identical for the films deposited by both methods. It is noted that there are two, new small peaks at 1170 cm^{-1} and 790 cm^{-1} (Si-O-Si) in the QAS film depsoited by RIR-MAPLE. These peaks are attributed to the reaction of the silane groups of QAS with water during target preparation; however, such a reaction has no impact on the biocidal function of the QAS and the change in the FTIR spectrum does not result from the laser-material interaction. The slight differencesin peak intensity observed

between the films deposited by the two methods result from variations in film thickness and/or atmospheric conditions (e.g., humidity) and are not related to RIR-MAPLE deposition. Therefore, these data indicated that no significant chemical degradation occurred during RIR-MAPLE deposition.

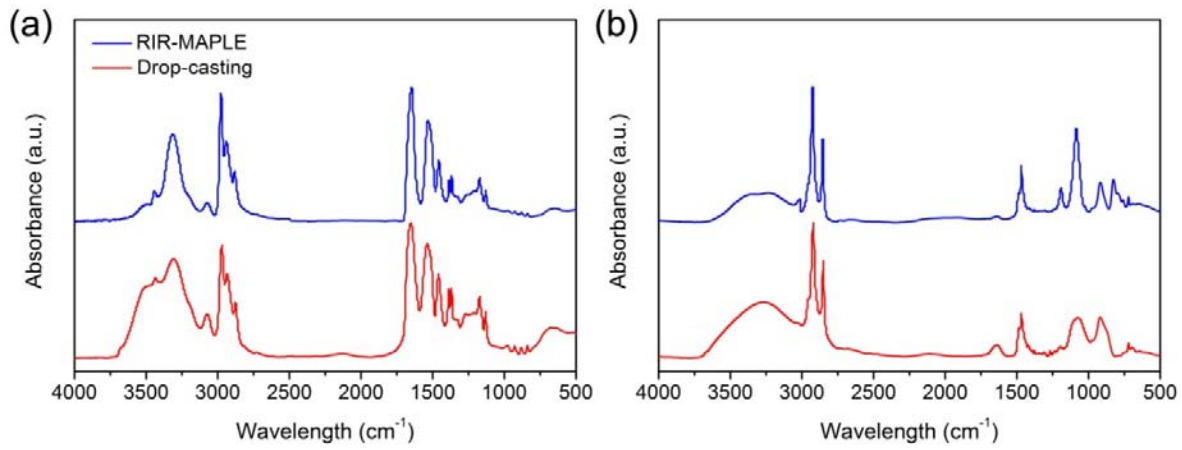

Figure S2. Comparisons of FTIR spectra of (a) PNIPAAm and (b) QAS deposited by RIR-MAPLE and drop casting.

3. Effect of incubation temperature on killing efficacy

We examined the effect of temperature on killing efficiency of the sample films, which were incubated in suspensions of *E. coli* or *S. epidermidis* at 37°C or 25°C for 2 h (**Figure S3**). The PNIPAAm/QAS hybrid films exhibited more effective killing efficiency at 37°C than those at 25°C ((79.7±6.1%*vs.* 51.3±3.3% for *E. coli* and 86.7±6.0% *vs.* 18.8±4.5% for *S. epidermidis*). In contrast, for the control films (QAS and PNIPAAm), the killing efficiency was similar at both 37°C and 25°C.

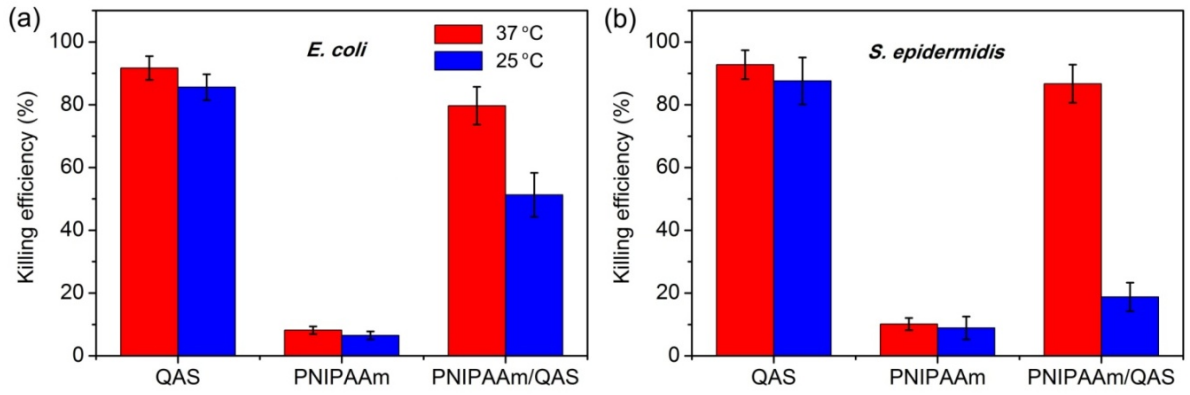

Figure S3. Killing efficiency of sample films against (a) *E. coli* and (b) *S. epidermidis* at different temperatures. The surfaces were incubated in suspensions of *E. coli* and *S. epidermidis* at 37°C or 25°C for 2 h. The killing efficiency was defined as the ratio of amount of dead bacteria and amount of total bacteria attached on these three surfaces at 37°C and 25°C. Error bars represent the standard deviation of the mean (n=3).

4. Stability of PNIPAAm containing films in aqueous solution

To test the stability of sample films deposited by RIR-MAPLE in water, we incubated the films in water at either 37°C or 25°C for 3 h and then examined the changes of the surface properties. As shown in **Figure S4**, there are no significant differences in film thickness and C/N ratio for QAS films, suggesting these films are relatively stable in water at all temperatures used in this study, which might be due to the strong hydrophobicity of QAS. In contrast, both PNIPAAm films and PNIPAAm/QAS films exhibited a significant decrease in film thickness after incubation in water at 25°C, indicating at least the partial dissolution of PNIPAAm into water. The dissolution of PNIPAAm was further probed by tapping mode AFM, in which obvious changes in the phase images were observed after incubation in water at 25°C (**Figure S5**).

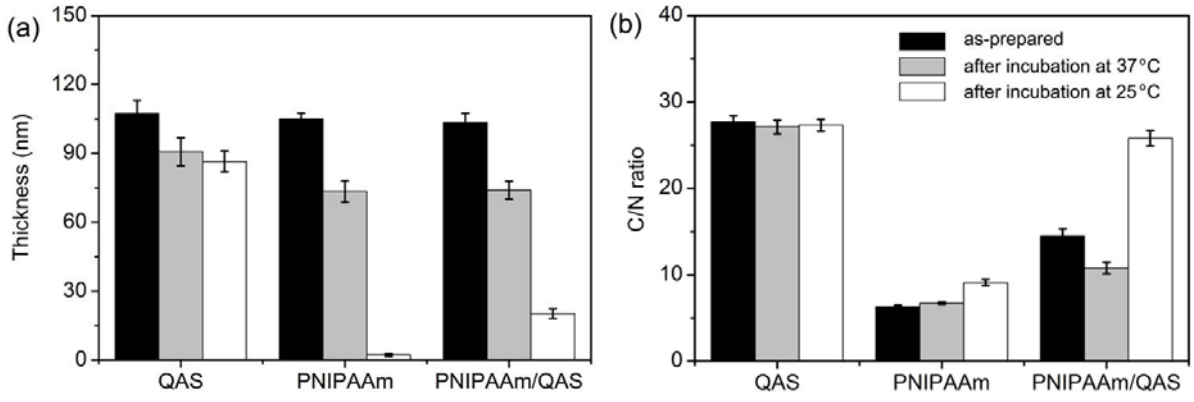

Figure S4. Changes of (a) film thickness and (b) surface chemical composition (C/N ratio) of sample films before and after incubation in water at different temperatures. Data consist of the mean ± standard error (n=3).

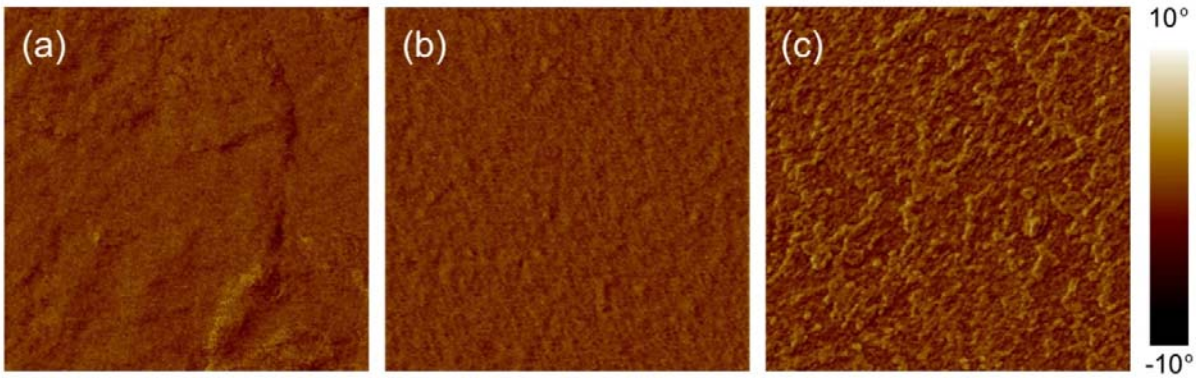

Figure S5. Tapping mode AFM phase images obtained in air of PNIPAAm/QAS film before (a) and after incubation in water at 37°C (b) or 25°C (c) for 3 h. The size of images is 1×1μm.

5. Effect of film thickness on surface properties

Three PNIPAAm/QAS hybrid films with different thickness (from ~10.3 nm to ~103.4 nm) were prepared by adjusting the deposition time during RIR-MAPLE growth. As shown in **Figure S6**, there are no significant differences in either killing efficiency or release ratio among these three PNIPAAm/QAS

hybrid films. Considering that the surface wettability is also similar for these films ($p>0.05$, **SI, Figure S7**), we assume that the topmost layer of PNIPAAm/QAS hybrid films is independent of thickness. This thickness-independent surface morphology is related to the nature of the deposition process in RIR-MAPLE, where the film is deposited continuously under the same condition.

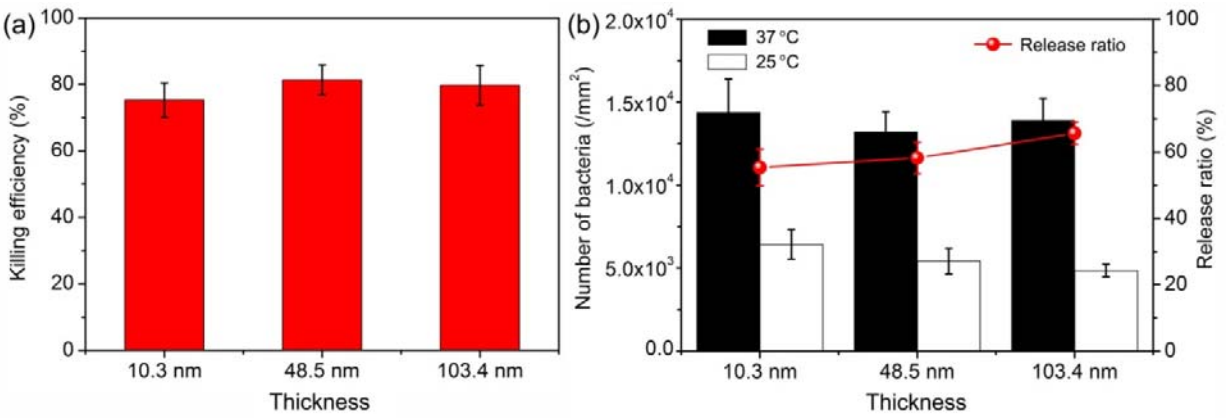

Figure S6. Comparison of (a) killing efficiency and (b) attachment and detachment of bacteria on PNIPAAm/QAS hybrid films with different film thickness. The surfaces were incubated in suspensions of *E. coli* at 37°C for 2 h and the average number of adhered cells was determined. Then the surfaces were rinsed with 0.85% NaCl solution and ultrapure water at 25°C and the remaining cells were counted. The bacterial release ratio is also shown. Error bars represent the standard deviation of the mean (n=3).

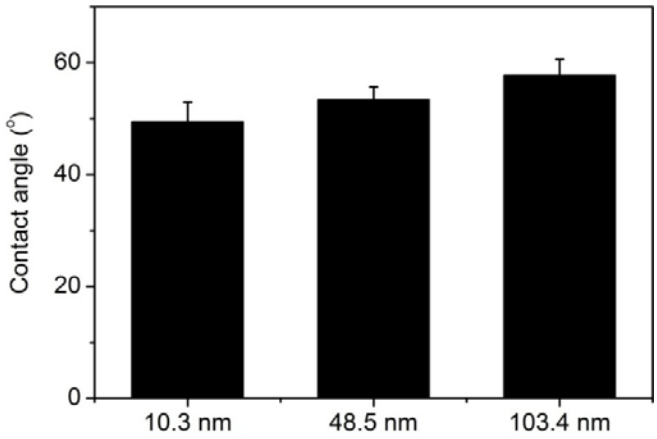

Figure S7. Comparison of water contact angle of PNIPAAm/QAS hybrid films with different film

thickness. Error bars represent the standard deviation of the mean (n=3). According to the result of t-test, the difference is insignificant ($p>0.05$).

6. Enhancement of stability by introduction of APTES

To test the stability of PNIPAAm/QAS/APTES ternary films deposited by RIR-MAPLE in water, we incubated these films in water at 25°C for either 2 h or 24 h and then examined the changes of the surface properties. As shown in **Figure S8**, there are no significant changes in film thickness and surface wettability of this hybrid film before and after incubation in cold water, suggesting the incorporation of APTES indeed increases the stability of the hybrid film.

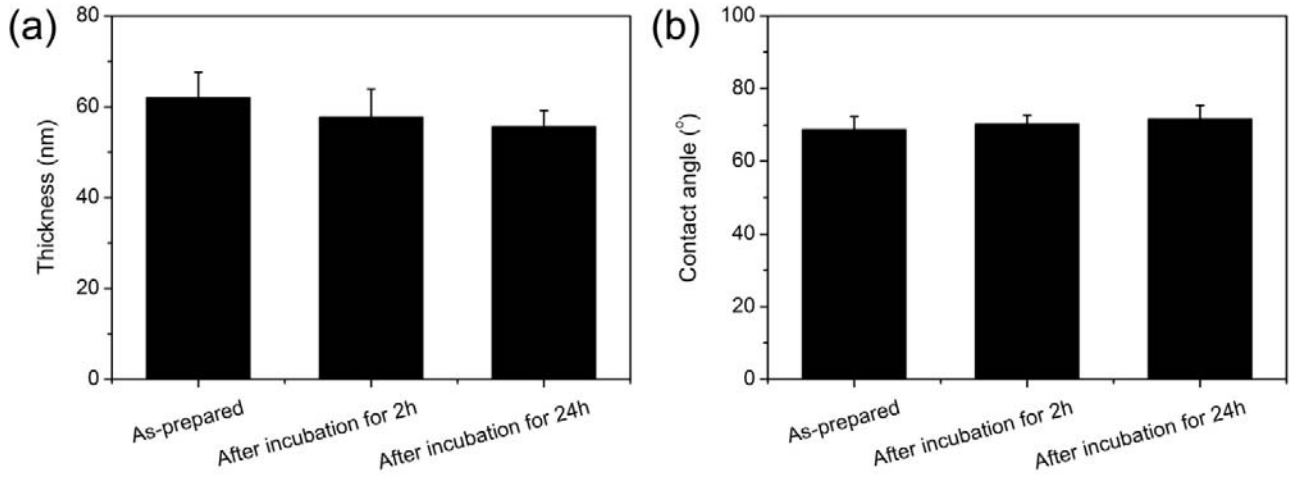

Figure S8. Changes of (a) film thickness and (b) water contact angle of PNIPAAm/QAS/APTES films before and after incubation in water at 25°C for different time periods. Data consist of the mean ± standard error (n=3).

References

1. Qurere, D. *Annu. Rev. Mater. Res.* **2008**, *38*, 71.

2. Wenzel, R. N. *Ind. Eng. Chem.* **1936**, *28*, 988