Bio-inspired Silicon Nanospikes Fabricated by Metal-Assisted Chemical Etching for Antibacterial Applications

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Antibacterial surfaces have wide applications in implanted medical devices and the textile industry. Recent studies have discovered that the wings of Cicada and dragon flies have nanopillars that can penetrate bacterial cells and are naturally evolved bactericidal surfaces [1]. Following this discovery, various nanofabrication methods have been used to fabricate bioinspired antibacterial surfaces such as reactive ion etching [2] and glancing angle deposition [3]. These two methods both require the use of expensive equipment and vacuum, hindering the practical application of antibacterial surfaces.

In this paper, we present the results of efficient killing of the bacteria *E. coli* on silicon nanospike surfaces fabricated using a low-cost metal-assisted chemical etching (MacEtch) approach. Moreover, we studied the influence of etching time to the morphology of the silicon nanospikes as well as to their bactericidal effects. We discovered that silicon samples prepared by 6 min of MacEtch provide the best bactericidal properties by having an optimal nanospike spacing similar to biological structures. We hypothesize that at this spacing, nanospike surface has enough number of contact points with the bacterial cell to damage the cell. While each contact point can induce certain tensile stress on the bacterial membrane, the overall effect of nanospikes on the bacterial in contact is stretching the bacterial membrane beyond a critical strain, causing bacterial death.

Figure 1 illustrates the mechanisms of the MacEtch. Silver ions in the etching solutions form dendrites on the silicon surface, which induce etching of silicon in contact with the silver dendrites. The silver dendrites sink down as the silicon underneath is etched. Finally, the silver dendrites is removed to render silicon nanospikes. Figure 2 shows the typical nanospike surface fabricated by 6 min of MacEtch in front view and titled view. The sample has an average spacing about 200 nm matching the spacing of the spikes on biological samples.

Figure 3(a) is the helium ion microscopy image of the lysed *E. coli* on the 6 min MacEtch sample without metal coatings. As shown in Figure 3(a), lysed *E. coli* cells lose their characteristic cell boundary and exhibit amorphous cell shapes. In contrast, Figure 3(b) shows a normal *E. coli* cell maintaining its boundary of cell wall on the same nanospike surface. Figure 4(a) shows the fluorescence image of *E. coli* on a sample with both smooth silicon and nanospike region. Figure 4(b) compares the bacterial count on smooth silicon and bacterial count on silicon nanospikes surface fabricated by 6 min MacEtch. There is a significant difference in the bacterial count, indicating the bactericidal nature of silicon nanospikes.

[1] E. P. Ivanova, et al., Small, vol. 8, 2489 (2012)
[2] E. P. Ivanova, et al., Nat Commun, vol. 4, 2838 (2013)

[3] S. Christina, et al., Nanotechnology, vol. 25, 195101 (2014)

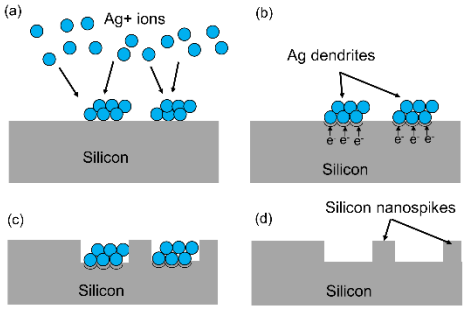

Figure 1: Schematics illustrating the mechanism of MacEtch

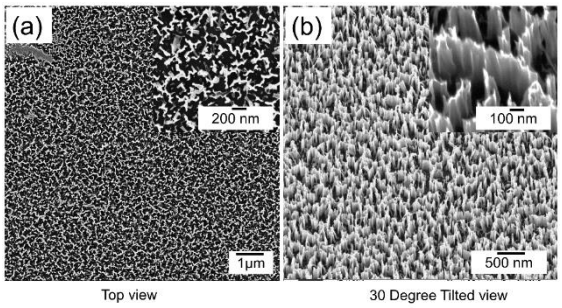

Figure 2: Helium Ion Microscope images of silicon nanospikes prepared by 6 min of MacEtch: (a) Front view; (b) 30 degree titled view

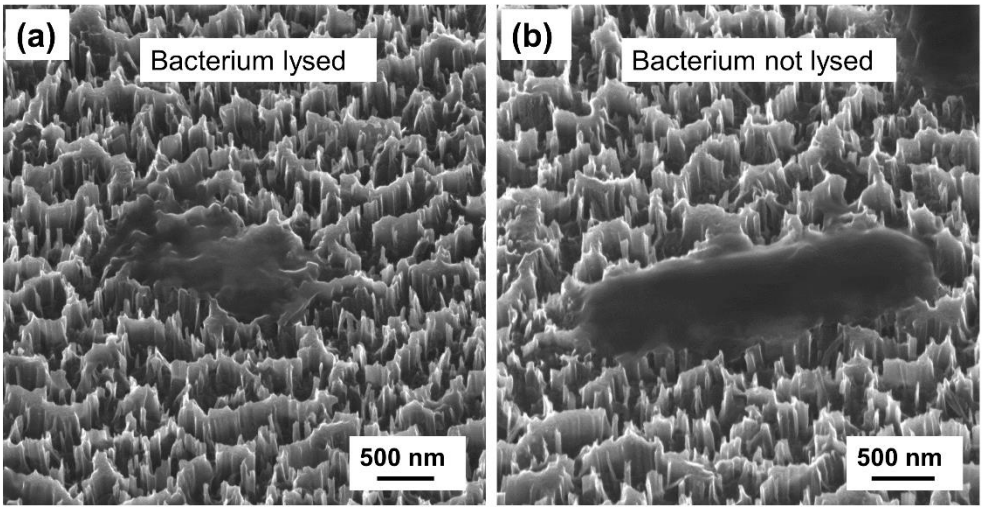

Figure 3: (a) 30 degree titled view of an *E. coli* bacterium lysed by 6 min MacEtched silicon nanospikes imaged by helium ion microscope; (b) 30 degree tilted view of an *E. coli* bacterium not lysed by same silicon nanospikes imaged by helium ion microscope

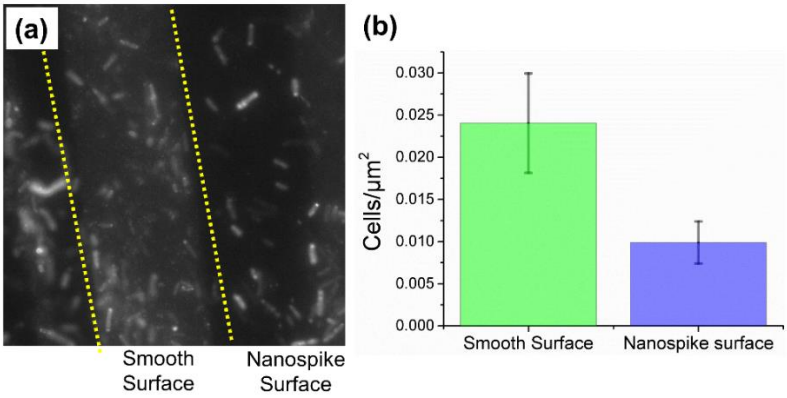

Figure 4: (a) Fluorescence image of *E. coli* bacteria on a surface with part of the region smooth without silicon nanospikes and part of the region with silicon nanospikes; Live bacteria fluorescence while dead bacteria do not fluoresce (b) Bacterial counts of live *E. coli* on silicon nanospike surface and on smooth silicon surface. Live bacteria on smooth surface outnumbers the live bacteria on nanospike surface significantly.