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Supporting Information

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Bioinspired Patterning with Extreme Wettability Contrast on TiO_2 Nanotube Array Surface: A Versatile Platform for Biomedical Applications

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Bioinspired Patterning with Extreme Wettability Contrast on TiO_2 Nanotube Array Surface: a Versatile Platform for Biomedical Applications

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Rewritable Patterned Superhydrophobicity on TNA Films. The superhydrophobic and superhydrophilic property can be reversible achieved again by alternating SAM and UV light irradiation respectively. Therefore, by controlling the site-seletive photocatalytic decomposition of low surface energy organic layer using UV irradiation, various surface patterns with high wettability contrast can be on-demand constructed on the same substrate (Figure S1). This process based on a robust biocompatible TiO_2 surface should offer a renewable, resource-saving, and environmentally-friendly methodology to the formation of wettability patterns for biomedical applications.

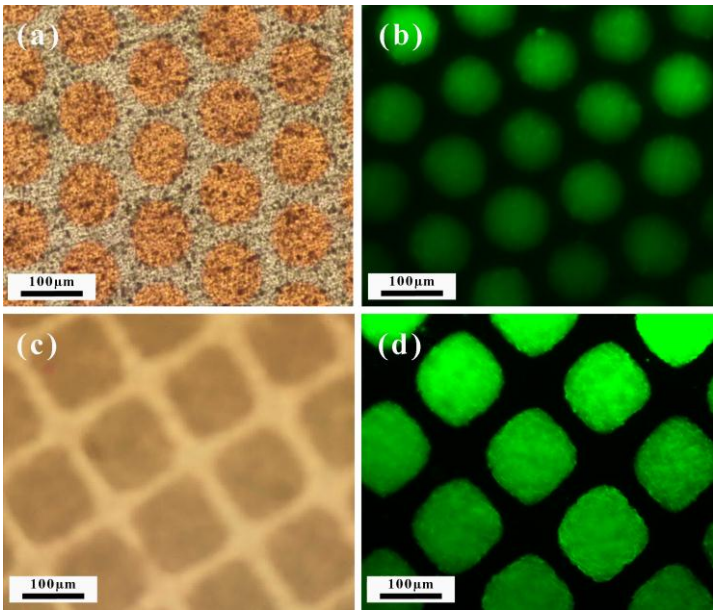

Figure S1. Optical and fluorescent images of the original (a, b) and regenerative (c, d) superhydrophilic-superhydrophobic micropatterns on the identical TNA surfaces.

Patterned Superhydrophobicity on other substrate. The hierarchical TiO_2 micro/nanoscale binary structures films were fabricated by electrochemically anodizing of titanium sheets (purity 99.5 %) in 0.01 M NH_4F electrolyte with Pt counter electrode (Figure S2a-c). The anodizing was carried out at 50 V for 1 h. The TiO_2 film was then rinsed with deionized water and air dried. The TiO_2 films were modified with PTES to achieve superhydrophobic property (see the inset of Figure S2a). The convenient patterned superhydrophobic technique in this work is also suitable to prepare high wettability contrast micropattern on such substrate (Figure S2d).

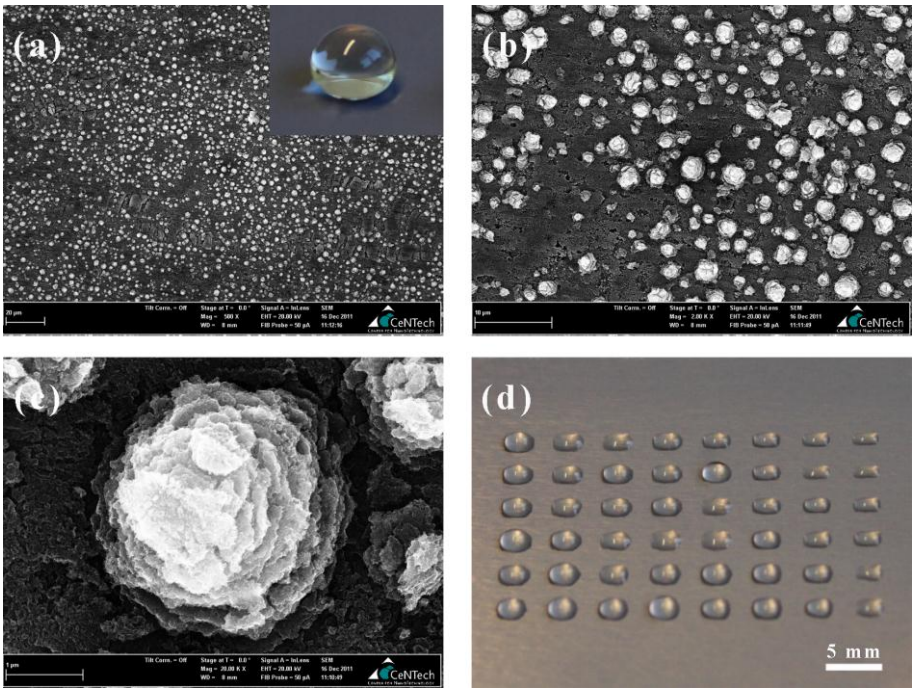

Figure S2. (a-c) SEM image of the micro/nanoscale binary structured TiO_2 film on titanium substrate by anodizing in 0.01 M NH_4F electrolyte with a voltage of 50 V for 1 h. The inset of (a) shows the optical image of a water droplet sitting on the resultant superhydrophobic surface. (d) Optical image of the as-prepared superhydrophilic-superhydrophobic micropattern according to the identical method reported in this work.

The smooth TiO_2 film was obtained by anodizing in 1 M H_2SO_4 at 20 V for 20 min. The hydrophilic-hydrophobic micropattern was fabricated by selective UV exposure of the PTES modified annealed TiO_2 film with the assistance of photomask. The static contact angle of the PTES modified smooth TiO_2 film before and after UV irradiation (366 nm) for 20 min is only about 110^o and 45^o, respectively. The cells show random distribution without preferred attachment on the smooth TiO_2 film with identical pattern consisted with hydrophobic-hydrophilic line. This verified the high contrast of wettability played a vital role for the highly selective attachment of cells.

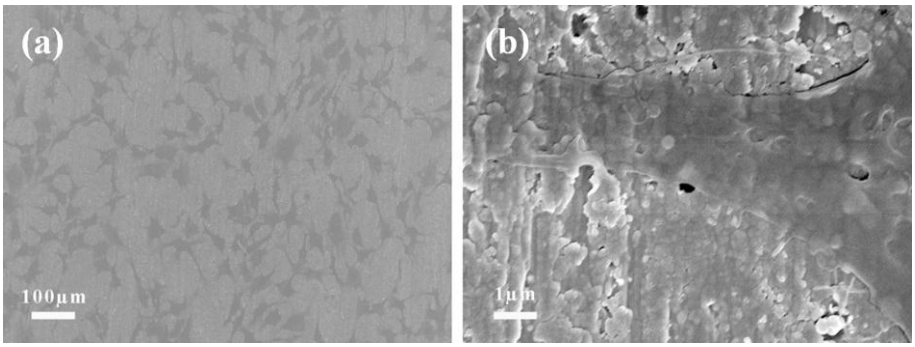

Figure S3. (a) SEM image of 3T3 cells adhesion on a smooth TiO_2 film with hydrophilic-hydrophobic square micropatterns (200 μm, 45 μm interval) for 24 h; (b) Magnified image.

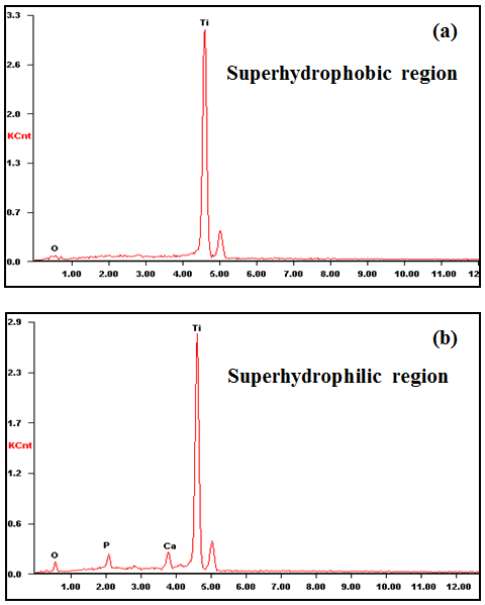

Figure S4. EDS results for the micropatterned CaP thin films grown on the corresponding superhydrophobic (a) and superhydrophilic (b) region.

The protein adsorption was analyzed by measuring the fluorescent intensity of FITC-BSA. The absorption peak intensity ratio (A_{280}/A_{490}) in pure FITC and FITC-BSA is approximately 37.3% and 80.2%, respectively. This change indicates the successful conjugation of FITC onto the BSA due to the solo absorption peak of BSA at 280 nm.

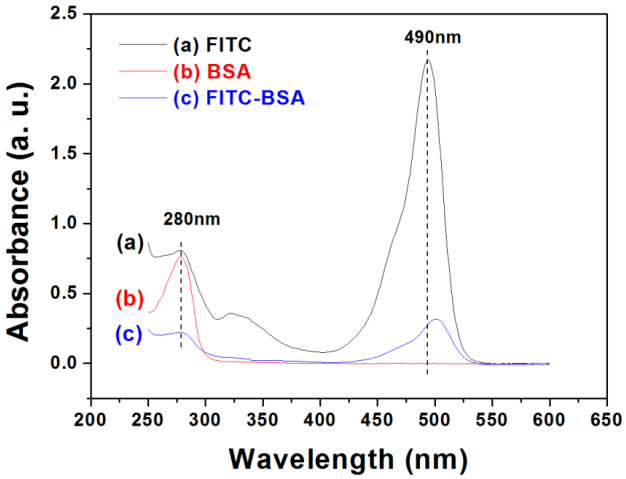

Figure S5. UV-Vis absorbance spectra of (a) FITC solution, (b) BSA solution, and (c) FITC-BSA solution.

Figure S6a shows the typical TEM image of the AgNP@TNA. From the image, we can find that AgNPs are uniformly coating on the outer and inner TNA wall. This can also be verified by the homogeneous AgNPs deposited on smooth TiO_2 surface (Figure S6b). These results indicated that uniform distributed Ag particles were deposited successfully among TNA.

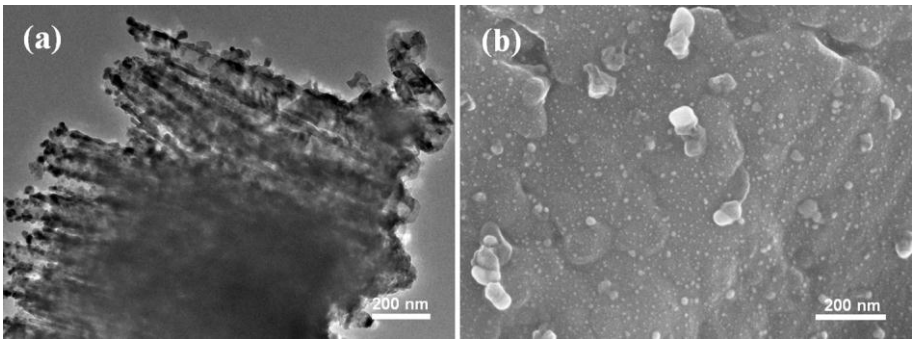

Figure S6. TEM image of Ag nanoparticles on TNA (a); SEM image of the Ag nanoparticles on the smooth TiO_2 prepared with an identical deposition process (b).

The fluorescent image shows significant reductions in the number of viable organisms of the AgNP@TNA (Figure S7a). On the contrary, *E. coli* is almost completely covered the TNA surface after dropping bacteria culture for 10 h (Figure S7b). This testing result indicates that the AgNP@TNA has a good anti-biofouling performance in the prevention of bacterial adhesion and biofilm formation. Moreover, the morphology of the *E. coli* changes apparently. As shown by SEM images (Figure S7c, d), the bacteria cells on AgNP/TNA are fragmented (thin and short in size) and show non-uniform color, suggesting that the integrity of the cell has been damaged. The decomposition of the cell membranes leads to leakage of the interior component, and hence the inactivation of the bacteria. These results are in good agreement with the optical observation of the antibacterial testing. A clear zone of growth inhibition is observed around the square silver-immobilized sample (inset of Figure S7a), displaying its good antibacterial efficacy, while the non-silver immobilized membrane surface is uniformly covered by the diffused *E. coli* (inset of Figure S7b).

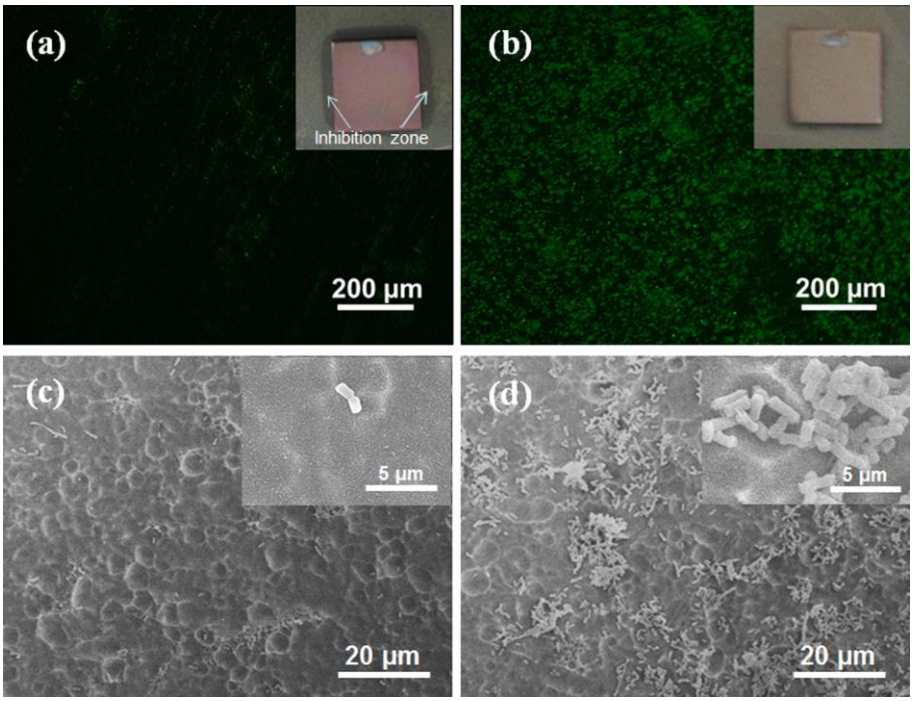

Figure S7. Typical fluorescent image of micropatterned AgNP@TNA film (a) and control TNA cultured with *E. coli* for 10 h and stained with Calcein (b). The corresponding SEM image of *E. coli* on AgNP@TNA (c) and TNA (d) surface. The insets of (a, b) show the optical images of *E. coli* incubated on agar plates, antibacterial performance of AgNP@TNA and control TNA for 24 h.