

# Robust, Transparent and Self-healing Superamphiphobic Films

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**ABSTRACT:** The technological implementation of superamphiphobic surfaces has been largely hindered by their stability issues caused by surface abrasion, corrosion, contamination and *etc.* The contradictory requirement on both decent roughness and robustness is still remain the major challenge for a well-performing superamphiphobic coating. In this work, a simple route of spraying the inks containing designed silica building-blocks are presented to preparing superamphiphobic coatings. The as-made films exhibit excellent super-repellency to various

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3 liquids and also enhanced robustness. The static contact angles (SCAs) for water (surface  
4 tension 72.1 mN/m) and dodecane (surface tension 25.3 mN/m) can reach  $166\pm 3^\circ$  and  $153\pm 3^\circ$ ,  
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6 respectively. Through controlling thickness of the films, the optical transmittance of the films  
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8 (400 nm thick) is close to that of glass. The mechanical properties of the films are significantly  
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10 strengthened for titania modified silica coatings, which are able to withstand a standard 2H pencil  
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12 scratching and sand flow impact. Moreover, efficient decomposition of organic substance  
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14 attached on the surfaces by photocatalysis has been demonstrated which enables the recovery of  
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16 superamphiphobic property of the contaminated films. Thus, these unique properties, robustness,  
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18 transparency and self-healing, *etc.*, combined with the low cost fabrication, make the  
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20 superamphiphobic coatings promising in various applications.  
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28 Inspired by biological species, such as water-repellent plants, <sup>1</sup> water striders, <sup>2</sup> nepenthes, <sup>3</sup>  
29 butterfly, <sup>4</sup> dragonfly <sup>5</sup> and so on, <sup>6-8</sup> the fine micro-nano structure with super-repellent property  
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31 could exert tremendous and fascinated applications in self-cleaning, <sup>9</sup> anti-smudge, <sup>10</sup> anticorrosion,  
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33 <sup>11</sup> anti-icing, <sup>12</sup> heart-lung machines, <sup>13</sup> and *etc.* <sup>14-15</sup> A super-repellent surface can reject bulk  
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35 liquids being spread on it, which exhibits a large static contact angle (SCAs $>150^\circ$ ) and small  
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37 sliding angles (SAs  $< 10^\circ$ ). A superhydrophobic surface is super-repellent to water, and a  
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39 superamphiphobic surface is super-repellent to both water and oil. The main fundamentals of the  
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41 solid wetting phenomenon, including the Young's model, <sup>16</sup> the Wenzel's model, <sup>17</sup> the Cassie-  
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43 Baxter's model <sup>18</sup> and so on, <sup>19-21</sup> can roughly illustrate the principle of building super-repellent  
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45 surfaces. Hierarchical structures coated with low surface energy materials can render  
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47 superhydrophobic surfaces. However, simply roughened surface is not sufficient to create  
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49 superamphiphobic property because oils have much lower surface tensions than water. In order to  
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51 build a superamphiphobic surface, a special structure, such as over-hang structure, doubly re-  
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3 entrant structure,<sup>22</sup> must be developed. So far, there have been many reports claiming that  
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5 superamphiphobic surfaces were created.<sup>22-27</sup> However, the superamphiphobic performance of  
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7 these surfaces varies with the types of oil that could have different and relatively low surface  
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9 tensions ( $\gamma$ ), and deteriorates dramatically with extremely low  $\gamma$  oils. Very few reports claimed  
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11 that the surfaces could super-repel the liquids that possess the  $\gamma$  as low as 25.3 mN/m  
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13 (dodecane) on the non-fabric flat substrates simply by building a special over-hang structure<sup>22-</sup>  
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To realize the technological application of superamphiphobic surfaces, three challenges need to be  
tackled. Firstly, aforementioned micro-nano over-hang structure<sup>22, 28</sup> must be built, which ensures  
high SCAs for liquids. Many methods,<sup>23, 27, 29-39</sup> such as etching, photolithographic, laser  
patterning, electrospinning, electrodeposition, templating, spray-coating, etc., have been utilized to  
construct superamphiphobic films. It is worth to note that using a low-cost, simple, efficient and  
facile process is essentially required for large scale production of the superamphiphobic films.  
Spraying coating, as a widely used film deposition technique in industry, could meet these  
requirements, if a specially-designed particles suspension deposition procedure is used. Different  
sized TiO<sub>2</sub> nanoparticles mixture (~60-200 nm and ~21 nm),<sup>38</sup> raspberry-like polymer particles,<sup>40</sup>  
silica nanotubes,<sup>41</sup> have been used to preparing over-hang structures. Secondly, the mechanical  
robustness for the films must be enhanced, which needs to withstand possible scratches and  
abrasions. In spite of the obvious advantages of spraying technology that can easily form delicate  
micro-nano structures via layer by layer construction, the adhesions between the film and the  
substrate and also inter-particles are particularly weak if without treatment. To date, the  
fluorinated polymers or other organic monomers are used as the binders to improve the

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3 mechanical property, <sup>25-26, 42-43</sup> which are not suitable for the long-term outdoor applications due  
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5 to the organic aging. Inorganic adhesives <sup>44</sup> are rarely used due to their high energy barrier of  
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7 covalent bonding; however, they are less susceptible to the property degradation in the outdoor  
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9 environment. Finally, the superamphiphobic films must have a long-term stability against  
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11 atmospheric contamination. Since the superamphiphobic surfaces are theoretically repellent only  
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13 to bulk liquids, tiny organic pollutants contained in the floating fog and smoke could attach to the  
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15 superamphiphobic surfaces, therefore altering the surface energy and gradually worsening super-  
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17 repelling performance. Applying photoactive agent, <sup>45-48</sup> such as TiO<sub>2</sub>, to the surfaces could  
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19 improve the stability against pollutants through photo decomposition of organic  
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21 contaminants, which provides self-healing ability to superamphiphobic surfaces.  
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28 Herein, this paper presents a simple and facile method to prepare the superamphiphobic films by  
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30 spray deposition of pre-designed silica building blocks. <sup>49</sup> By adjusting the degree of  
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32 agglomeration of the nano-SiO<sub>2</sub> particles, the over-hang structure of nanoparticles was obtained  
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34 and the resultant films show the SCAs as high as 153° for dodecane and 166° for water after the  
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36 films were fluorinated. The thickness of the films can be altered to maintain the  
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38 superamphiphobic property and simultaneously high transparency to the extent of over 89%. The  
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40 robustness of the film is enhanced to 2H hardness pencil scratching ((ASTM) D3363) after  
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42 incorporation of titania as the bolting crystal for the silica matrix. Moreover, we also demonstrate  
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44 the interesting self-healing phenomenon of the contaminated superamphiphobic surfaces after a  
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46 period of illumination under 1 sun solar simulator. The enhanced mechanical property, high  
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48 transparency and self-healing ability of superamphiphobic films could be attractive in many  
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50 applications in the future.  
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## 57 **RESULTS AND DISCUSSION**

## Film building-blocks and Superamphiphobic Coatings

For the porous films, the static contact angle,  $\theta^{\text{app}}$  ( $\theta^{\text{app}}$  is the apparent contact angle on the surface) can be explained by the Cassie model, whose equation has recently been rewritten as follows: 50

$$\cos\theta = f \cos\theta - 1 + (1)$$

where  $f$  is the fraction of the projected area of the solid surface in contact with the liquid,  $r_f$  the roughness of the solid surface that is in contact with water, and  $\theta$  the equilibrium contact angle on a smooth surface. To produce a superamphiphobic film with over-hang and continuous pore structure, one of the key issues is to produce a small  $f$  surface<sup>50</sup>. It was found that the nanoparticles with a certain degree of agglomeration in spray ink could serve as effective “building blocks” for stacking and reforming as desired micro-nano structure. The transmission electron microscopy (TEM) morphologies of the coatings prepared by spraying the inks containing the so-called “building blocks” are demonstrated in Figure 1 (a) to (e). Their morphologies vary from mono-dispersed nano spheres to spongia-like agglomerates. The sample P0 demonstrates spherical particles with the diameter of about 40-50 nm. These spherical particles were well dispersed in ethanol with no significant inter-particle connections. Adding CTAB surfactant into the solution at the beginning of the reaction between tetraethylorthosilicate (TEOS) and ammonium solution will result in the hydrophilic heads of CTAB attaching the formed SiO<sub>2</sub> nucleus and the hydrophobic tails connecting each other and therefore the agglomerates generate. The more CTAB in the system, the larger size the agglomerates would be. When 0.05g CTAB was added into the solution, the diameter of the particles (P1) in the coating was reduced to 10-20 nm (Figure 1 (b)), which could be attributed to the surfactant CTAB coated

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 3 on the SiO<sub>2</sub> nucleus via the interaction between the hydroxy groups of SiO<sub>2</sub> and the hydrophilic  
 4 ammonium head of the CTAB, refraining the SiO<sub>2</sub> particles from further growing up. Samples  
 5 P1-P3 present many nanoparticles (10-20 nm) agglomerating together into a spongia-like  
 6 structure, and the size of these particle agglomerates in the coatings increases (see the red dotted  
 7 circles) with the CTAB content in the spray inks and they are about 100-500 nm (Figure 1 (b),  
 8 P1), 0.5-1.5 μm (Figure 1 (c), P2), 2-4 μm (Figure 1 (d), P3), respectively. Further increasing  
 9 CTAB the silica particles become even larger blocks with the size of the agglomerates  
 10 approaching 5 μm (Figure 1 (e), P4). Figure 1 (f) shows the schematic diagram of the prepared  
 11 superhydrophobic and superamphiphobic surfaces. When spraying the inks with the different  
 12 degrees of agglomeration, the nanostructures of the films are quite different. The nanoparticles  
 13 are agglomerated together becoming micro particles, and when these agglomerated particles are  
 14 sprayed on the substrate, the micro-nano over-hang structures are constructed. For the  
 15 superamphiphobic films, the formation of micro-nano over-hang structure is a key point.  
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35 The SCAs of liquids having the different surface tensions on the as-made films are shown in Figure  
 36 2 (a). These liquids include water, glycol, oleic acid, hexadecane and dodecane with the surface  
 37 tensions of 72 mN/m, 48.4 mN/m, 33.8 mN/m, 27.3 mN/m and 25.3 mN/m respectively. It was  
 38 found that the SCAs of the liquids decrease with the decrease of surface tension ( $\gamma$ ) from water to  
 39 dodecane. The SCAs of these liquids on the glass (G) are all less than 90°, but on the PFTS-coated  
 40 glasses (PFTS=1H, 1H, 2H, 2H-perfluorodecyltrichlorosilane), the SCAs of these liquids increase  
 41 obviously, with the highest value of 114° for water (Sample F/G in Fig 2 (a)). As shown in the  
 42 Figure 2 (a) (yellow dotted box), the F/P0 film only has the super-repellence for water,  $\theta_{appwater}$   
 43 =163±3°; F/P1 film is super-repellent both to water and glycol,  $\theta_{appwater}$  =164±3°,  $\theta_{appglycol}$  =152±3°;  
 44 F/P2 film has the good superamphiphobic property for water, glycol and oleic  
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3 acid,  $\theta_{\text{appwater}} = 165 \pm 3^\circ$ ,  $\theta_{\text{appglycol}} = 162 \pm 3^\circ$ ,  $\theta_{\text{appoleic acid}} = 157 \pm 3^\circ$ ; It needs to be noted that F/P3 film shows  
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5 excellent superamphiphobic property for all liquids (see the red dotted box),  $\theta_{\text{appwater}} = 166 \pm 3^\circ$ ,  
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8  $\theta_{\text{appglycol}} = 164 \pm 3^\circ$ ,  $\theta_{\text{appoleic acid}} = 162 \pm 3^\circ$ ,  $\theta_{\text{apphexadecane}} = 161 \pm 3^\circ$ ,  $\theta_{\text{appdodecane}} = 153 \pm 3^\circ$ . From the film F/P0 to the  
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10 film F/P3, the SCAs of the same liquids increase. The improved superamphiphobic properties are  
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12 probably due to the generation of micro-nano over-hang topographies of films prepared by using  
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14 different silica building blocks.  
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18 Figure 2 (b)-(f) shows the SEM images of the films made by spray-coating the particles P0-P4,  
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20 respectively. The insets in Figure 2 (b)-(f) show the SEM images of the corresponding films  
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22 with higher amplification. The morphology of the films becomes rougher from the films F/P0 to  
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24 F/P3. It is observed that Film F/P0 has the cracks (Figure 2 (b)), which is due to the violent  
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26 vaporization of ethanol after the film was sprayed on the substrate. The temperature of the  
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28 substrate during coating could generate thermal stress in the films and thus influence the  
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30 topography of the films (Figure S1-S2). The best substrate temperature is found to be 200 °C.  
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32 The SEM image of the film F/P0 (Figure 2 (b) inset) shows that the film is composed of many  
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34 nano spherical particles that are closely packed. The film F/P1 (Figure 2 (c)) possesses a similar  
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36 morphology to F/P0 at low magnification and also shows the cracks. However, the observation  
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38 by high magnification SEM reveals that a refined nanostructure with pore channels starts to form.  
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40 It is observed that the film F/P2 (Figure 2 (d)) has no cracks, which is because the holes  
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42 generated in the SiO<sub>2</sub> agglomeration are larger than those holes observed in the films F/P0 and  
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44 F/P1, and the vapor could escape from the holes and thus the thermal stress is released in the  
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46 porous film. The pores in the film F/P3 and over-hang structure (dotted red circles in Figure 2  
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48 (e)) can be obviously observed in Figure 2 (e). It is also observed that the over-hang structure is  
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50 composed of many small SiO<sub>2</sub> nanoparticles in F/P3 that were not observed in the samples F/P0,  
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3 F/P1 and F/P2. The formation of over-hang structure is due to, firstly, the micro-size  
4 agglomerates, and secondly, the removal of CTAB. Although micro-size holes were formed in  
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6 the film F/P4 (Figure 2 (f)), the large blocks of agglomerated nanoparticles could not  
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8 completely cover the substrate and nano particles structure is too large so that the low surface  
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10 tension liquids can easily penetrate to the bottom of the film, leading to the fact that the film  
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12 F/P4 can only super-repel water. It is conspicuous that the morphologies of the 5 films are  
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14 different from each other, which can be attributed to the variation of CTAB content and the  
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16 difference of resultant microstructures in the silica building blocks. As shown in Figure 1, the  
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18 degree of the particle agglomeration is enhanced when more CTAB are added. The bigger  
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20 chunks of particles in the SiO<sub>2</sub> building-blocks are the easier to form micron-sized porous  
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22 films. At the same time, the removal of CTAB that entangled with silica can also produce nano  
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24 holes in the films. The best superamphiphobic film F/P3 should be ascribed to the addition of  
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26 proper amount of CTAB, which results in the proper degree of agglomeration of SiO<sub>2</sub>  
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28 nanoparticles. The SEM cross section image (Figure S3) of the films F/P0 – F/P3 and stylus  
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30 profiler curves (Figure S4) obviously show more micro-nano over-hang structures of the  
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32 surfaces in F/P3, which allows more air trapped in this film, resulting in a smaller value of the  $f$   
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34 in Equation (1). In the case of the same liquid, the smaller value of the  $f$  will lead to larger  $\theta^{\text{app}}$   
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36 when the  $r_f$  remains no change in Equation (1).  
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### 47 **Highly Transparent Superamphiphobic Films**

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50 High transparency of the superamphiphobic films enables them to find applications in visual  
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52 windows in buildings, cars, displays and etc. However the designed micro-nano over-hang  
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54 structure that brings film roughness normally causes intensive light scattering, which greatly  
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56 reduces the transparency. Although the thicknesses of the films P0-P4 are all about 5  $\mu\text{m}$  (Figure  
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3 S3), the transmittance of the films is widely various (Figure S5 and S6). According to Uv-Vis  
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5 measurements (Figure S6), the transmittance of the films P0, P1, P2, P3 and P4 are about 89.3%,  
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7 90.4%, 80.4%, 73.6%, and 81%, respectively. Film P3 has the lowest transmittance, which can  
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9 be attributed to its special micro-nano over-hang structure, in which small particles agglomerate  
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11 forming micron-size particles and many holes inside resulting in strong light scattering, though it  
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13 shows the best superamphiphobic performance among all the films.  
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18 To improve the transmittance of the film P3, the thickness of the film P3 was reduced by using  
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20 the diluted spraying ink. Figure 3 (a) shows the images of the as-made superamphiphobic films  
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22 that have different thicknesses and have water (containing methyl blue), olive oil (yellow),  
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24 hexadecane, dodecane drops on top of them. The Uv-vis characterization (Figure 3 (b)) suggests  
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26 that the average transmittance between wavelength 350nm to 800nm is 89% for P3-C1 (395 nm  
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28 thick), which is very close to the glass substrate, 90.3%. Only P3-C4 (3559 nm thick) can super-  
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30 repel the low surface tension liquid, dodecane, with transparency up to 73.6%. The detailed data  
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32 of SCAs results are shown in Figure 3 (c). It can be noticed that the highly transparent samples  
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34 can still be superamphiphobic for water (blue) and olive oil (yellow) with very low haze (Figure  
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36 3 (c)).  
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43 As shown in Figure 3 (d), the average film thickness is 395nm, 1595nm, 2491nm, and 3559nm  
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45 for P3-C1, P3-C2, P3-C3 and P3-C4, respectively. The film thickness increases with SiO<sub>2</sub>  
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47 content in the spraying ink because in every single fog drop in spraying liquid contains more  
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49 SiO<sub>2</sub> particles. Using the inks with higher SiO<sub>2</sub> particle content would also result in more SiO<sub>2</sub>  
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51 particles compiling in the same area leading to larger roughness. Figure 3 (d) shows that the  
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53 average height of the peaks is ~486 nm for film P3-C1, ~2,072 nm for film P3-C2, ~4,473 nm  
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55 for film P3-C3, ~6,300 nm for film P3-C4, respectively. The average interval of the peaks is  
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3 ~21.3 Jim, ~23.4 Jim, ~ 21.4 Jim, ~20.62 Jim for the films P3-C1, P3-C2, P3-C3, P3-C4,  
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5 respectively. There would have more air trapped in the films that have higher peaks and more  
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7 over-hang structures. The liquids are harder to penetrate the thicker films and reach to the bottom  
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9 if the film possesses stronger peaks in over-hang structure, which also results in larger light  
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11 scattering and less transparency.  
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### 16 **Robust and Self-healing Superamphiphobic Films**

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19 In outdoor environment, superamphiphobic surfaces need to survive harsh conditions, like sand  
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21 abrasion by wind and the adsorption of small organic molecules, which can change the  
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23 roughness and the surface tension of the film leading to the loss of efficacy. In order to improve  
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25 the mechanical properties of the films, titanium diisopropoxide bis 2, 4-pentanedionate (TAA) was  
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27 added to the SiO<sub>2</sub> system to act as a binder of SiO<sub>2</sub> particles after it was pyrolysed. The films  
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29 obtained with the addition of different TAA are referred as P3-T0, P3-T1, P3-T2, P3-T3 and P3-  
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31 T4 (see Experimental for details). To investigate the mechanical resistance of the films with the  
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33 addition of TAA, sand abrasion test (Figure 4 (a)-(c)) and pencil test (Figure 4 (d)) were  
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35 performed. Sand grains (200g, 10g/s) with a diameter of 0.6 to 0.8 mm impinged the P3-T3  
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37 surface from a height of 24 cm. Figure 4 (b) and (c) are the microscope images of the films P3-T0  
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39 (without TAA) and P3-T3 after sand abrasion. The film P3-T0 after the abrasion test was partially  
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41 peeled off (the red dotted circles in Figure 4 (b)), indicating that the P3-T0 silica surfaces were not  
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43 sufficiently robust to withstand the impact of sand abrasion. The mechanical property of the film  
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45 P3-T3 was greatly improved, with only a small impact on the film being observed (Figure 4 (c),  
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47 the red dotted circles). However, although the films partially destroyed by the sand abrasion, the  
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49 superamphiphobic property of the films is intact with  $\theta^{\text{app}}_{\text{olive oil}} = 156^\circ$  (Figure 4 (b)),  $\theta^{\text{app}}_{\text{olive oil}} =$   
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51  $154^\circ$  (Figure 4 (c)). Figure 4 (d) shows the curves of stylus profiler of  
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3 the pencil scratch on the films P3-T0, P3-T1, P3-T2, P3-T3, and P3-T4, respectively. The pencil  
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5 scratches left obvious marks on the films P3-T0, P3-T1, P3-T2. The marks by pencil scratch on  
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7 the films P3-T3 and P3-T4 could not be obviously observed while film P3-T0 was totally  
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9 scraped off (see the Figure S7 and S8), indicating that the mechanical strength of the films was  
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11 improved upon the addition of the appropriate amount of TiO<sub>2</sub> binder.  
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16 Furthermore, the inclusion of TiO<sub>2</sub> adds photocatalytic ability which enables recoverability of the  
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18 superamphiphobic films degraded by organic contamination. Figure 4 (e) shows the Uv-vis curves  
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20 of the film P3-T3 with and without methylene blue (Mb and 0 Mb) after photocatalytic  
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22 decomposition of Mb for different illumination time (0-90 min). The spectral absorption (500-600  
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24 nm) of Mb was weakened when the time of the light exposure prolongs. Figure 4 (f) is the image  
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26 and SCAs of the water and olive oil on the different P3-T3 films (0 Mb, 0 min, 90 min). The  
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28 SCAs of the water and olive oil on the P3-T3 without Mb (0 Mb) is 163° and 159°, respectively.  
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30 However when the P3-T3 film coated with Mb, the liquid-repellent property decreases and  
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32 therefore the superamphiphobic ability losses,  $\theta_{\text{appwater}}^{\text{app}}=102^\circ$ ,  $\theta_{\text{olive oil}}^{\text{app}}=66^\circ$ , which is attributed to  
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34 the contamination of the surface. The photocatalytic TiO<sub>2</sub> can decompose the small hydrocarbon  
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36 materials, and after the illumination for 90 min, the Mb almost totally disappears. The most  
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38 important phenomenon is that the superamphiphobic property was fully recovered,  $\theta_{\text{appwater}}^{\text{app}}=160^\circ$ ,  
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40  $\theta_{\text{olive oil}}^{\text{app}}=154^\circ$ . This excellent self-healing property is very practical for outdoor environment  
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42 where micro/nano organic pollutants are adsorbed on the surface.  
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50 Figure 5 (a) is the SEM image of the film P3-T3. It shows the basic over-hang structure still  
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52 existing on the surface of the film after the addition of TAA. Its low and high resolution TEM  
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54 images show the edge of the big particles (red dotted blocks) in Figure 5 (b). The calculation  
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56 from the distinct lattice fringes shows that the distance between the two crystal planes is about  
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3 0.350 nm, which is the (101) face of anatase. There are many similar small black particles around  
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5 the big particles, which are assigned to anatase (yellow dotted circles) in the TEM images. The big  
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7 particles are surrounded by the nano-TiO<sub>2</sub> particles, and the diameter of the nano-anatase is about  
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9 10-20 nm (yellow dotted circles). Such configuration is effective to improve the  
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11 mechanical property of the superamphiphobic film. The superamphiphobic properties will be  
12  
13 decreased if too much TAA are added because the holes previously existed in the film (Figure  
14  
15 5(a)) will be filled with the small anatase particles, which decreases the volume of the over-hang  
16  
17 structure. The P3-T3 film is found to be able to super-repel both water and oils, but the film P3-  
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19 T4 with more addition of TAA can super-repel only water (Figure S9). Hence, appropriate  
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21 amount of the bolting titania is crucial to obtain robust and superamphiphobic films.  
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28 Figure 5 (c) shows the schematic diagram of how the mechanical properties of  
29  
30 superamphiphobic films are strengthen and how photocatalytic function performs by the addition  
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32 of anatase. The superamphiphobic films are sintered at 550 °C, at which temperature SiO<sub>2</sub> cannot  
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34 be sintered, however, this temperature is high enough to crystallize TiO<sub>2</sub> so that it can help bolt  
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36 SiO<sub>2</sub> particles together as shown in Figure 5 (c), which leads to the increase of the mechanical  
37  
38 property of the films. TiO<sub>2</sub> can also act as a photocatalyst to assist the decomposition of organic  
39  
40 contaminants attached on the superamphiphobic surfaces. When the TiO<sub>2</sub> absorbs UV light,  
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42 electron-hole pairs will be generated, which will oxidize the organic substances on the  
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44 superamphiphobic surfaces, resulting in the decomposition of the organic contaminant.  
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50 The superhydrophobic windows have the potential applications as self-cleaning surfaces. Film  
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52 P1 and a plain glass slide were both placed in outdoor environment for 30 days. Figure S10  
53  
54 shows the results of the self-cleaning tests. It has shown that after test in smoggy weather in  
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56 Wuhan, the glass was covered with dirt while the P1 film is still clean and remains  
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3 superhydrophobic property. And the spray-coating method is easy for large scale production of  
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5 the superamphiphobic films. A demonstration of 10\*10 cm glass with superhydrophobic coating  
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7 (Figure S11) shows well super repellent property to water (added methyl blue), yoghurt,  
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9 perhydrol, sulfuric acid, glycerol, oleic acid, olive oil, and diiodomethane drops, and also  
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11 extremely high transparency and homogeneity is obtained.  
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## 19 **CONCLUSIONS**

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22 In summary, we present a facile route by spraying the inks containing the micro-sized silica  
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24 agglomerates, a designed-structure building block, on glasses to form superamphiphobic films  
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26 that possess robust, transparent and self-healing properties. The morphology, the degree of  
27  
28 agglomeration, organic/inorganic ratio and particle size of the prepared silica building-blocks  
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30 are adjusted by the amount of CTAB added in the precursor solution, which are crucial for  
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32 obtaining low f factor and thus large SCAs for liquids. Optimized films demonstrated  
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34 superamphiphobic properties. The best film could super-repel the oil with the surface tension as  
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36 low as 25.3mN/m, and its SCA for water as high as 166°. For a film with the average thickness  
37  
38 395 nm, its transmittance can be as high as 89% close to that of glass substrates (90.3%).  
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41 Furthermore, the introduction of inorganic binder of crystallized anatase can help cement silica  
42  
43 building blocks, which largely improves the mechanical property of the film (withstanding 2H  
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45 pencil test). Moreover this unique nano structure also provides a photocatalytic property and can  
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47 decompose organic contaminants upon exposing to lighting.  
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## 54 **EXPERIMENTAL SECTION**

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## Materials

Tetraethylorthosilicate (TEOS), cetyltrimethylammonium bromide (CTAB, > 99%), ethanol (> 99.7%), olive oil, oleic oil, ammonia solution (25%-28%), hexane (> 97%), glycol, methylene blue were obtained from Sino Pharm Chemical Reagent Co. Ltd. Dodecane (>99%), hexadecane (98%), 1H,1H,2H,2H-perfluorodecyltrichlorosilane(PFTS) were purchased from Aladdin. Titanium diisopropoxide bis 2, 4-pentanedionate (TAA, 75wt% in isopropyl alcohol) was obtained from Alfa Aesar. All of the mentioned reagents were used as received.

## Experimental procedure

*Preparation of Different Agglomerated Silica Nanoparticles:* a certain amount of CTAB was dissolved in a mixed solution composed of 4 mL ammonia solution and 80 mL ethanol. The mixture was stirred with a magnetic stirrer for 5 min till the CTAB was fully dissolved. 2 ml of TEOS was dissolved in 80 ml ethanol. This TEOS solution was quickly dripped into the CTAB solution. The resulting mixture was stirred at 40 °C for 12 h. The obtained solid-liquid mixture was dried in air at 80 °C for 12 h. SiO<sub>2</sub> particle agglomerates with 5 different sizes were obtained by using the different amounts of the CTAB (0 g, 0.05 g, 0.15 g, 0.25 g and 0.35 g) and denoted as P0, P1, P2, P3 and P4, respectively.

*Preparation of Different Superamphiphobic Films:* The obtained (P0, P1, P2, P3 and P4) SiO<sub>2</sub> particle agglomerates (0.3 g) were ultrasonically dispersed in 35 ml ethanol solution, respectively. Soda-lime-silica glasses were used as substrates that were washed with ultrapure water and ethanol. The cleaned substrates were heated to about 200 °C, and then 4 ml of ultrasonically-dispersed SiO<sub>2</sub> particles ink were sprayed onto an area of 2.5 x2.5 cm<sup>2</sup> substrate at a distance of

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3 15 cm at a rate of 4 ml/min. The coated glass substrates were sintered in air at 550 °C for 1 h  
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5 and cooled naturally. The coated substrates after sintered were dipped into hexane solution  
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7 containing 1 wt% PFTS for 1 min, dried naturally in air for 30 min and then the coated  
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9 substrates were put onto a heating platform at 420 °C for 3 min to volatilize redundant PFTS.  
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13 *Prepare Different Transparent Superamphiphobic Films:* A certain amount of P3 particles (0.05  
14 g, 1.8 wt%; 0.1 g, 3.6 wt%; 0.2 g, 7.2 wt% and 0.3 g, 10.8 wt%) were ultrasonically dispersed in  
15  
16 35 ml ethanol, and the spraying and fluorinating processes are the same as mentioned above.  
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18 The obtained films were denoted as P3-C1, P3-C2, P3-C3, P3-C4, respectively. Furthermore, in  
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20 order to enhance the robust of the films, P3 particles (0.3 g) were ultrasonically dispersed in 35  
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22 ml ethanol, and then a certain amount of TAA (0, 200  $\mu$ l, 400  $\mu$ l, 600  $\mu$ l, 800  $\mu$ l) were added in  
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24 4 ml P3 particles in ethanol before spraying. The obtained films were denoted as P3, P3-T1, P3-  
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26 T2, P3-T3, P3-T4, respectively.  
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33 *Characterization of the Coatings:* The morphologies of the particles and the films were  
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35 examined with transmission electron microscope (TEM, JEM-2100F STEM/EDS), scanning  
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37 electron microscope (SEM, ULTRA PLUS-43-13) and optical microscope (Olympus BX51).  
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39 The contact angle of various liquids on the films was measured by Contact Angle tester (Theta  
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41 Lite, Biolin Scientific) in the sessile mode at room temperature. The model of the stylus profiler  
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43 is Dektakxt. The transmittance of the films was measured by the ultraviolet and visible  
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45 spectrophotometer (Uv-Vis, PerkinElmer). The pencil scratching test was carried out using a  
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47 Pencil Hardness Tester according to the State Standard Testing Method (GB/T6739-1996,  
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49 equivalent of American Society for Testing and Materials (ASTM) D3363). The pencil was held  
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51 firmly against the film at a 45° angle and pushed forward by the tester at a speed of 0.5 mm/s.  
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3 The light source for photocatalytic degradation is from the Class AAA Solar Simulators  
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5 (94023A, Newport).  
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## 10 11 12 **FIGURES CAPTIONS**

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15 **Figure 1.** (a), (b), (c), (d), and (e) are the TEM images of the as-obtained particles P0, P1, P2, P3  
16 and P4 on carbon nets, respectively. P0 contains spherical particles (40-50 nm), P1-P3 contain the  
17 spongia-like agglomerates of SiO<sub>2</sub> nanoparticles (10-20 nm). P4 contains larger agglomerates  
18 (red dotted circles) of SiO<sub>2</sub> nanoparticles (200 nm); (f) the schematic diagram of prepared  
19 superhydrophobic and superamiphiphobic surfaces. The different sized nanoparticles create  
20 different sized agglomerates, which wereobtained by adjusting the content of CTAB. The  
21 resultant films are either superhydrophobic or superamiphiphobic.  
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33 **Figure 2.** (a) the SCAs of different liquids: Water, Glycol, Oleic acid, Hexadecane, Dodecane on  
34 glass (G), PFTS coated glass (F/G), PFTS/P0 coated glass (F/P0), PFTS/P1 coated glass (F/P1),  
35 PFTS/P2 coated glass (F/P2), PFTS/P3 coated glass (F/P3), PFTS/P4 coated glass (F/P4); (b), (c),  
36 (d), (e), and (f) the low and high amplification (the insets on top right corner) SEM images of the  
37 as-obtained films F/P0, F/P1, F/P2, F/P3, F/P4, respectively; (g) the picture of the liquid droplets  
38 on the F/P3 film (water was added methyl blue to improve the comparison).  
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48 **Figure 3.** Optical measurements of the films: P3-C1, P3-C2, P3-C3 and P3-C4, (a) Optical  
49 pictures of the liquids, water (added methyl blue) and olive oil (yellow), hexadecane, dodecane  
50 on the superamiphiphobic glasses ; (b) Transmittance of the surfaces; (c) SCAs of the different  
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3 liquids on the surfaces; (d) stylus profiler of the surfaces (the inset of the Figure 3 (d) is the  
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5 expansion of the vertical coordinate when horizontal coordinate remains unchanged).  
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9 **Figure 4.** (a) Optical picture of sea sand used for the sand abrasion tests (the average grain size is  
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11 between 0.6-0.8 mm ), and the inset is the schematic diagram of sand abrasion tests; (b) and (c)  
12  
13 Optical microscope images of the films P3-T0 and P3-T3 showing sand abrasion areas (red dotted  
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15 cycles) and without and the insets are the SCAs of the olive oil drops deposited on the films after  
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17 sand impingement); (d) stylus profiler of the pencil scratch on the films P3-T0, P3-T1, P3-T2, P3-  
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19 T3, and P3-T4, respectively; (e) the Uv-Vis transmittance of Film P3-T3 with methylene blue  
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21 (Mb) photocatalytically degraded at different illumination time (0, 30, 60, and 90 min); (f) the  
22  
23 optical images and SCAs of the water and olive oil on the FilmP3-T3 (0 Mb  
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25 presents no methylene blue; 0 min is the film with Mb under no illumination; 90 min is the film  
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27 with Mb under a 90 min illumination).  
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33 **Figure 5.** (a) SEM image of the P3-T3; (b) TEM image of SiO<sub>2</sub> particles bonded by TiO<sub>2</sub>; high  
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35 resolution TEM image of Film P3-T3 (the yellow dotted circles are the anatase); (c) schematic  
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37 diagram of SiO<sub>2</sub> strengthen by anatase and photo degradation mechanism, (CB, conduction band;  
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39 VB, valence band).  
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#### 44 **Displayed equations**

$$45 \cos\theta = f \cos\theta - 1 + \quad (1)$$

#### 46 **ASSOCIATED CONTENT**

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## Supporting Information.

The following files are available free of charge.

brief description (file type, *i.e.*, PDF)

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12 Any additional relevant notes should be placed here.  
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## 32 33 **ABBREVIATIONS**

34  
35 CTAB, cetyltrimethylammonium bromide; SCAs, static contact angles;CVD, chemical vapour  
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37 deposition; TEOS, tetraethyl orthosilicate; TAA, titanium diisopropoxidebis 2,4-pentanedionate;  
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39 Mb, methylene blue; CB, conduction band; VB, valence band; PFTS, 1H,1H,2H,2H-  
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41 perfluorodecyltrichlorosilane.  
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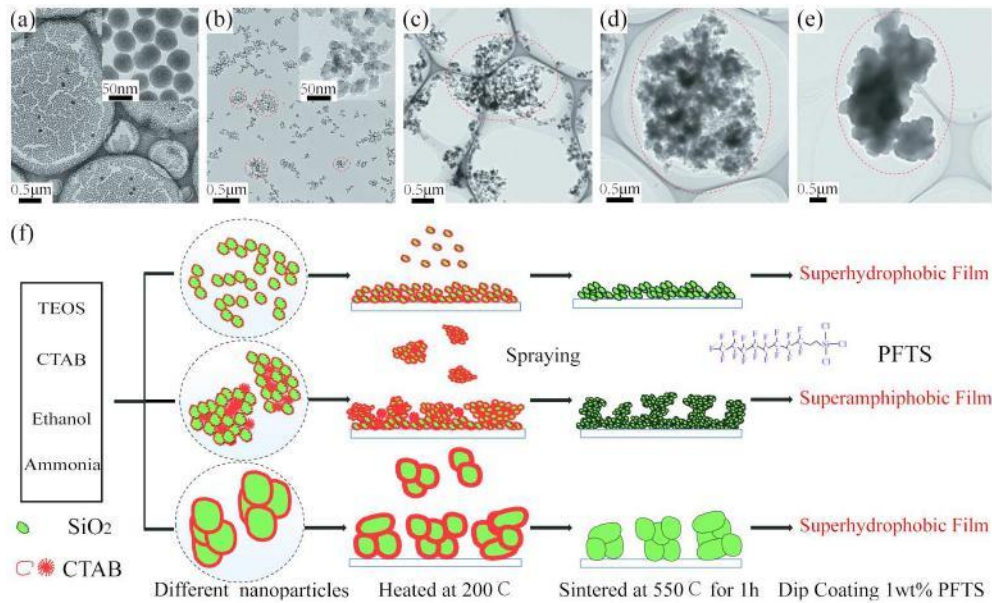


Figure 1. (a), (b), (c), (d), and (e) are the TEM images of the as-obtained particles P0, P1, P2, P3 and P4 on carbon nets, respectively. P0 contains spherical particles (40-50 nm), P1-P3 contain the spongia-like agglomerates of SiO<sub>2</sub> nanoparticles (10-20 nm). P4 contains larger agglomerates (red dotted circles) of SiO<sub>2</sub> nanoparticles (200 nm); (f) the schematic diagram of prepared superhydrophobic and superamphiphobic surfaces. The different sized nanoparticles create different sized agglomerates, which were obtained by adjusting the content of CTAB. The resultant films are either superhydrophobic or superamphiphobic.

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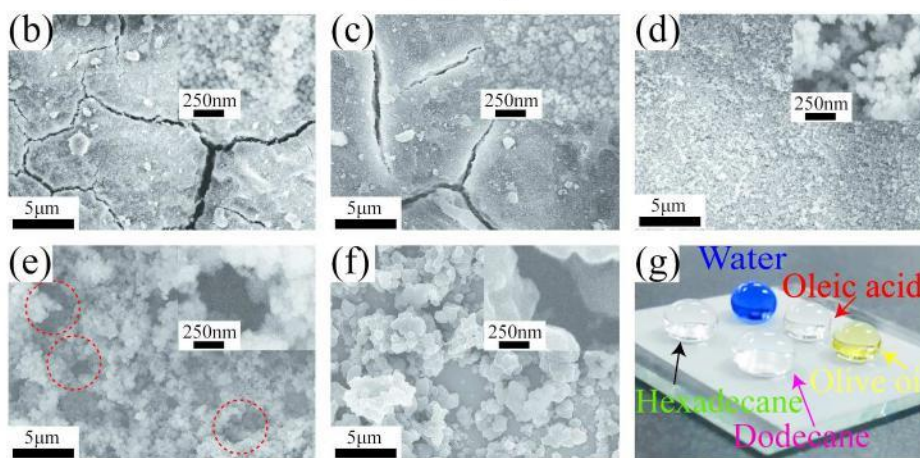
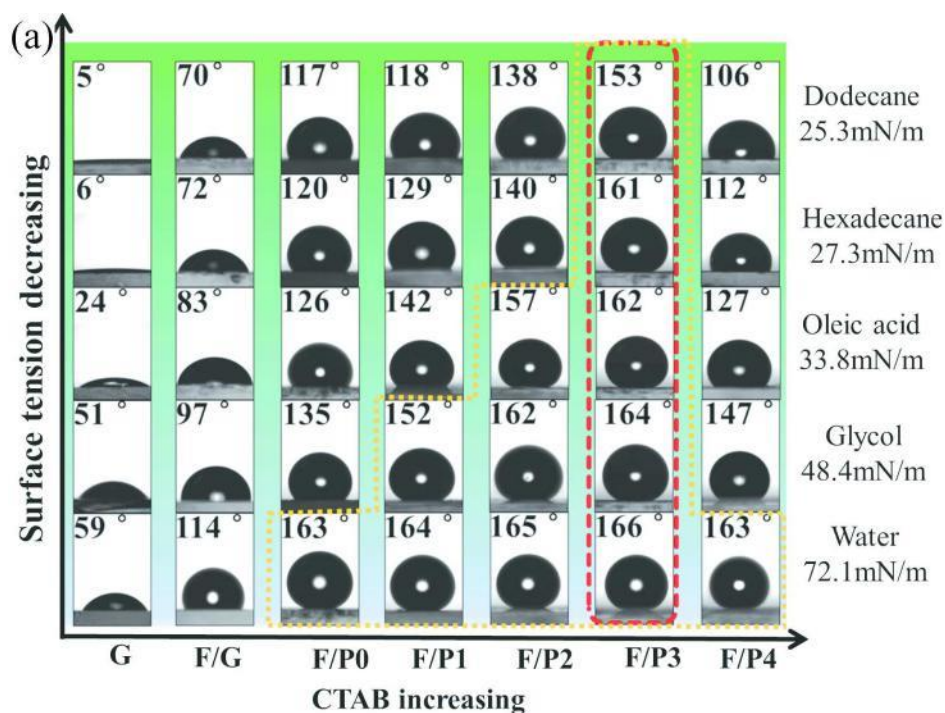


Figure 2. (a) the SCAs of different liquids: Water, Glycol, Oleic acid, Hexadecane, Dodecane on glass (G), PFTS coated glass (F/G), PFTS/P0 coated glass (F/P0), PFTS/P1 coated glass (F/P1), PFTS/P2 coated glass (F/P2), PFTS/P3 coated glass (F/P3), PFTS/P4 coated glass (F/P4); (b), (c), (d), (e), and (f) the low and high amplification (the insets on top right corner) SEM images of the as-obtained films F/P0, F/P1, F/P2, F/P3, F/P4, respectively; (g) the picture of the liquid droplets on the F/P3 film (water was added methyl blue to improve the comparison).

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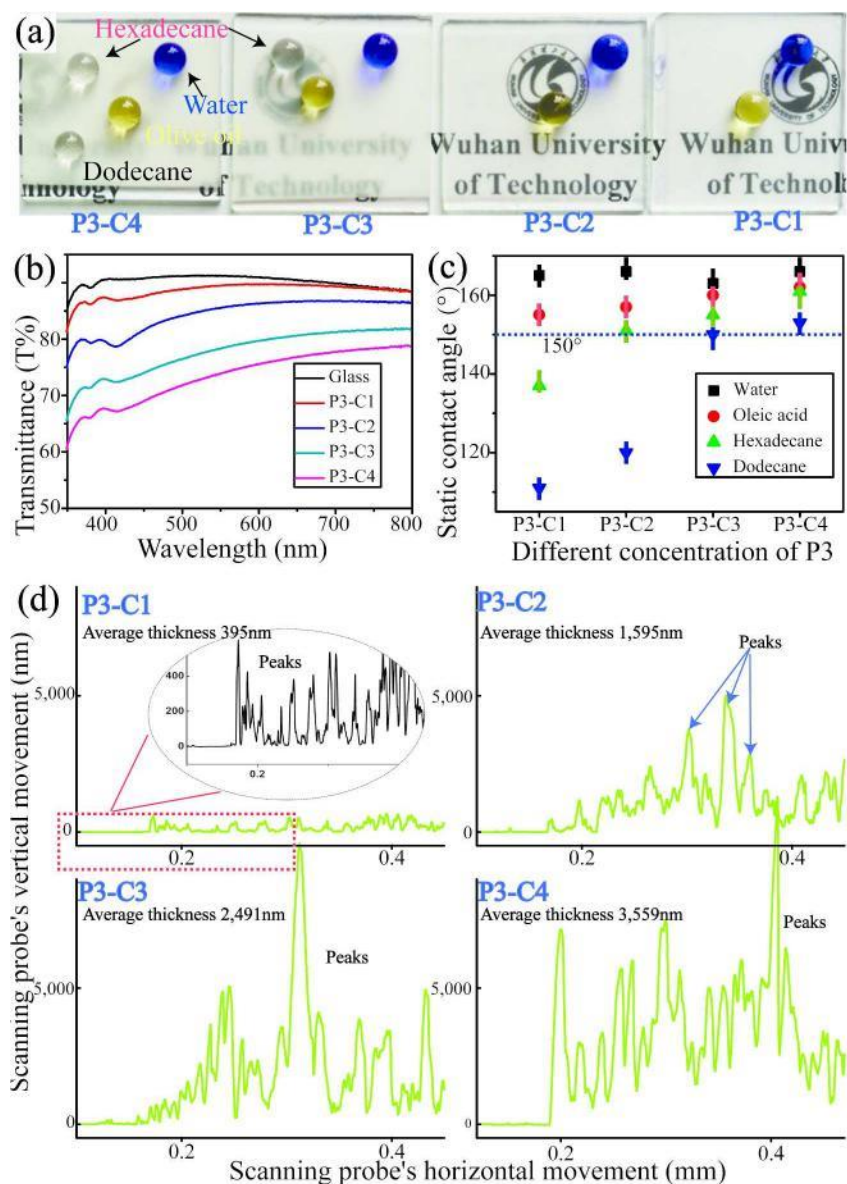


Figure 3. Optical measurements of the films: P3-C1, P3-C2, P3-C3 and P3-C4, (a) Optical pictures of the liquids, water (added methyl blue) and olive oil (yellow), hexadecane, dodecane on the superamphiphobic glasses ; (b) Transmittance of the surfaces; (c) SCAs of the different liquids on the surfaces; (d) stylus profiler of the surfaces (the inset of the Figure 3 (d) is the expansion of the vertical coordinate when horizontal coordinate remains unchanged).

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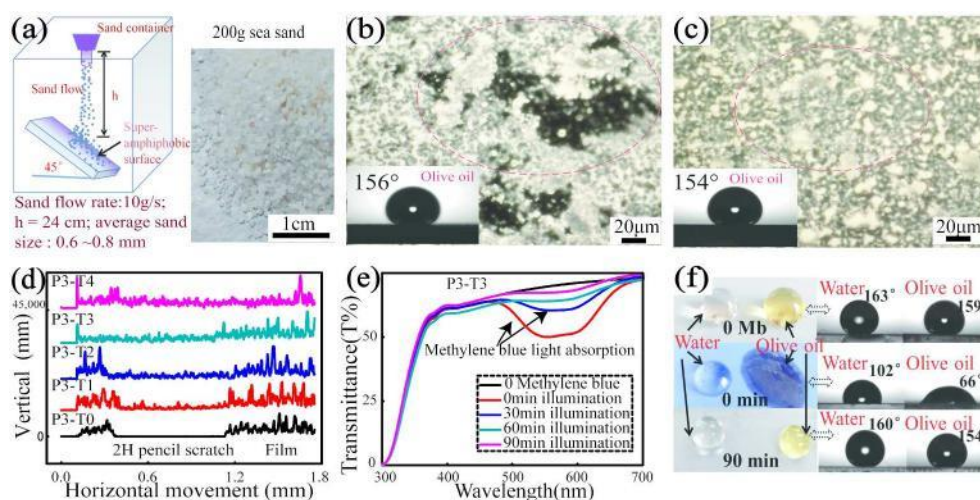


Figure 4. (a) Optical picture of sea sand used for the sand abrasion tests (the average grain size is between 0.6-0.8 mm), and the inset is the schematic diagram of sand abrasion tests; (b) and (c) Optical microscope images of the films P3-T0 and P3-T3 showing sand abrasion areas (red dotted circles) and without and the insets are the SCAs of the olive oil drops deposited on the films after sand impingement; (d) stylus profiler of the pencil scratch on the films P3-T0, P3-T1, P3-T2, P3-T3, and P3-T4, respectively; (e) the UV-Vis transmittance of film P3-T3 with methylene blue (Mb) photocatalytically degraded at different illumination time (0, 30, 60, and 90 min); (f) the optical images and SCAs of the water and olive oil on the film P3-T3 (0 Mb presents no methylene blue; 0 min is the film with Mb under no illumination; 90 min is the film with Mb under a 90 min illumination).

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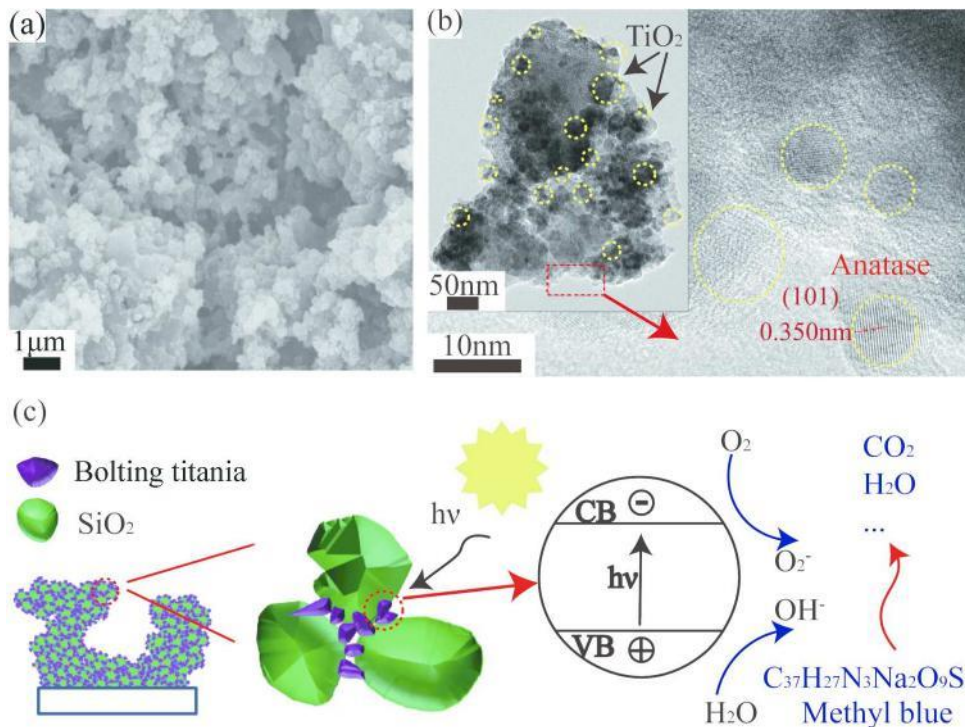


Figure 5. (a) SEM image of the P3-T3; (b) TEM image of SiO<sub>2</sub> particles bonded by TiO<sub>2</sub>; high resolution TEM image of film P3-T3 (the yellow dotted circles are the anatase); (c) schematic diagram of SiO<sub>2</sub> strengthened by anatase and photo degradation mechanism, (CB, conduction band; VB, valence band).

212x160mm (300 x 300 DPI)

# Robust transparent superamphiphobic coatings on non-fabric flat substrates with inorganic adhesive titania bonded silica

Wen, Min

2017-04-03

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Wen M, Zhong J, Shuangjie Z, et al., Robust transparent superamphiphobic coatings on non-fabric flat substrates with inorganic adhesive titania bonded silica, *Journal of Materials Chemistry A*, Volume 5, Issue 18, Pages 8352 – 8359.

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