# Pigmented Self-Cleaning Coatings with Enhanced UV Resilience *via* the Limitation of Photocatalytic Activity and its Effects

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# **Electronic supplementary material (ESI<sup>†</sup>)**

## S1 Experimental details

**Materials:** Sylgard-184 (Silicone elastomer) was purchased from Ellsworth Adhesive Ltd. Multi-purpose adhesive was purchased from 3M. Industrial grade superglue (medium viscosity) was purchased from Tool Station. Titanium Dioxide (Aeroxide P25, 21nm), cerium oxide (<25nm), triethylamine (>99%) and 1H, 1H, 2H, 2H-perfluorooctyltriethoxysilane (98%) were purchased from Sigma Aldrich. Hexane (HPLC grade) and ethanol (analytical reagent grade) were purchased from Fisher Scientific Limited.

**Preparation of superhydrophobic TiO**<sub>2</sub>/CeO<sub>2</sub>-FAS: Nanoparticles (0.5 g) were added to a solution of 1H, 1H, 2H, 2H-perfluorooctyltriethoxysilane (0.196 mmol, 0.076 mL) in ethanol (12.5 mL) and mechanically stirred for 1 hour. A catalytic amount of triethylamine (7.94 mmol, 1.1 mL) was added to CeO<sub>2</sub>/1:10 solutions to encourage formation of the monolayer. Hexane (2 mL) and multi-purpose adhesive (4 mL) were mixed together. One layer of this solution was pipetted over a glass substrate to obtain full coverage and left to dry for 30 seconds before spraying. The nanoparticle sol was spray-coated onto the glass substrate (three layers), and allowed for dry for 15 minutes.

**Preparation of superhydrophobic TiO**<sub>2</sub>/CeO<sub>2</sub>-PDMS: Nanoparticles (2.91 mmol; total mass of 0.50g for exclusive CeO<sub>2</sub> and 1:10 coatings, and a total mass of 0.23g for exclusive TiO<sub>2</sub> coatings) were suspended in ethanol (10 mL). A Sylgard-184 solution (10:1 mass ratio of base and curing agent; for CeO<sub>2</sub> coatings 0.2/0.02g and for TiO<sub>2</sub> coatings 0.15g/0.015g) dissolved in hexane (10 mL) was made up and mixed to ensure complete dissolution. The silicone/hexane solution was added to the nanoparticle sol and mechanically stirred for 3 hours before spraying. A temperature probe was set to 50°C and a layer of PDMS solution (0.22g PDMS/10 mL hexane) was spray-coated onto a hot glass substrate and left for 30 minutes. Following this, the temperature probe was then set to 125°C and the nanoparticle sol was spray-coated onto the hot glass substrate (two layers) and left for a further 30 minutes.

**Spray coating process:** The spray-coating processes were carried out using a compression pump and artist spray gun at a pressure of 2 bar. All spraying was carried out approximately 4 cm away from the surface.

**UV degradation process:** Samples were exposed to UV irradiation using a UV lamp of 365nm wavelength (8W power), which was situated 6.8 cm above coated slides.

Materials characterization: Surface morphologies of coatings were analysed using a scanning electron microscope (SEM) (JEOL JSM-7001F) operating at an acceleration voltage of 20 kV. This instrument had a built-in INCA X-act EDX detector. Samples were vacuum sputter coated in a thin layer of chromium to improve electrical conductivity. A transmission electron microscope (JEOL 2100F) was used at an acceleration voltage of 200 kV in both transmission (TEM) mode and scanning transmission (S/TEM) mode using a CEOS GmbH "CESCOR" aberration correction system. FTIR measurements were taken using a Bruker Optics' Vertex 70 over a range of 450 to 4000 cm<sup>-1</sup>. UV-Vis diffuse reflectance spectra were obtained using a Cary 5000 UV-Vis-NIR Spectrometer in the range of 200-600 nm. Static WCA measurements were taken using a DSA100 Expert Drop Shape Analyser using sessile drop and Young-Laplace operating modes (manual setting);  $6 \,\mu$ L water droplets were used and 5 WCA measurements were taken per sample. Tilting angles were recorded manually by dropping a water droplet on the surface and tilting the surface, recording the angle at which the droplet began to roll; an average was taken over 5 areas. Water bouncing videos were recorded using a Sony Cyber-shot DSC-RX10 III digital camera (shooting at 1000 frames per second) and an average of 4 videos per coating was used to calculate bounces. 6  $\mu$ L water droplets were dispensed from a 30 gauge dispensing tip positioned 20 mm above the substrate surface.

#### S2 Movies

**Movie S1**: Water bouncing video 1:10-PDMS. Details of set-up found in the experimental section.

### S3 Alternating TiO<sub>2</sub>:CeO<sub>2</sub> mass ratios

TiO <sub>2</sub> :CeO <sub>2</sub> ratio	10:1	5:1	2:1	1:1	1:2	1:5	1:10
with FAS							
CA 0hr UV (°)	159	158	160	160	161	161	162
CA 16hr UV (°)	0	0	0	0	125	155	157

Table S1. Measured WCA's of various ratios of TiO<sub>2</sub>:CeO<sub>2</sub> in FAS composite films.

\*Preliminary results; WCA's measured using an Ipevo USB camera and digital protractor.

Coatings that contained an equal or greater mass of  $TiO_2$  displayed significantly less UV stability, as can be seen by the large reduction in WCA after only 16 hours of UV irradiation. This can be explained by the strong photocatalytic behaviour of  $TiO_2$  degrading the self-assembled monolayer of FAS surrounding nanoparticles, hence, all superhydrophobicity was lost.

### **S4 Film pigmentation**



**Fig. S1.** Physical appearance (left to right: TiO<sub>2</sub>-PDMS, PDMS).

of PDMS composite coatings CeO<sub>2</sub>-PDMS and 1:10-



Fig. S2. UV-Vis diffuse reflectance spectra of TiO<sub>2</sub>-PDMS, CeO<sub>2</sub>-PDMS and 1:10-PDMS.

 $TiO_2$  nanostructured coatings displayed increased reflectance at wavelengths above 328 nm and significant reflectance above 353nm. For CeO<sub>2</sub>-PDMS, increased reflectance was observed at wavelengths above 357nm. When combining  $TiO_2$  and CeO<sub>2</sub> (1:10-PDMS), reflectance began to rise at wavelengths above 352nm, demonstrating that a fraction of  $TiO_2$  can improve white



pigmentation of CeO<sub>2</sub>-based coatings.

**Fig. S3.** UV-Vis diffuse reflectance spectra of  $TiO_2$ -FAS, CeO<sub>2</sub>-FAS and 1:10-FAS. For  $TiO_2$ -FAS reflectance began to increase at 328 nm and showed a steep rise at 351 nm. Generally, lower reflectance was observed for CeO<sub>2</sub> nanostructured films; reflectance began to increase at 361 nm for CeO<sub>2</sub>-FAS and at 354 nm for 1:10-FAS. Ceria containing FAS composite films appeared to be more transparent than other coatings.

### S5 FTIR



Fig. S4. FTIR spectra of PDMS composite films before UV irradiation tests.

All vibrational stretches were as expected. In CeO<sub>2</sub>-PDMS and 1:10-PDMS spectra a peak at 698 cm<sup>-1</sup> can be seen due to Ce-O stretching. Vibrational peaks representative of PDMS can be seen in all spectra; 2960 cm<sup>-1</sup> owed to asymmetric -CH<sub>3</sub> stretching in Si-CH<sub>3</sub>, 1257 cm<sup>-1</sup> representative of the -CH<sub>3</sub> symmetric deformation of Si-CH<sub>3</sub>, 1060 cm<sup>-1</sup> characteristic of the Si-O-Si stretching mode and at 790 cm<sup>-1</sup> corresponding to –CH<sub>3</sub> rocking and Si-C stretching in Si-CH<sub>3</sub>, respectively. <sup>1</sup>



**Fig. S5.** FTIR spectra of FAS composite films before UV irradiation tests. Inset magnified version of overlaid FTIR spectra.

As FAS molecules only form a self-assembled monolayer around nanoparticles, FTIR signals were expected to be relatively weak. Expected signals were present in all films; ~2995-2810 cm<sup>-1</sup> representative of -CH<sub>2</sub> stretching vibrations and 1238 cm<sup>-1</sup>, 1193 cm<sup>-1</sup>, 1143 cm<sup>-1</sup> and 1065 cm<sup>-1</sup> characteristic of -CF<sub>2</sub> vibrations, with additional peaks below 1000 cm<sup>-1</sup> corresponding to C-F<sub>3</sub> bands.<sup>2</sup>



Fig. S6. FTIR spectra of TiO<sub>2</sub>-FAS before and after 90 minutes of UV irradiation (365 nm).



Fig. S7. FTIR spectra of TiO<sub>2</sub>-PDMS before and after 96 hours of UV irradiation (365 nm).

Vibrational peaks for FAS composite coatings were seen to decrease in intensity after irradiation which can be owed to the degradation of the self-assembled monolayer surrounding inorganic nanoparticles. Spectra of PDMS composite coatings displayed vibrational peaks of a similar intensity before and after irradiation. However, an increasing hydroxyl peak could be seen at  $\sim 3250$  cm<sup>-1</sup>, suggesting that partial degradation of PDMS may have begun to occur after 96 hours irradiation.

#### **S6 Electron microscopy**



**Fig. S8.** TEM images of 'as received' (a) P25  $TiO_2$  nanoparticles (21 nm) and (b)  $CeO_2$  (<25 nm). Scale bars shown.

Transmission electron microscopy (TEM) was used to image the 'as received' individual nanoparticles, P25 TiO<sub>2</sub> and CeO<sub>2</sub> nanoparticles used in coatings; average diameters were measured to be 24  $\pm$  7 nm and 27  $\pm$  14 nm, respectively. TiO<sub>2</sub> particles were predominantly uniform in size and shape, whereas CeO<sub>2</sub> nanoparticles displayed a greater distribution in size and irregularity in shape.



Fig. S9. Side on SEM micrographs of TiO<sub>2</sub>-PDMS showing (a) the measured average film thickness and (b) a large microstructure measuring 43  $\mu$ m. Scale bars shown.

Surface morphologies were analysed *via* SEM; irregular microstructures ranging up to 43  $\mu$ m can be observed throughout the surface coating from partial agglomeration of particles during the sol-gel/spray-coating processes, resulting in substantial hierarchical surface roughness which is required when fabricating highly water repellent materials. An average film thickness

was estimated to be between 12-16  $\mu$ m for the TiO<sub>2</sub>-PDMS coating, structured from a 4  $\mu$ m PDMS base layer and nanoparticle coating measured to be between 8-12  $\mu$ m.



**Fig. S10.** SEM micrographs showing the surface morphology of (a) TiO<sub>2</sub>-PDMS (b) CeO<sub>2</sub>-PDMS and (c) 1:10-PDMS at high magnification. Scale bars shown.

Furthermore, the combined effect of natural particle agglomeration and coating particles (both  $TiO_2$  and  $CeO_2$ ) with an optimal thickness of polymer, resulted in difficulties when attempting to image individually coated nanoparticles as particle definition was lost. A better representation of individual nanoparticles is displayed in Figure 2e, which displays an S-TEM image of PDMS coated TiO<sub>2</sub> nanoparticles (polymer thickness 7 ± 2 nm).

Film					
	СК	O K	Si K	Ti K	Ce K
TiO <sub>2</sub> -PDMS	28.12	50.14	15.01	6.73	-
CeO <sub>2</sub> -PDMS	40.34	35.78	12.51	-	11.37
1:10-PDMS	27.68	43.70	12.11	3.77	12.74

**Table S2.** EDS data before UV irradition of TiO<sub>2</sub>-PDMS, CeO<sub>2</sub>-PDMS and 1:10-PDMS, confirming the presence of all expected elements.



**Fig. S11.** SEM micrographs showing the surface morphology of (a) TiO<sub>2</sub>-FAS, (b) CeO<sub>2</sub>-FAS and (c) 1:10-FAS. Scale bars shown.

# S7 Increasing wt% of PDMS



Fig. S12. Graph highlighting the relationship between WCA and wt% of PDMS polymer in TiO<sub>2</sub>-PDMS.

As the wt% of PDMS in  $TiO_2$ -PDMS films was increased form 10 wt % to 40 wt%, the films respective WCA's were seen to steadily increase. However, this was followed by a sharp decrease in WCA as the wt % of PDMS was increased beyond this, as a result of loss of surface porosity.

## **S8** Self-cleaning



**Fig. S13.** Removal of artificial dirt (MnO) *via* a single water droplet deposited onto the films surface after films had endured 96 hours of irradiation (left to right: TiO<sub>2</sub>-PDMS, 1:10-PDMS and CeO<sub>2</sub>-PDMS).

Coatings were seen to retain their self-cleaning abilities after irradiation when tested with simulated dirt particles. A single water droplet was deposited onto films and was observed to remove MnO from the surface of coatings.

## **S9** Water bouncing tests



**Fig. S14.** Photographs displaying the behaviour of a 6  $\mu$ L water droplet dispensed 20 mm above the surface which had been coated with 1:10-PDMS. Methylene blue was used to aid visualisation and did not interfere with bouncing.

The interaction of water with PDMS composite surfaces was captured using a high-speed camera (1000 Frames per second). 6  $\mu$ L water droplets were dispensed from a 30 gauge dispensing tip positioned 20 mm above the substrate surface, as this had previously been determined as the height where water droplets carry maximum momentum.<sup>3</sup> Water bouncing was used as an alternative method to characterise superhydrophobicity. The average number of water bounces was found to be typically proportional to the observed WCA of any given coating; TiO<sub>2</sub>-PDMS displayed 11-12 water bounces, CeO<sub>2</sub>-PDMS displayed 12 water bounces and 13-14 bounces was observed for 1:10-PDMS (Movie S1). This can be explained by a greater distribution in particle size from a combination of two inorganic oxides utilized in 1:10-PDMS. Therefore, surface roughness was amplified, enhancing the air-liquid interfacial area and limiting water adhesion to the surface coating.

#### References

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