

## Superhydrophobic and White Light-Activated Bactericidal Surface through a Simple Coating

Gi Byoung Hwang, adnan Patir, Elaine Allan, Sean P. Nair, and Ivan P. Parkin

*ACS Appl. Mater. Interfaces*, **Just Accepted Manuscript** • DOI: 10.1021/acsami.7b05977 • Publication Date (Web): 31 Jul 2017

Downloaded from <http://pubs.acs.org> on August 7, 2017

### Just Accepted

“Just Accepted” manuscripts have been peer-reviewed and accepted for publication. They are posted online prior to technical editing, formatting for publication and author proofing. The American Chemical Society provides “Just Accepted” as a free service to the research community to expedite the dissemination of scientific material as soon as possible after acceptance. “Just Accepted” manuscripts appear in full in PDF format accompanied by an HTML abstract. “Just Accepted” manuscripts have been fully peer reviewed, but should not be considered the official version of record. They are accessible to all readers and citable by the Digital Object Identifier (DOI®). “Just Accepted” is an optional service offered to authors. Therefore, the “Just Accepted” Web site may not include all articles that will be published in the journal. After a manuscript is technically edited and formatted, it will be removed from the “Just Accepted” Web site and published as an ASAP article. Note that technical editing may introduce minor changes to the manuscript text and/or graphics which could affect content, and all legal disclaimers and ethical guidelines that apply to the journal pertain. ACS cannot be held responsible for errors or consequences arising from the use of information contained in these “Just Accepted” manuscripts.

# Superhydrophobic and White Light-Activated Bactericidal Surface through a Simple Coating

Gi Byoung Hwang <sup>a</sup>, Adnan Patir <sup>a</sup>, Elaine Allan <sup>b</sup>, Sean Nair <sup>b</sup>, and Ivan P. Parkin <sup>a\*</sup>

*<sup>a</sup>Materials Chemistry Research Centre, Department of Chemistry, University College London, 20 Gordon Street, London, WC1H 0AJ, United Kingdom*

*<sup>b</sup>Division of Microbial Diseases, UCL Eastman Dental Institute, University College London, 256 Gray's Inn Road, London WC1X 8LD, United Kingdom*

\* To whom correspondence should be addressed.

E-mail: i.p.parkin@ucl.ac.uk Tel: 44(0)207 679 4669

**Abstract**

Bacterial adhesion and proliferation on surface give a challenge in medical and industrial fields. Here, a simple one-step technique is reported to fabricate self-cleaning and antibactericidal surfaces. White, blue, and violet paints were produced using titanium dioxide nanoparticles, 1H, 1H, 2H, 2H-perfluorooctyltriethoxysilane (PFOTES), crystal violet, toluidine Blue O, and ethanol solution. All of the painted surfaces showed superhydrophobicity in air, and even after hexadecane oil contamination, they retained water repellency and self-cleaning properties. In an assay of bacterial adhesion, significant reductions (>99.8%) in the number of adherent bacteria were observed for all the painted surfaces. In bactericidal tests, the painted surfaces demonstrated not only bactericidal activity against *S. aureus* and *E. coli* in the dark but also induced very potent photosensitisation (>4.4 log reduction in the number of viable bacteria on violet painted surface) under white light illumination. The technique that we developed here is general, and can be used on a wide range of substrates such as paper, glass, polymers, and others.

**Keyword:** self-cleaning surface, bactericidal activity, superhydrophobic surface, *E. coli*, and *S. aureus*

## Introduction

Bacteria are one of the oldest life forms on our planet and they have developed a variety of adaptive mechanisms for the colonization of surfaces over millions of years<sup>1</sup>. Bacterial biofilms on surfaces are known to produce adverse effects in a variety of situations. In water-based industries, including water treatment and distribution, paper manufacturing, and the operation of cooling towers, biofilms reduce water quality by influencing taste and odour and they cause corrosion of the pipe-line resulting in equipment damage<sup>2-3</sup>. In the medical field, biofilms are important contributors to hospital acquired infections (HAIs) which are the fourth leading causes of death in the U. S<sup>4-5</sup>. Pathogenic bacteria are able to survive on surfaces within healthcare facilities for several weeks and they can be transmitted through touch by hospital workers and patients<sup>6-7</sup>. According to a report by the U.S. Center for Disease Control and Prevention (CDC) in 2007, approximately 1.7 million patients in hospitals acquired HAIs and 99,000 of these patients died during hospitalization. Further, 60-70% of HAIs were related to bacterial contamination of hospital surfaces or medical devices<sup>8-10</sup>.

Superhydrophobic surfaces are able to reduce bacterial adhesion, and biofilm formation and provide easy removal of bacterial cells<sup>11</sup>. Many techniques to produce superhydrophobic surfaces have been suggested including surface modification using nanoparticles, photolithography, mesoporous polymer, surface etching resulting in nanoscale surface roughness, and chemical modification<sup>12-16</sup>. However, some of these techniques require harsh conditions or complex fabrication processes, thus limiting the substrate type and geometry. Moreover, superhydrophobic surfaces are easily destroyed by mild abrasive force and readily contaminated by oil resulting in loss of water repellency<sup>17-18</sup>.

1  
2  
3  
4  
5  
6  
7  
8  
9  
10  
11  
12  
13  
14  
15  
16  
17  
18  
19  
20  
21  
22  
23  
24  
25  
26  
27  
28  
29  
30  
31  
32  
33  
34  
Bactericidal surfaces kill bacteria on contact <sup>19</sup>. Such surfaces have been widely investigated for potential use in healthcare facilities, in industry, and even the home. The most common and arguably, the most important use of bactericidal surfaces is for hospital surfaces or medical devices to prevent HAIs <sup>20-22</sup>. Many techniques have been suggested for application to surfaces including silver- or copper-coated surfaces <sup>19, 23-25</sup>, and photosensitive surfaces using light activated antimicrobial agents (LAAAs) <sup>6, 26</sup>. Recently surface treatments using light-activated antimicrobial agents, crystal violet (CV), methylene blue (MB) and toluidine blue O (TBO) have been investigated<sup>27-29</sup>. The dyes generate reactive singlet oxygen (<sup>1</sup>O<sub>2</sub>) and free radicals when they are exposed to a visual light, and the <sup>1</sup>O<sub>2</sub> and free radicals produce adverse effects on bacteria resulting in cell death<sup>28</sup>. Previous studies showed that CV, MB, and TBO can be impregnated into soft polymers thorough a swell-encapsulation-shrink process, and the dyed polymers possess potent photobactericidal activity under white light <sup>30-32</sup>.

35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60  
New attempts at developing hybrid materials have been conducted in order to improve bactericidal performance whilst maintaining prevention of bacteria attachment. Previous studies showed that the combination of superhydrophobic materials with either photocatalysts or antibacterial nanoparticles such as silver, copper, and silica retained superhydrophobicity or at least hydrophobicity. However, they typically show no photocatalytic reaction and only relatively weak bactericidal activity, indicating those materials were not effectively combined <sup>11, 33-39</sup>. We have developed hybrid materials with increased bactericidal performance and with the ability to prevent bacterial attachment. In this study, a new paint formulation with dual functional properties of self-cleaning and white light-activated bactericidal activity is described. The paints that we developed here are quite general, and can be easily applied to

1  
2  
3  
4 various surfaces such as glass, paper, plastic and others. Furthermore, they function even  
5  
6 after contaminated by hexadecane oil.  
7  
8

## 9 **Experimental section**

### 10 **Preparation of white, blue, and violet paints**

11  
12  
13  
14 Solution A: 1.0 g of 1H, 1H, 2H, 2H-perfluorooctyltriethoxysilane (PFOTES,  
15  
16  $C_8F_{13}H_4Si(OCH_2CH_3)_3$ , Sigma-Aldrich, St. Louis, MO, USA) was dispersed in 99.0 g of pure  
17  
18 ethanol (EDM Millipore Co., Billerica, MA, USA), and for 10 min, the mixture was agitated.  
19  
20

21  
22 White paint: 4.0 g of  $TiO_2$  nanoparticles (Degussa P 25) were mixed with 40 mL of  
23  
24 solution A with constant agitation, and then, for 5 min the mixture was sonicated and  
25  
26 vortexed for 5 min  
27

28  
29 Blue paint: 4.0 g of  $TiO_2$  nanoparticles (Degussa P 25), and 40 mg of toluidine blue O  
30  
31 (TBO, Sigma-Aldrich, St. Louis, MO, USA) were dispersed in 40 mL of solution A with  
32  
33 constant agitation, and then, for 5 min the mixture was sonicated and vortexed for 5 min.  
34

35  
36 Violet paint: 4.0 g of  $TiO_2$  nanoparticles (Degussa P 25), and 40 mg of crystal violet (CV,  
37  
38 Sigma-Aldrich, St. Louis, MO, USA) were dispersed in 40 mL of solution A with constant  
39  
40 agitation, and then, for 5 min the mixture was sonicated and for 5 min, it was vortexed.  
41  
42

### 43 **Water repellency and self-cleaning in air**

44  
45 450  $\mu$ L of paint was inoculated on the glass slides ( $2.5 \times 7.5$  cm), the slides were tilted until  
46  
47 whole surfaces were coated, and dried in the dark room for 3 h. After drying, the samples  
48  
49 were washed using deionized (DI) water to ensure removal of non-combined CV or TBO. To  
50  
51 test water repellency, 0.5 mL of deionized (DI) water was fallen on to the treated samples at a  
52  
53 height of  $\sim 20$  mm. To test the self-cleaning property of the samples, iron oxide powder was  
54  
55 loaded on to the samples to mimic dirt, and then 1 ml of DI water was fallen on to the  
56  
57  
58  
59  
60

1  
2  
3  
4 samples using a pipette. The water repellency and self-cleaning tests were recorded using a  
5  
6 smartphone camera (Galaxy S5, Samsung Electronics Co., Ltd, Suwon, South Korea)  
7  
8

### 9 **Water contact angle measurement of white, blue, and violet painted surfaces in air**

10  
11 As shown in Figure S1, the equilibrium water contact angle on the paint coated samples  
12 was examined by a contact angle meter (First Ten Angstroms, Inc., Portsmouth, Virginia,  
13 USA). A DI water droplet (volume 5  $\mu\text{L}$ ) was put onto the surface of samples, images were  
14 captured on and analyzed by Surftens 4.5 software. The contact angle hysteresis was  
15 measured using “add and remove volume” method. The contact angle hysteresis was  
16 investigated by the variation of advanced angle and receding angle <sup>40</sup>.  
17  
18  
19  
20  
21  
22  
23  
24

### 25 **Water contact angle measurement of the painted surface in hexadecane**

26  
27 The painted samples were immersed in hexadecane and droplets of DI water containing  
28 Congo red dye (Sigma-Aldrich, St. Louis, MO, USA) were put onto the treated and untreated  
29 sample. It was photographed from the side and then analyzed by Surftens 4.5 software.  
30  
31  
32  
33  
34

### 35 **Water repellency and self-cleaning in air after hexadecane contamination**

36  
37 To make oil-contaminated surfaces, the painted glass slides were dipped in hexadecane,  
38 and then, from a height of  $\sim 20$  mm, 0.5 mL of DI water containing Congo red dye was  
39 dropped on to the surface of the samples which were tilted at an angle of  $20^\circ$ .  
40  
41  
42  
43

44 for the self-cleaning test of the oil-contaminated sample, vanadium oxide powder was  
45 placed on to the contaminated samples and then 0.5 ml DI water was fallen on to samples  
46 which were tilted at an angle of  $20^\circ$  using pipette.  
47  
48  
49  
50

### 51 **Measurement of UV-vis spectrum**

52  
53 As shown in Figure S2, the UV-vis absorption spectra for the paint coated samples were  
54 examined by UV-Vis Spectrometer (PerkinElmer Inc., Winter St., CT, USA). Absorption was  
55 examined in the wavelengths of 400–900 nm.  
56  
57  
58  
59  
60

### SEM and AFM Analysis

Scanning Electron Microscopy (SEM, JEOL Inc., Peabody, MA, USA) was used to observe the surface morphology of the paint coated samples at an accelerating voltage of 5 kV. Images were captured using SEMAfore software. Fine gold particles were deposit onto sample to eliminate surface charging. Atomic force microscopy (AFM, EeasyScan 2 AFM, Nanosurf, Liestal, Switzerland) was employed to determine a roughness of the sample surface and it was investigated using tapping mode.

### Bactericidal testing

For bactericidal testing, the surface of glass slides was coated by 450  $\mu$ L paint and then dried in the dark room for 3h. The bactericidal activity of the samples was investigated in *Escherichia coli* ATCC 25922 and *Staphylococcus aureus* NCTC 13143. *E. coli* and *S. aureus* were stored at  $-70^{\circ}\text{C}$  in brain-heart-infusion broth (BHI broth, Oxoid Ltd., Hampshire, England, UK) with 20% glycerol and incubated on MacConkey agar (Oxoid Ltd., Hampshire, England, UK) and Mannitol salt agar (Oxoid Ltd.), respectively. One bacterial colony was inoculated into 10 ml BHI broth and cultured in shaking incubator (200 rpm) at  $37^{\circ}\text{C}$ . After incubation for 18 h, the bacteria were harvested by centrifugation ( $21^{\circ}\text{C}$ , 5000 rpm for 10 min), washed using 10 mL of phosphate buffered saline (PBS), and centrifuged again to recover the bacteria which were re-suspended in 10 mL of PBS. The washed suspension was diluted 1000-fold in order to obtain  $\sim 10^6$  colony forming units per millilitre (CFU/mL). As shown in Figure S3, 75  $\mu$ L of bacterial suspension was inoculated onto sterilized glass slide ( $2.5 \times 7.5$  cm), the glass slide was overturned and plated on the paint coated sample. The samples were loaded in petri dishes with wet paper to keep humidity, and they were exposed to white light. another set of samples was placed in the dark room. White light intensity ranged from 3900 to 5300 lx, and the emission wavelength ranged from 400 to 730 nm



1  
2  
3  
4 (Figure S4). The samples were located into 40 mL PBS after white light exposure, and mixed  
5  
6 using a vortex mixer for 1 min to ensure that the bacteria were recovered from the surface of  
7  
8 the sample. The bacterial suspension was concentrated into 450  $\mu$ L by centrifugation (5000  
9  
10 rpm at 21 °C for 20 min), plated onto agar; (MacConkey agar for *E. coli*, and mannitol salt  
11  
12 agar for *S. aureus*). After 24 h incubation at 37 °C, the bacteria colonies on the plates were  
13  
14 counted.  
15  
16

### 17 18 **Test of bacterial adhesion**

19  
20 The adhesion of *E. coli* and *S. aureus* was tested on the glass control and the paint coated  
21  
22 samples. Glass slides were dipped into paint solution and then dried in the dark room for 3 h.  
23  
24 After being washed using DI water, the samples were placed vertically in 30 mL of bacterial  
25  
26 suspension containing  $\sim 10^{10}$  CFU for 3 min, and then were placed into 30 ml of PBS and  
27  
28 vortexed for 1 min to be sure that all bacteria were recovered from the surface of the sample.  
29  
30 The bacterial suspension was concentrated into 450  $\mu$ L by centrifugation (5000 rpm at 21 °C  
31  
32 for 20 min), serially diluted and plated on to agar. After 24 h incubation at 37 °C, the bacteria  
33  
34 colonies on the plates were counted.  
35  
36  
37  
38

### 39 40 **Preparation of paint and double side tape treated glass slides and robust test**

41  
42 As shown Figure S5, double side tapes were attached onto glass slides. and then the tape  
43  
44 attached samples were coated by white, blue, violet paints. The coated samples were placed  
45  
46 in dark room for 6 h. After drying, the painted sample was place onto sandpaper (CAMI grit  
47  
48 no. 150) and weight of 40 g was placed on the glass. The painted glass moved back and forth  
49  
50 for 8 cm along ruler. This process defined as one cycle. The water contact angle of the treated  
51  
52 sample was examined at each cycle.  
53  
54  
55

### 56 57 **Water repellency and stability tests of white, blue, and violet particles**

1  
2  
3  
4 The white, violet, and violet particles were produced by ethanol evaporation and top-down  
5 process (grinding process). To determine water repellency of the particles, the particles were  
6 attached to the surface of glass slide using double sided tape and then droplets of DI water  
7 containing Congo red dye were dropped on to the particles. The particles were dropped into  
8 DI water to determine leaching of CV or TBO dye and 10  $\mu$ L of DI water containing Congo  
9 red dye was placed on the surface of the particles which were floated on DI water.  
10  
11  
12  
13  
14  
15  
16  
17

### 18 **Statistical analyses**

19  
20 T-test statistical analysis on results was conducted by SPSS software (version 12.0, SPSS, Inc  
21 ., Chicago, IL, USA)  
22  
23  
24

## 25 **Results and Discussion**

26  
27  
28 As shown in Figure 1(a), white, blue, and violet paints were produced. Glass slides were  
29 painted and then dried in the dark room for 3 h. After drying, samples were washed using  
30 deionized (DI) water to remove non-combined CV or TBO. The white paint maintained its  
31 color after drying, however, the color became more or less intense in the case of the blue or  
32 violet paints. Scanning electron microscopy (SEM) Atomic force microscopy (AFM) were  
33 used to examine the surface of the samples and these showed that the  $\sim 21$  nm  $\text{TiO}_2$   
34 nanoparticles in the paint were agglomerated<sup>41</sup> and the painted surface has a roughness of  
35  $\sim 1000$  nm (Table 1).  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46

47  
48 The UV-vis absorbance spectra of the unpainted control and painted glass slides were  
49 measured over the wavelengths of 400–900 nm (Figure 2). The white paint did not show a  
50 major absorbance peak between 400–900 nm, while the blue and violet paints showed major  
51 absorbance peaks at 589 and 590 nm, respectively, corresponding to the CV and TBO. The  
52 adsorption features of CV and TBO in the wavelength of 400–750 nm may explain their role  
53 on photosensitizer using white light.  
54  
55  
56  
57  
58  
59  
60

1  
2  
3  
4  
5 The water contact angle of the control and painted glass was measured. As shown in Figure  
6  
7 3 (a), the control gave water contact angles of  $5.9^\circ$ , indicating superhydrophilic character.  
8  
9 However, the painted glass surfaces gave the water contact angles higher than  $160^\circ$ ,  
10  
11 indicating that they are superhydrophobic (Table 1)<sup>37</sup>. To determine the water repellence of  
12  
13 the paints, 0.5 mL of water was dropped on to the samples. As shown in Movie S1–4 and  
14  
15 Figure S6, water droplets were trapped on the surface of the control glass slide whereas the  
16  
17 water droplets simply rolled off without wetting the surface on all the painted surfaces. The  
18  
19 water rolling phenomenon resulted from superhydrophobicity of the paints giving a high  
20  
21 water contact angle ( $>160^\circ$ ) and low roll off angle ( $<5^\circ$ ). The self-cleaning experiment  
22  
23 represented that after water falling, the dirt contained within the water remained on the  
24  
25 surface of the control material while the droplets rolled off on the treated surface, they carried  
26  
27 away the dirt. (Movie S5–8 and Figure S7). This phenomenon can be explained in that the  
28  
29 rough surface with low surface energy significantly reduces the contact between water  
30  
31 droplet and the surface. This considerably reduces the adhesion force of water and surface.  
32  
33 Thus, the dirt was washed away by the droplets because adhesion of dirt to the surface is  
34  
35 much weaker than that of water droplet to the dirt<sup>42</sup>.  
36  
37  
38  
39  
40  
41

42  
43 Previous studies showed that superhydrophobic surfaces lose their water repellency after  
44  
45 being partially contaminated by oil<sup>18, 43</sup>. This is because oil, a lower surface tension than  
46  
47 water, penetrated into the surface. As shown Figure 3 (b), a test of the water repellency of the  
48  
49 samples immersed in hexadecane oil showed that water droplets still formed spheres on the  
50  
51 painted surface, indicating a water contact angle of  $>160^\circ$ . When samples were immersed  
52  
53 into the oil, hexadecane permeated within the surface. Thus, water droplets were supported  
54  
55 by both the oil and the surface structure, and formed a sphere. After the oil contamination,  
56  
57 water droplets simply slid off on the painted surfaces and their self-cleaning property was  
58  
59  
60

1  
2  
3  
4 retained (Movie S9–16 and Figure S8–9). When the painted surfaces were exposed to  
5  
6 hexadecane, the oil penetrated within the surfaces<sup>44</sup>. This produces lubricating film on the  
7  
8 painted surface, resulting in slippery surfaces<sup>45</sup>.  
9

10  
11 To determine bacterial adhesion to the control and painted glass surfaces, suspensions of  
12  
13 *Staphylococcus aureus* NCTC 13143 (containing  $\sim 1.2 \times 10^{10}$  CFU) and *Escherichia coli*  
14  
15 ATCC 25922 (containing  $\sim 1.1 \times 10^{10}$  CFU) were used. Figure 4 shows the number of *S.*  
16  
17 *aureus* and *E. coli* attached to the surface of the control and painted surfaces.  $4.5 \times 10^7$  CFU  
18  
19 of *S. aureus* were adhered to the surface of the control material and statistically significant  
20  
21 decreases ( $>99.9\%$ ,  $P < 0.01$ ) in the numbers of *S. aureus* were apparent on the white ( $3.2 \times$   
22  
23  $10^4$  CFU), blue ( $1.9 \times 10^4$  CFU), and violet painted surfaces ( $1.6 \times 10^4$  CFU). A significant  
24  
25 decrease in bacteria attachment was also confirmed with *E. coli* for all three painted surfaces  
26  
27 compared to the control (unpainted) surface and significant differences were observed in the  
28  
29 numbers of adherent bacteria between the different painted surfaces (the number of bacteria  
30  
31 attached onto all of painted surface:  $P < 0.01$ ). The number of *E. coli* adhered to the surface of  
32  
33 the control glass was  $2.0 \times 10^7$  CFU, whereas the numbers on the white, blue, and violet  
34  
35 painted surfaces were  $4.9 \times 10^3$ ,  $2.4 \times 10^5$ , and  $5.7 \times 10^4$  CFU, respectively. The reduction in  
36  
37 bacterial adhesion is attributed to the superhydrophobicity of the paints. When a  
38  
39 superhydrophobic surface is immersed, most of its surface is occupied by fine air bubbles.  
40  
41 The air bubbles significantly reduce contact between bacteria and the surface, and the  
42  
43 bacteria are unable to cross the air-water interfaces as a result of surface tension<sup>42</sup> (Figure  
44  
45 S10). These results indicate that even though superhydrophobic surfaces are not able to  
46  
47 prevent bacterial adhesion completely, they could significantly retard biofilm formation by  
48  
49 inhibiting the adhesion.  
50  
51  
52  
53  
54  
55  
56  
57

58 Figure 5 shows (a) the bactericidal activity of the samples against *S. aureus* in the dark and  
59  
60

1  
2  
3  
4 in white light. After 3 h in the dark, the number of viable bacteria decreased significantly on  
5  
6 the white, blue, and violet painted surfaces compared to the control material (P-value <0.05),  
7  
8 and among them, violet paint showed the best bactericidal activity achieving a 1.1 log  
9  
10 reduction in bacterial numbers compared to a 0.3 and 0.9 log reduction observed for the white  
11  
12 and blue painted surfaces, respectively. In white light, the painted surfaces showed increased  
13  
14 bactericidal activity compared to the same material in the dark. After 3 h white light exposure,  
15  
16 a 2.3 log and 3.2 log reduction in the numbers of viable bacteria were confirmed on white and  
17  
18 blue paint, respectively, compared to the control material and on the violet painted surface,  
19  
20 the numbers of viable bacteria fell to below the detection limit (<10 CFU). All of the painted  
21  
22 materials showed increased bactericidal activity in the light compared to the dark, achieving a  
23  
24 0.7, 2.4 and 3.4 log differences in bacterial numbers for the white, blue, and violet paints,  
25  
26 respectively.  
27  
28  
29  
30  
31  
32

33 Figure 5 (b) shows the bactericidal activity of the paints against *E. coli* in dark and in the  
34  
35 white light. In contrast to *S. aureus*, after 4 h in the dark, no reduction in the number of viable  
36  
37 bacteria was confirmed on any of the painted surfaces, and even after 4 h of white light  
38  
39 exposure, the number of viable bacteria did not decrease on either the control or white  
40  
41 painted surfaces. But, a statistically significant reduction in the number of viable *E. coli* was  
42  
43 confirmed on the blue and violet painted glass (P-value < 0.01 at both blue and violet painted  
44  
45 glasses). Compared to the control material, a 2.6 log reduction in the numbers of viable  
46  
47 bacteria were confirmed on the blue painted surface, and on the violet painted surface, the  
48  
49 numbers of viable bacteria had fallen to below the detection limit (>5 log reduction).  
50  
51  
52  
53

54 TiO<sub>2</sub> nanoparticles, CV, and TBO used in this study are known to have some bactericidal  
55  
56 activity in the absence of light<sup>27, 46-47</sup>. Testing of the bactericidal activity of our materials  
57  
58 against *S. aureus* in the dark showed that TiO<sub>2</sub> nanoparticles, CV, and TBO keep their  
59  
60

1  
2  
3  
4 intrinsic bactericidal property after being incorporated into paint. However, the paints did not  
5  
6 have bactericidal activity against *E. coli* in the dark, and despite the longer exposure to white  
7  
8 light compared to *S. aureus*, *E. coli* was less susceptible overall. It is likely that the difference  
9  
10 in susceptibility between *S. aureus*, a Gram-positive bacterium, and *E. coli*, a Gram-negative  
11  
12 bacterium, is due to their different cell wall structure. The cell wall of Gram-positive bacteria  
13  
14 consists of a thick peptidoglycan layer, and only one membrane (plasma membrane) whereas  
15  
16 Gram-negative bacteria have a more complex cell wall with a relatively thin layer of  
17  
18 peptidoglycan, but an outer membrane in addition to the plasma membrane. The outer  
19  
20 membrane of Gram-negative bacteria is known to reduce the permeability of many molecules  
21  
22  
23  
24  
25  
26  
27  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60  
48 and is often responsible for resisting chemical agents 49.

After white light exposure, all of the paints showed enhanced bactericidal activity compared to the same material in the dark. However, compared with the blue and violet paints, the activity of white paint was relatively weak. White paint mainly consists of TiO<sub>2</sub> nanoparticles which are a UV light-activated antimicrobial agent (LAAA), and the photobactericidal activity of TiO<sub>2</sub> is ascribed to OH<sup>-•</sup> radicals and other reactive oxygen species (ROS) induced by the light source<sup>21, 50-51</sup>. As TiO<sub>2</sub> is activated by ultraviolet (UV) light<sup>52</sup> which accounts for a tiny portion of the total radiation in white light, this may explain why the white paint demonstrated less photobactericidal activity than the blue and violet paints. The potent photobactericidal activity of blue and violet paints is due to TBO and CV which are well known white light-activated antimicrobial agents (WLAAA). Under white light conditions, the CV or TBO molecules are excited to a triplet state via an intersystem crossing from a slightly higher energy, shorter lived excited singlet state. The triple state molecules can undergo quenching by molecular oxygen including singlet oxygen (<sup>1</sup>O<sub>2</sub>) formation or interaction with biomolecules in the vicinity generating radical species<sup>30</sup>. The

1  
2  
3  
4  $^1\text{O}_2$  and radical species are thought to kill bacteria by oxidative damage to cellular  
5 membranes, intracellular proteins and DNA <sup>29, 53</sup>. Despite using an identical amount of  
6  
7 WLAAA (CV: 40 mg, TBO: 40 mg) in the paints, the bactericidal activity of the blue and  
8  
9 violet paints differed; the reduction of viable bacteria on violet paint was >1.24 log higher  
10  
11 than that of blue paint. This indicates that the violet paint produces more free radical species  
12  
13 or singlet oxygen species more than the blue paint, resulting in better kill.  
14  
15  
16  
17

18 Nano- or micro scale surface structures and superhydrophobic coatings are easily destroyed  
19 because of their mechanical weakness resulting in loss of hydrophobicity and this limits their  
20  
21 widespread application. In this study, robust superhydrophobic and antimicrobial surfaces  
22  
23 were produced using double side tape (Sellotape, Cheshire, UK) and the paints and they were  
24  
25 tested at an extremely environmental condition. The painted sample was placed onto  
26  
27 sandpaper (CAMI grit no. 150) and 40 g weight was loaded on to the sample. The applied  
28  
29 force on samples was approximately 21.3 kg/m<sup>2</sup>. The sample was then moved back and forth  
30  
31 for 8 cm along a plastic ruler. One back and forth movement was defined as one abrasion  
32  
33 cycle. Figure 6 (a) shows that the sand paper abrasion test against white, blue, and violet  
34  
35 painted glass slides. Previous studies showed that the water contact angle of the robust  
36  
37 surface decreased by 13–15 ° after repeating abrasion test. <sup>54-55</sup> However, 10 cycles test in this  
38  
39 study showed that after repeating abrasion, the painted surfaces retained a water contact  
40  
41 angles of >158 °, low rolling off angle (<0.5 °) and contact angle hysteresis (<3.4 °), indicating  
42  
43 that they are still superhydrophobic. Their colors and the coating thickness of 55 μm were  
44  
45 also retained (Figure S11). The white, violet, and violet particles were made through ethanol  
46  
47 evaporation and top-down process. As shown in Figure 6 (b), the particles retained their  
48  
49 respective colors and measurement of the water contact angle showed that the particles  
50  
51 remained superhydrophobic. CV and TBO dyes used in this study were soluble in water.  
52  
53  
54  
55  
56  
57  
58  
59  
60

1  
2  
3  
4 However, dye leaching from the particles was not observed. In ethanol, porous TiO<sub>2</sub>  
5 nanoparticles absorb dye molecules <sup>56</sup>, and the PFOTES molecules covalently bond to the  
6 surface of TiO<sub>2</sub> nanoparticles <sup>57-58</sup>. Thus, a PFOTES molecules are bonded on the surface of  
7 the dye absorbed TiO<sub>2</sub>, the nanoparticles have superhydrophobic and the light activated  
8 properties (Figure S12).  
9  
10  
11  
12  
13  
14  
15

16  
17 Previous studies have shown that combination of superhydrophobic agents and bactericidal  
18 nanoparticles resulted in no or weak antimicrobial activity although they retained high  
19 hydrophobicity. This might be because the superhydrophobic polymer coating reduce the  
20 contact surface area between antimicrobial substances and bacteria <sup>11, 33-39</sup>. We addressed the  
21 problem by the combination of TiO<sub>2</sub>, WLAAA and PFOTES. As a result, bacteria are killed  
22 by ROS diffused from surface containing WLAAA under white light condition.  
23  
24  
25  
26  
27  
28  
29  
30

## 31 **Conclusion**

32  
33  
34 This study reports new paints possessing both self-cleaning and white light-activated  
35 bactericidal properties. Compared to previous techniques for bactericidal surfaces and  
36 superhydrophobic surfaces, the technique developed in this study has several advantages: (i).  
37 the paints are easily made; (ii) surface treatment with the paints is simple and fast as  
38 commercial paint; (iii) the surfaces have dual functions after one simple process and (iv) the  
39 paints can be applied to a wide range of substrates including glass (Figure 1(b)), paper, and  
40 plastic (Figure S13). It is expected that these paints may be useful for healthcare and  
41 industrial facilities, as well as being applicable in the home for decoration.  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52

## 53 **Supporting information**

- 54  
55  
56 1. Water repellent test of samples. 2. Self-cleaning testing of samples. 3. Water repellent test  
57 of samples after hexadecane contamination. 4. Self-cleaning testing of samples after  
58 hexadecane contamination. 5. Intensity distribution of the white light which. 6.  
59  
60



1  
2  
3  
4 Comparison of the paint coating thickness before and after abrasion test. 7. Chemical  
5 structures on the combinations of TiO<sub>2</sub> nanoparticle/PFOTES, and TiO<sub>2</sub>  
6 nanoparticle/PFOTES /TBO, and TiO<sub>2</sub> nanoparticle/ PFOTES/CV. 8. White, blue, violet  
7 painted plastics (plastic toys) and papers.  
8  
9  
10  
11  
12  
13  
14  
15  
16  
17  
18  
19  
20  
21  
22  
23  
24  
25  
26  
27  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60

## Reference

- 1
  - 2
  - 3
  - 4
  - 5
  - 6
  - 7
  - 8
  - 9
  - 10
  - 11
  - 12
  - 13
  - 14
  - 15
  - 16
  - 17
  - 18
  - 19
  - 20
  - 21
  - 22
  - 23
  - 24
  - 25
  - 26
  - 27
  - 28
  - 29
  - 30
  - 31
  - 32
  - 33
  - 34
  - 35
  - 36
  - 37
  - 38
  - 39
  - 40
  - 41
  - 42
  - 43
  - 44
  - 45
  - 46
  - 47
  - 48
  - 49
  - 50
  - 51
  - 52
  - 53
  - 54
  - 55
  - 56
  - 57
  - 58
  - 59
  - 60
- (1) Kraigsley, A. M.; Finkel, S. E., Adaptive Evolution in Single Species Bacterial Biofilms. *FEMS Microbiol. Lett.* 2009, 293, 135-40.
- (2) Islander, R. L.; Deviny, J. S.; Mansfeld, F.; Postyn, A.; Shih, H., Microbial Ecology of Crown Corrosion in Sewers. *J. Environ. Eng.* 1991, 117, 751-770.
- (3) Mahapatra, A.; Padhi, N.; Mahapatra, D.; Bhatt, M.; Sahoo, D.; Jena, S.; Dash, D.; Chayani, N., Study of Biofilm in Bacteria from Water Pipelines. *J. Clin. Diagn. Res.* 2015, 9, DC09-11.
- (4) Boyce, J. M., Environmental Contamination Makes an Important Contribution to Hospital Infection. *J. Hosp. Infect.* 2007, 65, 50-54.
- (5) Bagihalli, G. B.; Avaji, P. G.; Patil, S. A.; Badami, P. S., Synthesis, Spectral Characterization, in Vitro Antibacterial, Antifungal and Cytotoxic Activities of Co(II), Ni(II) and Cu(II) Complexes with 1,2,4-Triazole Schiff Bases. *Eur. J. Med. Chem.* 2008, 43, 2639-49.
- (6) Page, K.; Wilson, M.; Parkin, I. P., Antimicrobial Surfaces and Their Potential in Reducing the Role of the Inanimate Environment in the Incidence of Hospital-Acquired Infections. *J. Mater. Chem.* 2009, 19, 3819.
- (7) Ayliffe, G. A. J.; Collins, B. J.; Lowbury, E. J. L.; Babb, J. R.; Lilly, H. A., Ward Floors and Other Surfaces as Reservoirs of Hospital Infection. *J. Hyg.* 2009, 65, 515.
- (8) Castelli, P.; Caronno, R.; Ferrarese, S.; Mantovani, V.; Piffaretti, G.; Tozzi, M.; Lomazzi, C.; Rivolta, N.; Sala, A., New Trends in Prosthesis Infection in Cardiovascular Surgery. *Surg. Infect.* 2006, 7 Suppl 2, S45-7.
- (9) Monina, K. R. Centers for Disease Control and Prevention Public Health Reports. Healthcare-Associated Infections and Deaths in U.S. Hospitals; 2007.
- (10) Bryers, J. D.; Ratner, B. D., Biomaterials Approaches to Combating Oral Biofilms and Dental Disease. *BMC oral health* 2006, 6 Suppl 1, S15.
- (11) Zhang, X.; Wang, L.; Levänen, E., Superhydrophobic Surfaces for the Reduction of Bacterial Adhesion. *RSC Adv.* 2013, 3, 12003.
- (12) Sarkar, D. K.; Saleema, N., One-Step Fabrication Process of Superhydrophobic Green Coatings. *Surf. Coat. Technol.* 2010, 204, 2483-2486.
- (13) Zhang, H.; Lamb, R.; Lewis, J., Engineering Nanoscale Roughness on Hydrophobic Surface—Preliminary Assessment of Fouling Behaviour. *STAM* 2005, 6, 236-239.
- (14) Wang, H.; Fang, J.; Cheng, T.; Ding, J.; Qu, L.; Dai, L.; Wang, X.; Lin, T., One-Step Coating of Fluoro-Containing Silica Nanoparticles for Universal Generation of Surface Superhydrophobicity. *Chem. Commun.* 2008, 7, 877-9.
- (15) Yang, H.; Jiang, P., Self-Cleaning Diffractive Macroporous Films by Doctor Blade Coating. *Langmuir* 2010, 26, 12598-604.
- (16) Furstner, R.; Barthlott, W.; Neinhuis, C.; Walzel, P., Wetting and Self-Cleaning Properties of Artificial Superhydrophobic Surfaces. *Langmuir* 2005, 21, 956-61.
- (17) Zimmermann, J.; Reifler, F. A.; Fortunato, G.; Gerhardt, L.-C.; Seeger, S., A Simple, One-Step Approach to Durable and Robust Superhydrophobic Textiles. *Adv. Funct. Mater.* 2008, 18, 3662-3669.
- (18) Zhu, Q.; Chu, Y.; Wang, Z.; Chen, N.; Lin, L.; Liu, F.; Pan, Q., Robust Superhydrophobic Polyurethane Sponge as a Highly Reusable Oil-Absorption Material. *J. Mater. Chem. A* 2013, 1, 5386.
- (19) Hasan, J.; Crawford, R. J.; Ivanova, E. P., Antibacterial Surfaces: the Quest for a New Generation of Biomaterials. *Trends Biotechnol.* 2013, 31, 295-304.
- (20) Chen, X.; Schluesener, H. J., Nanosilver: a Nanoproduct in Medical Application. *Toxicol. Lett.* 2008, 176, 1-12.
- (21) Daoud, W. A.; Xin, J. H.; Zhang, Y.-H., Surface Functionalization of Cellulose Fibers with Titanium Dioxide Nanoparticles and Their Combined Bactericidal Activities. *Surf. Sci.* 2005, 599, 69-75.
- (22) Noimark, S.; Allan, E.; Parkin, I. P., Light-Activated Antimicrobial Surfaces with Enhanced Efficacy Induced by a Dark-Activated mechanism. *Chem. Sci.* 2014, 5, 2216.
- (23) Roe, D.; Karandikar, B.; Bonn-Savage, N.; Gibbins, B.; Roulet, J. B., Antimicrobial Surface Functionalization of Plastic Catheters by Silver Nanoparticles. *J. Antimicrob. Chemother.* 2008, 61, 869-76.
- (24) Grass, G.; Rensing, C.; Solioz, M., Metallic Copper as an Antimicrobial Surface. *Appl. Environ. Microbiol.* 2011, 77, 1541-7.
- (25) Salgado, C. D.; Sepkowitz, K. A.; John, J. F.; Cantey, J. R.; Attaway, H. H.; Freeman, K. D.; Sharpe, P. A.; Michels, H. T.; Schmidt, M. G., Copper Surfaces Reduce the Rate of Healthcare-Acquired Infections in the Intensive Care Unit. *Infect. Control Hosp. Epidemiol.* 2013, 34, 479-86.
- (26) Ramsden, J. J., Photocatalytic Antimicrobial Coatings. *Nanotechnol. Percept.* 2015, 11, 146-168.

- 1  
2  
3  
4  
5  
6  
7  
8  
9  
10  
11  
12  
13  
14  
15  
16  
17  
18  
19  
20  
21  
22  
23  
24  
25  
26  
27  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60
- (27) Naik, A.J.T.; Ismail, S.; Kay, C.; Wilson, M.; Parkin, I. P., Antimicrobial Activity of Polyurethane Embedded with Methylene blue, Toluidine Blue and Gold Nanoparticles against *Staphylococcus aureus*; Illuminated with White Light. *Mater. Chem. Phys.* 2011, 129, 446-450.
- (28) Sehmi, S. K.; Noimark, S.; Bear, J. C.; Peveler, W. J.; Bovis, M.; Allan, E.; MacRobert, A. J.; Parkin, I. P., Lethal Photosensitisation of *Staphylococcus aureus* and *Escherichia coli* using Crystal Violet and Zinc Oxide-Encapsulated Polyurethane, *J. Mater. Chem. B*, 2015,3, 6490-6500.
- (29) Ozkan, E.; Allan, E.; Parkin, I. P., The antibacterial Properties of Light-Activated Polydimethylsiloxane Containing Crystal Violet. *RSC Adv.* 2014, 4, 51711-51715.
- (30) Noimark, S.; Bovis, M.; MacRobert, A. J.; Correia, A.; Allan, E.; Wilson, M.; Parkin, I. P., Photobactericidal Polymers; the Incorporation of Crystal Violet and Nanogold into Medical Grade Silicone. *RSC Adv.* 2013, 3, 18383.
- (31) Piccirillo, C.; Perni, S.; Gil-Thomas, J.; Prokopovich, P.; Wilson, M.; Pratten, J.; Parkin, I. P., Antimicrobial Activity of Methylene Blue and Toluidine Blue O Covalently Bound to a Modified Silicone Polymer Surface. *J. Mater. Chem.* 2009, 19, 6167.
- (32) Noimark, S.; Dunnill, C. W.; Kay, C. W. M.; Perni, S.; Prokopovich, P.; Ismail, S.; Wilson, M.; Parkin, I. P., Incorporation of Methylene Blue and Nanogold into Polyvinyl Chloride Catheters; a New Approach for Light-Activated Disinfection of Surfaces. *J. Mater. Chem.* 2012, 22, 15388.
- (33) Ozkan, E.; Crick, C. C.; Taylor, A.; Allan, E.; Parkin, I. P., Copper-Based Water Repellent and Antibacterial Coatings by Aerosol Assisted Chemical Vapour Deposition. *Chem. Sci.* 2016, 7, 5126-5131.
- (34) Berendjchi, A.; Khajavi, R.; Yazdanshenas, M. E., Fabrication of Superhydrophobic and Antibacterial Surface on Cotton Fabric by Doped Silica-Based Sols with Nanoparticles of Copper. *Nanoscale Res. Lett.* 2011, 6, 594.
- (35) Chung, J. S.; Kim, B. G.; Shim, S.; Kim, S. E.; Sohn, E. H.; Yoon, J.; Lee, J. C., Silver-Perfluorodecanethiolate Complexes Having Superhydrophobic, Antifouling, Antibacterial Properties. *J. Colloid Interface Sci.* 2012, 366, 64-9.
- (36) Shateri Khalil-Abad, M.; Yazdanshenas, M. E., Superhydrophobic Antibacterial Cotton Textiles. *J. Colloid Interface Sci.* 2010, 351 (1), 293-8.
- (37) Tang, H.; Wang, H.; He, J., Superhydrophobic Titania Membranes of Different Adhesive Forces Fabricated by Electrospinning. *J. Phys. Chem C* 2009, 113, 14220-14224.
- (38) Yamauchi, K.; Yao, Y.; Ochiai, T.; Sakai, M.; Kubota, Y.; Yamauchi, G., Antibacterial Activity of Hydrophobic Composite Materials Containing a Visible-Light-Sensitive Photocatalyst. *J. Nanotech.* 2011, 2011, 1-7.
- (39) Privett, B. J.; Youn, J.; Hong, S. A.; Lee, J.; Han, J.; Shin, J. H.; Schoenfisch, M. H., Antibacterial Fluorinated Silica Colloid Superhydrophobic Surfaces. *Langmuir* 2011, 27, 9597-601.
- (40) Chang, F.-M.; Hong, S.-J.; Sheng, Y.-J.; Tsao, H.-K., High Contact Angle Hysteresis of Superhydrophobic Surfaces: Hydrophobic Defects. *Appl. Phys. Lett.* 2009, 95, 064102.
- (41) Lu, Y.; Sathasivam, S.; Song, J.; Crick, C. R.; Carmalt, C. J.; Parkin, I. P., Repellent materials. Robust self-Cleaning Surfaces that Function When Exposed to either Air or Oil. *Science* 2015, 347, 1132-5.
- (42) Truong, V. K.; Webb, H. K.; Fadeeva, E.; Chichkov, B. N.; Wu, A. H.; Lamb, R.; Wang, J. Y.; Crawford, R. J.; Ivanova, E. P., Air-Directed Attachment of Cocci Bacteria to the Surface of Superhydrophobic Lotus-Like Titanium. *Biofouling* 2012, 28, 539-50.
- (43) Tuteja, A.; Choi, W.; Mabry, J. M.; McKinley, G. H.; Cohen, R. E., Robust Omniphobic Surfaces. *PNAS* 2008, 105, 18200-5.
- (44) Shang, B.; Wang, Y.; Peng, B.; Deng, Z., Bioinspired Polydopamine Particles-Assisted Construction of Superhydrophobic Surfaces for Oil/Water Separation. *J. Colloid Interface Sci.* 2016, 482, 240-51.
- (45) Wong, T. S.; Kang, S. H.; Tang, S. K.; Smythe, E. J.; Hatton, B. D.; Grinthal, A.; Aizenberg, J., Bioinspired self-repairing slippery surfaces with pressure-stable omniphobicity. *Nature* 2011, 477, 443-7.
- (46) Verdier, T.; Coutand, M.; Bertron, A.; Roques, C., Antibacterial Activity of TiO<sub>2</sub> Photocatalyst Alone or in Coatings on *E. coli*: The Influence of Methodological Aspects. *Coatings* 2014, 4, 670-686.
- (47) Komerik, N.; Wilson, M., Factors Influencing the Susceptibility of Gram-Negative Bacteria to Toluidine Blue O-Mediated Lethal Photosensitization. *J. Appl. Microbiol.* 2002, 92, 618-623.
- (48) Tortora, G.; Funke, R. B.; Case, L. C., *Microbiology; An Introduction*. Addison-Wesley Longman, Inc.: New York, 2001.
- (49) Fu, G.; Vary, P. S.; Lin, C. T., Anatase TiO<sub>2</sub> Nanocomposites for Antimicrobial Coatings. *J. Phys. Chem B* 2005, 109, 8889-98.
- (50) Zhao, L.; Chu, P. K.; Zhang, Y.; Wu, Z., Antibacterial Coatings on Titanium Implants. *J. Biomed. Mater. Res. B Appl. Biomater.* 2009, 91, 470-80.
- (51) Visai, L.; De Nardo, L.; Punta, C.; Melone, L.; Cigada, A.; Imbriani, M.; Arciola, C. R., Titanium Oxide

1  
2  
3  
4 Antibacterial Surfaces in Biomedical Devices. *Int. J. Artif. Organs* 2011, 34, 929-46.

5 (52) Hashimoto, K.; Irie, H.; Fujishima, A., TiO<sub>2</sub> Photocatalysis: a Historical Overview and Future Prospects.  
6 *Jpn. J. Appl. Phys.* 2005, 44, 8269-8285.

7 (53) Maisch, T., Resistance in Antimicrobial Photodynamic Inactivation of Bacteria. *Photochem. Photobiol. Sci.*  
8 2015, 14, 1518-26.

9 (54) Wang, G.; Liu, S.; Wei, S.; Liu, Y.; Lian, J.; Jiang, Q., Robust Superhydrophobic Surface on Al Substrate  
10 With Durability, Corrosion Resistance and Ice-Phobicity. *Sci. Rep.* 2016, 6, 20933.

11 (55) Wang, N.; Lu, Y.; Xiong, D.; Carmalt, C. J.; Parkin, I. P., Designing Durable and Flexible  
12 Superhydrophobic Coatings and Its Application in Oil Purification. *J. Mater. Chem. A* 2016, 4, 4107-4116.

13 (56) Luo, X.; Kim, J. H.; Ahn, J. Y.; Lee, D.; Kim, J. M.; Lee, D. G.; Kim, S. H., Electrospraying-Assisted Rapid  
14 Dye Molecule Uptake on the Surfaces of TiO<sub>2</sub> Nanoparticles for Speeding Up Dye-Sensitized Solar Cell  
15 Fabrication. *Sol. Energ. Mat. and Sol. Cells* 2016, 144, 411-417.

16 (57) Cech, J.; Taboryski, R., Stability of FDTS Monolayer Coating on Aluminum Injection Molding Tools. *Appl.*  
17 *Surf. Sci.* 2012, 259, 538-541.

18 (58) Barlow, S. M.; Raval, R., Complex Organic Molecules at Metal Surfaces: Bonding, Organisation and  
19 Chirality. *Surf. Sci. Rep.* 2003, 50, 201-341.  
20  
21  
22  
23  
24  
25  
26  
27  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60

## Table Legend

Table 1. water contact angle, rolling off angle, contact angle hysteresis, and surface roughness of untreated, white painted, blue painted, and violet painted surfaces.

## Figure Legends

Fig. 1 (a) white, blue, and violet paint solutions, and (b) the painted glass slides and SEM and AFM images of the painted glass samples

Fig. 2. UV-vis absorption spectra of an unpainted glass slide (control), and glass slides painted with white, blue, and violet paints. Absorption spectra were collected at wavelengths 400–900 nm.

Fig. 3. Water contact angle of control, and the painted glasses in (a) air and (b) hexadecane <sup>1</sup>WCA:  
Water Contact Angle

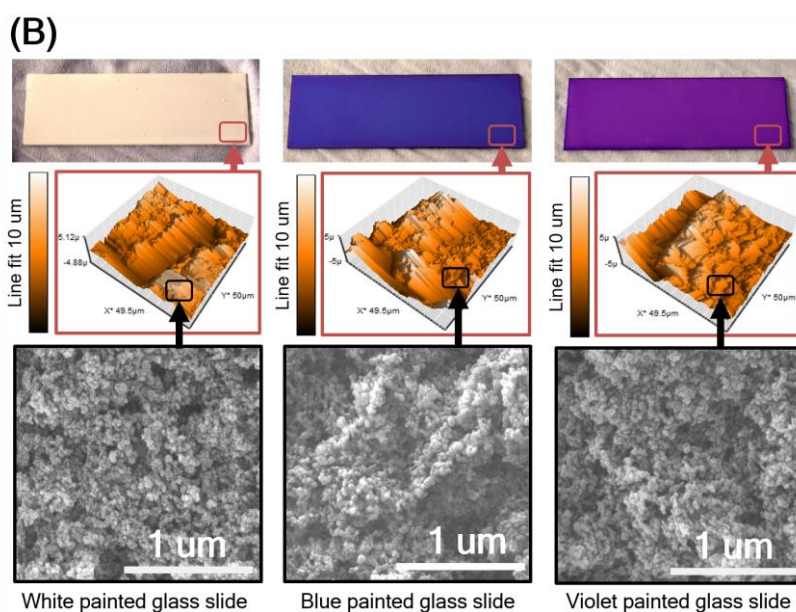
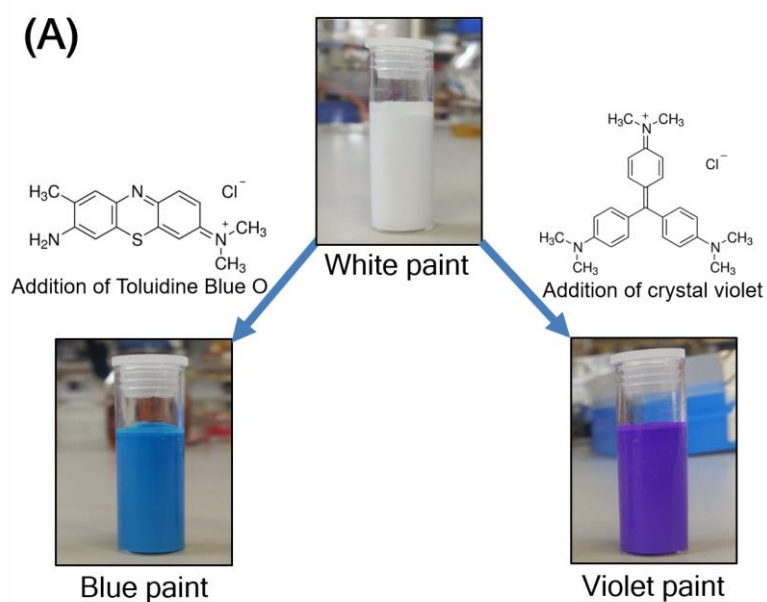
Fig. 4. Numbers of (a) *S. aureus* and (b) *E. coli* adhering to the surface of control, white, blue, and violet painted glass slides. The painted glass slides were immersed into bacterial solution for 3min.

Fig. 5. Bactericidal activity of unpainted glass slide (control) and white, blue, and violet painted glass slides against (a) *S. aureus* and (b) *E. coli*: samples inoculated with bacteria were exposed to light intensities ranging from 3900 to 5300 lx for 3 h and 4 h, respectively. In all tests, the temperature was maintained at a constant 20 °C.

Fig. 6. (a) Sand paper abrasion test of the paint and double side tape treated glass slides and (b) water repellent and stable tests of white, blue, and violet particles.

Table 1. water contact angle, rolling off angle, contact angle hysteresis, and surface roughness of untreated, white painted, blue painted, and violet painted surfaces.

Sample	Water contact angle (°)	Rolling off angle (°)	Contact angle hysteresis (°)	Surface roughness (Sa, nm)
Untreated surface (glass slide)	5.9 ± 0.6	n/a	n/a	5.1 ± 0.8
White painted surface	164.4 ± 2.2	0 ± 0	0.4 ± 0.5	1150.7 ± 610.5
Blue painted surface	163.6 ± 1.6	0 ± 0	0.8 ± 0.6	1046.1 ± 757.6
Violet painted surface	163.1 ± 1.8	0 ± 0	0.9 ± 1.0	1027.8 ± 61.9



47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60

Fig. 1 (a) white, blue, and violet paint solutions, and (b) the painted glass slides and SEM and AFM images of the painted glass samples

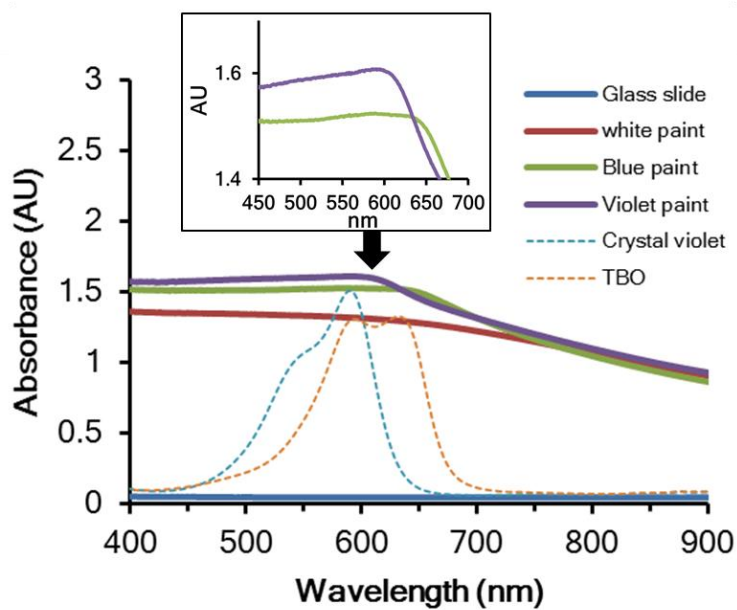


Fig. 2. UV-vis absorption spectra of an unpainted glass slide (control), and glass slides painted with white, blue, and violet paints. Absorption spectra were collected at wavelengths 400–900 nm.



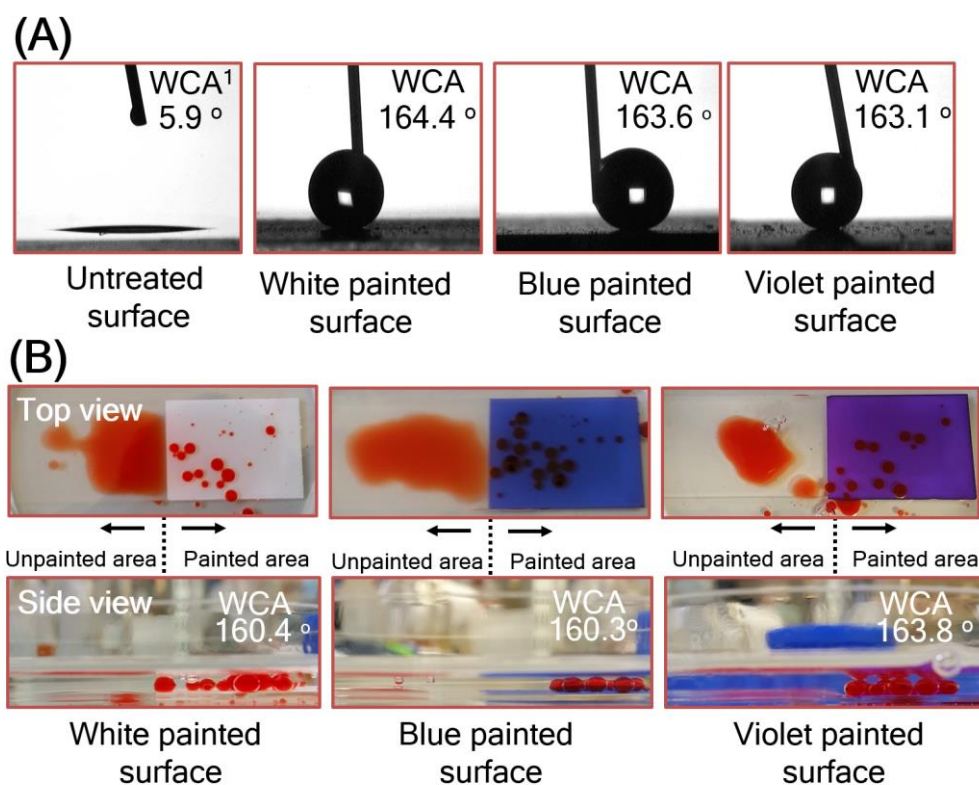


Fig. 3. Water contact angle of control, and the painted glasses in (a) air and (b) hexadecane

<sup>1</sup>WCA: Water Contact Angle

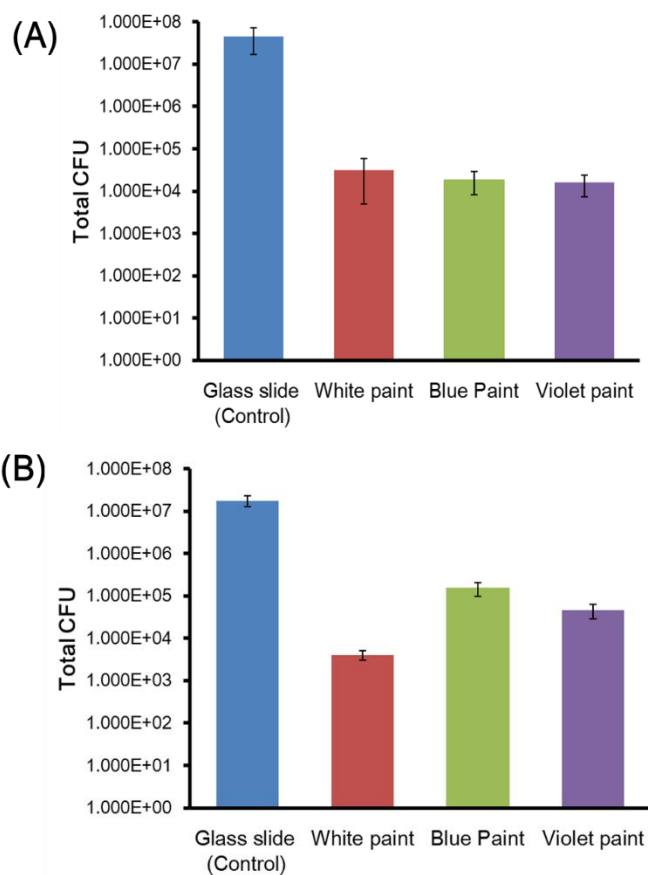


Fig. 4. Numbers of (a) *S. aureus* and (b) *E. coli* adhering to the surface of control, white, blue, and violet painted glass slides. The painted glass slides were immersed into bacterial solution for 3min.

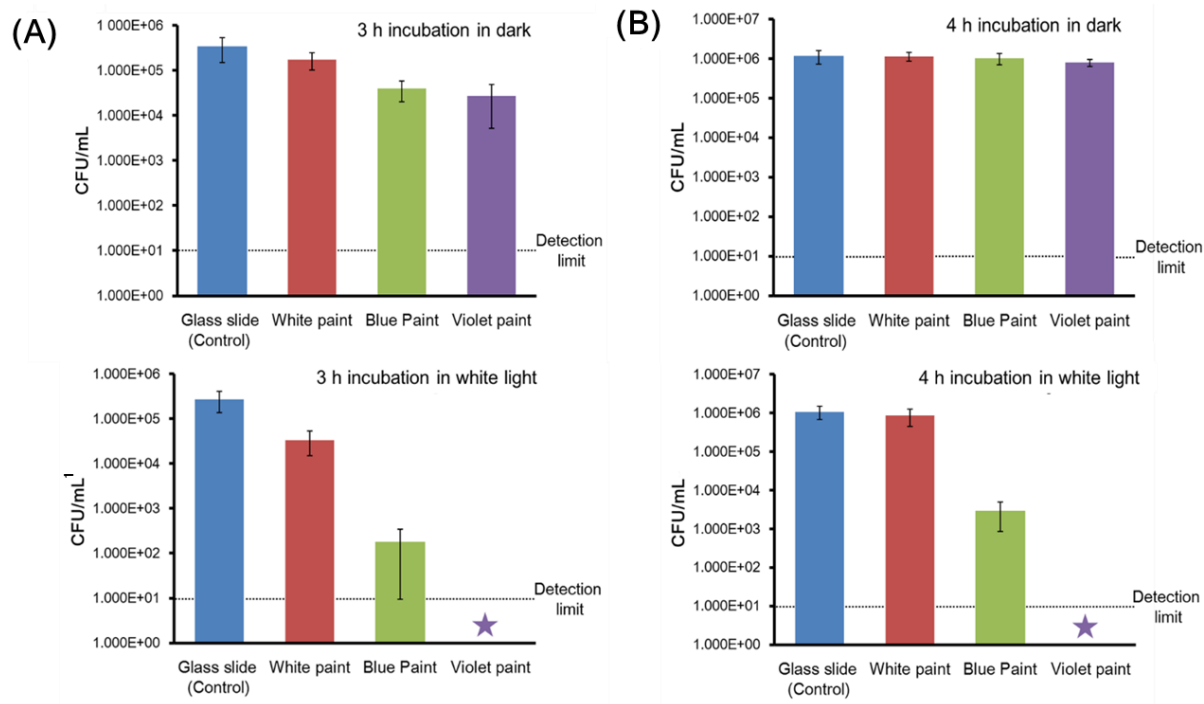


Fig. 5. Bactericidal activity of unpainted glass slide (control) and white, blue, and violet painted glass slides against (a) *S. aureus* and (b) *E. coli*: samples inoculated with bacteria were exposed to light intensities ranging from 3900 to 5300 lx for 3 h and 4 h, respectively. In all tests, the temperature was maintained at a constant 20 °C.

<sup>1</sup> Colony forming unit/ mL: Colony forming Unit (CFU) is derived from viable counting whereby a single bacterial colony is assumed to have arisen from a single bacterium

★ Detection limit: <10 CFU

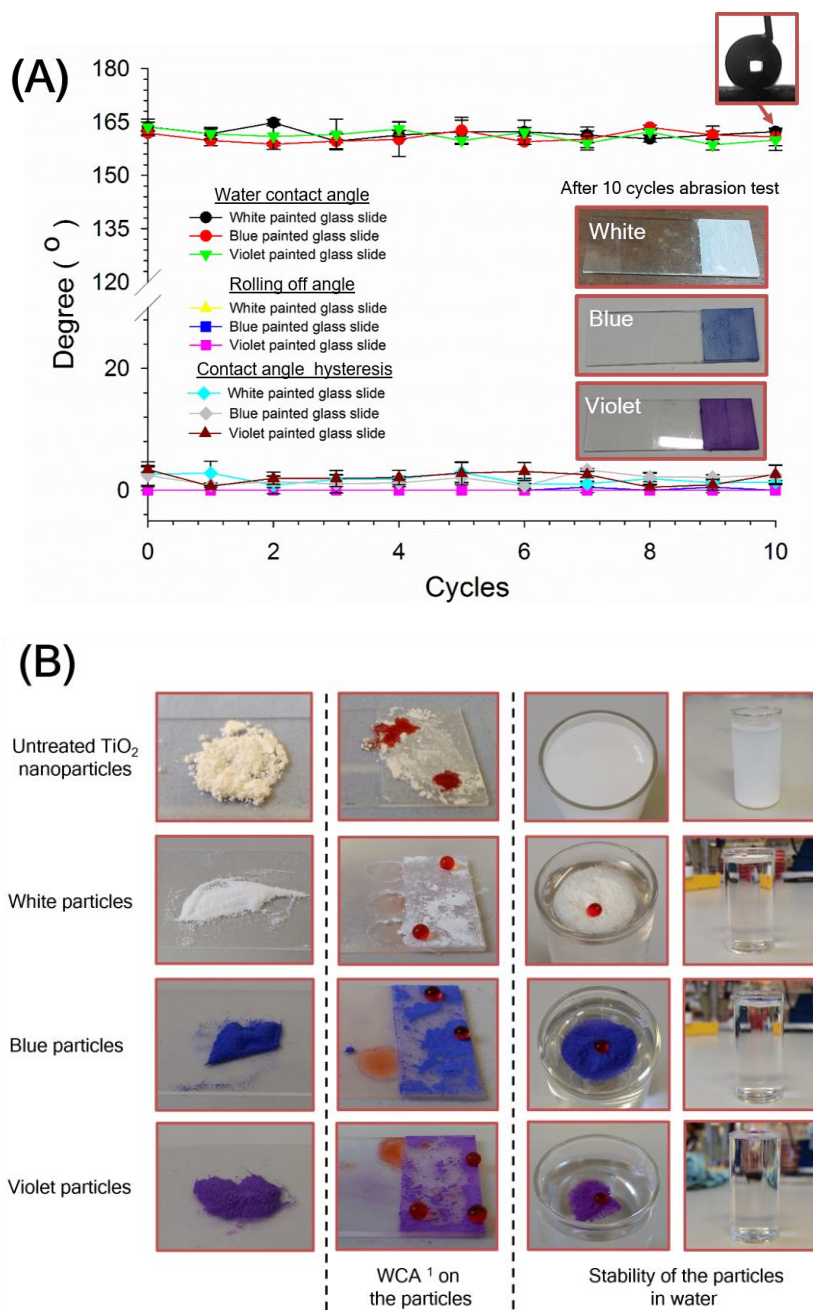


Fig. 6. (a) Sand paper abrasion test of the paint and double side tape treated glass slides and (b) water repellent and stable tests of white, blue, and violet particles.

<sup>1</sup>WCA: Water Contact Angle

## Graphical abstract

