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Pigmented self-cleaning coatings with enhanced UV resilience *via* the limitation of photocatalytic activity and its effects†

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Self-cleaning superhydrophobic surfaces are a highly sought-after class of materials which have the potential to be hugely beneficial to many commercial industries. A prospective application is within the paints and coatings industry. However, photo-degradation of titanium dioxide-based (TiO_2) coatings often limits the practical implementation of applied superhydrophobic coatings. Here, we present a facile process for fabricating pigmented superhydrophobic nanomaterials which display excellent UV durability, owed to the synergistic effect of using cerium oxide (CeO_2) nanoparticles and a silicone elastomer, polydimethylsiloxane (PDMS). Composite coatings resisted photo-degradation after 250 hours of intense UV irradiation (over 100 days under ambient conditions) and continued to exhibit promising self-cleaning properties.

Design, System, Application

A combination of high-level surface roughness and a low surface-energy material is crucial when designing highly water repellent materials. A target use of these materials is as self-cleaning paints as metal oxide nanoparticles not only provide pigmentation, but can also act as nanoparticle scaffolds to generate the hierarchical roughness required. However, the brightest white pigment, titanium dioxide (TiO_2), is highly photocatalytic in the presence of UV light. Hence, irreversible surface wettability is expected and the search for alternative pigments is ongoing. Here, we demonstrate that highly water repellent coatings can be both pigmented and exert UV stability. We probe the synergistic effect of (i) using less photoactive metal oxide nanoparticles as the primary pigment (cerium oxide, CeO_2) and (ii) employing a low surface-energy silicone elastomer to coat nanoparticles, on UV stability. Moreover, we directly compare the benefits of using CeO_2 *vs.* TiO_2 nanoparticles as both polymeric and molecular composites. Long term testing has verified the enhanced UV resilience and functional self-cleaning properties of films post-irradiation, compared to conventional TiO_2-based coatings which loose functionality after short irradiation periods. There is potential for these materials to be applied as self-cleaning paints/coatings where there is a requirement for coatings to be aesthetically pleasing.

1. Introduction

Highly water repellent materials with water contact angles (WCA) exceeding 150° have recently gained interest as applied self-cleaning coatings across various industrial and commercial areas.[1–6] The combined effect of low surface energy materials and hierarchical surface roughness, forces water droplets to bead up into near-spherical droplets and roll off the surface carrying with them any surface-bound contaminants (lotus effect).[7,8] Engineering of nano- and micro-surface structures from inorganic nanoparticles, followed by post-treatment with an organic coating (molecular or polymeric), is an inexpensive and commonly used fabrication route to generate superhydrophobic materials.[9,10] However, the components used when designing superhydrophobic coating formulations and the chemical composition that these are applied in has be shown to be critical for the durability and visual properties of the resultant coatings.[11]

Titanium dioxide (TiO_2) is a wide bandgap semiconductor oxide (band gap: 3.2 eV) that is essential for pigmented coatings due to its high refractive index and known optical properties; a combination of which enables the maximum scattering of visible light in TiO_2-based nanomaterials.[12,13] These factors make titania the brightest white pigment in common use and is thereby crucial to the paint and coatings industries.[14] Hence, pigmented self-cleaning coatings display huge potential in any industrial and/or commercial area that considers aesthetics to be important.[15] However, as semi-conducting oxide nanoparticles are inherently photocatalytic, exposure to UV radiation liberates charge carriers which subsequently migrate to the surface of particles to carry out redox reactions on any surface adsorbed organic matter, breaking it down into active radicals.[16] Therefore, environmentally induced change to surface

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wettability is a major concern for any superhydrophobic materials that utilize TiO_2 nanoparticles and has been shown to take place when exposing coatings to UV irradiation (mimicking solar radiation).[17–21]

TiO_2-Based superhydrophobic suspensions have been widely reported as potential external surface anti-contamination coatings (*via* self-cleaning mechanism).[22–24] Lu *et al.* detailed an ethanolic suspension of dual sized TiO_2 nanoparticles coated with perfluorooctyltriethoxysilane that was highly versatile (used to coat textiles, paper, glass and steel) and displayed excellent self-cleaning properties, retaining superhydrophobicity even during immersion in oil.[25] Although pigmented superhydrophobic coatings have been successfully developed, integrating UV stability into TiO_2-based coatings still remains challenging. Nishimoto *et al.* reported TiO_2 modified with self-assembled monolayers of octadecylphosphonic acid undergoing a transformation from superhydrophobic (WCA of 173.6°) to superhydrophilic (near 0°) after just 10 minutes of UV irradiation.[26] Qing *et al.* reported a superhydrophobic thin film designed from polydimethylsiloxane/fluoroalkylsilane (PDMS/FAS)-TiO_2 composite displaying a significant reduction in WCA from 162.3° to 75.6° after 20 minutes UV irradiation.[27] Two different approaches have been used here to fabricate TiO_2-based superhydrophobic films, yet both provide minimal UV durability, undoubtedly highlighting the importance of chemical composition. Furthermore, Ding *et al.* reported a superhydrophobic self-cleaning coating fabricated by blending TiO_2 nanoparticles with fluorinated polysiloxane co-polymers. The direct blending of nanoparticles into the polymer results in a UV durable material. However, its practical application is limited by the inflexibility of the polymer casting technique, and cost/regulatory issues relating to the commercial application of the fluorinated co-polymer system.[28] Generally, successful fabrication routes to UV durable TiO_2-based nanomaterials frequently involve the use of fluorinated chemicals, multi-step modification processes, or the requirement for specialised equipment, all of which can be expensive and/or environmentally hazardous.

Herein, we present a simplistic, low-cost spray-coating method used to fabricate pigmented self-cleaning superhydrophobic coatings that are highly impervious to UV degradation. Previously, we reported a three-phase interchangeable formulation system (nanoparticles, polymer and solvent), where we investigated how the polymer : nanoparticle ratio could impact the resultant materials properties.[11] As a further development, we have shown how this can be applied to two pigmented metal oxide systems (individually and blended) to provide long-term UV stability to otherwise rapidly degrading materials. Furthermore, by blending TiO_2 and cerium oxide (CeO_2) particles together, we demonstrate that it's possible to manipulate the resultant pigmentation of these superhydrophobic coatings while retaining UV stability, which to our knowledge has not been reported in the literature. The coating formulations combine CeO_2 nanoparticles with a molecular coating, fluoroalkylsilane (FAS), and a thermoset polydimethylsiloxane (PDMS) polymer coating to probe the enhancement in UV durability of these composites in comparison to traditional TiO_2-based systems (for both molecular and polymeric systems, Fig. 1). CeO_2 has been reported to exhibit limited interaction with water as a result of shielding of its unfilled 4f orbital, in addition to showing rapid recombination of charge carriers owing to a high concentration of oxygen defects.[29,30] Hence, it was anticipated that films incorporating CeO_2 would display limited photodegradation when compared to that of exclusively TiO_2. WCA's as high as 168° were attained, with negligible change after extensive periods of intense UV irradiation (365 nm, 8 W power).

2. Experimental

2.1. Materials

Sylgard-184 (silicone elastomer) was purchased from Ellsworth Adhesive Ltd. Multi-purpose adhesive was purchased from 3M. Titanium dioxide (Aeroxide P25, 21 nm), cerium oxide (<25 nm), triethylamine (>99%) and 1*H*,1*H*,2*H*,2*H*-perfluorooctyltriethoxysilane (98%) were purchased from Sigma Aldrich. Hexane (HPLC grade) and

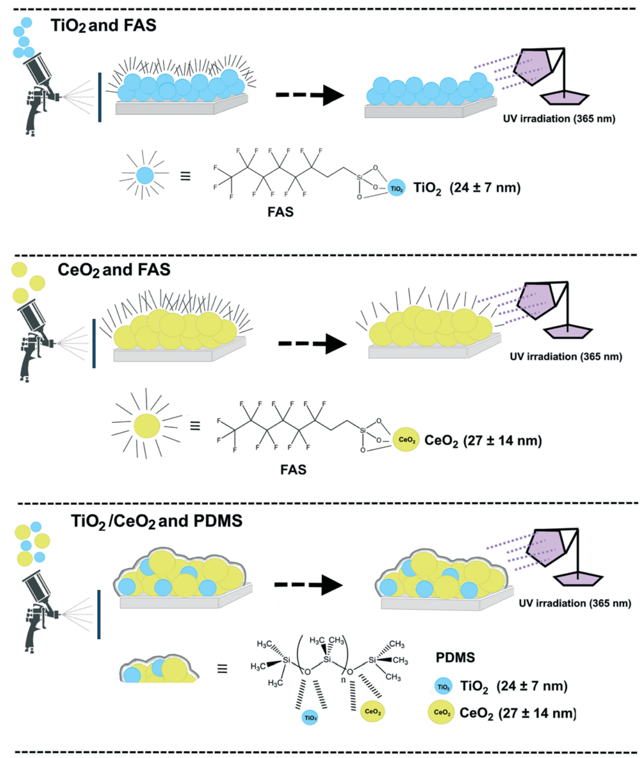

Fig. 1 Schematic illustration depicting the rapid degradation of FAS coated TiO_2 composite films under UV illumination (top), the reduced degradation rate observed when FAS coated CeO_2 nanoparticles are employed in place of TiO_2 (middle) and PDMS coated TiO_2/CeO_2 composite films, which were observed to be highly durable with respect to UV irradiation (bottom).

ethanol (analytical reagent grade) were purchased from Fisher Scientific Limited.

2.2. Preparation of superhydrophobic TiO_2/CeO_2-FAS films

Nanoparticles (0.5 g) were added to a solution of 1*H*,1*H*,2*H*,2*H*-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_2/1 : 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.

2.3. Preparation of superhydrophobic TiO_2/CeO_2-PDMS films

Nanoparticles (2.91 mmol; total mass of 0.50 g for exclusive CeO_2 and 1 : 10 coatings, and a total mass of 0.23 g for exclusive TiO_2 coatings) were suspended in ethanol (10 mL). A Sylgard-184 solution (10 : 1 mass ratio of base and curing agent; for CeO_2 coatings 0.2/0.02 g and for TiO_2 coatings 0.15 g/0.015 g) 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 (0.22 g 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 (three layers) and left for a further 30 minutes.

2.4. 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.

2.5. UV degradation process

Samples were exposed to UV irradiation using a UV lamp of 365 nm wavelength (8 W power), which was situated 6.8 cm above coated slides that were in a container (22 cm in width and 31 cm in length).

2.6. 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^{-1}. 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 baseline setting); 6 μL water droplets were used and 5 WCA measurements were taken and averaged 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 μL water droplets were dispensed from a 30 gauge dispensing tip positioned 20 mm above the substrate surface.

3. Results and discussion

3.1. FAS coatings

FAS-modified TiO_2 composite films were fabricated to probe the UV resilience of molecularly coated TiO_2 nanomaterials. The resultant coatings appeared to be homogenous and visually bright white, confirmed *via* UV-vis diffuse reflectance. Films were subject to intense UV exposure periods, where any photo-induced loss in superhydrophobicity could be monitored *via* a decreasing WCA. Based on the average total UVA irradiance in a month being approximately 3.09 ± 1.91 W m^{-2}, it has been estimated that using a UVA source of this intensity (117.30 W m^{-2}, 365 nm) has the solar equivalent of 35 days outdoor exposure.[31] Initially a WCA of 162° ± 2 was observed, which was rapidly reduced to 4° ± 6 after a short period (90 minutes) of irradiation. This transition was also tracked using FTIR, where a reduction in the intensity of peaks representative of FAS could be seen (see ESI†). Irradiation of semiconducting oxide nanoparticles (including TiO_2) liberates photo-generated holes (h^+) and electrons (e^-) which migrate to perform redox reactions on surface adsorbed species, thereby, breaking down all organic matter into active radicals.[32,33] Hence, TiO_2-FAS displayed an anticipated loss in functionality, as the self-assembled monolayer of FAS was subsequently degraded.

To impart greater UV stability, analogous CeO_2-based coatings (CeO_2-FAS) were fabricated and were irradiated continuously for a period of 96 hours. It was anticipated that the inclusion of CeO_2 would actively extend the time it took for coatings to lose their functionality, as CeO_2 is known to promote electron–hole recombination and thus depress the production of active radicals. CeO_2-FAS nanostructured films withstood the full duration of 96 hours irradiation, showing a loss in superhydrophobicity only within the final 24 hours (WCA decreased from initial reading of 166° ± 1 to 148° ± 15). This highlights clearly that coatings which employ CeO_2 nanoparticles as the primary pigment are remarkably less photocatalytically active. Although, films were no longer observed to be visually bright white due to CeO_2 being inherently pale yellow (see ESI†). Furthermore, increased water adherence to the surface was evident after 72 hours, implying a change in wetting state from the Cassie–Baxter state to the Wenzel state due to a reduction in the liquid–vapour interfacial area beneath the droplet. Hence, long term use as applied pigmented self-cleaning coatings in their current form would remain very challenging, due to the rapid degradation of the self-assembled monolayer of organic molecules.

3.2. PDMS coatings

Although a noticeable improvement in UV stability was reported when replacing TiO_2 nanoparticles with CeO_2, we wanted to further improve this by introducing a thermoset silicone elastomer (PDMS). Generally, polymeric coatings provide greater control over composite optimisation due to the extensive network of intermolecularly bonded polymer chains, of which the thickness can be tuned accordingly (unlike self-assembled monolayers of molecules). Exclusive TiO_2 (TiO_2-PDMS) and exclusive CeO_2 (CeO_2-PDMS) composite coatings were fabricated. Prior to particle coating deposition, the substrate was first spray-coated with a layer of PDMS and partially cured; this provided a water repellent base (fully cured during second spray coating), aimed at increased hydrophobicity and physical durability.

When carrying out duplicate degradation tests to those used when examining FAS systems, TiO_2-PDMS with an optimal polymer thickness surrounding nanoparticles initially displayed a WCA of 164° ± 1 (CAH = 1.5°). Negligible change was observed after 96 hour of irradiation, decreasing to only 163° ± 2 (CAH = 2°) and exhibiting a significant enhancement in UV stability. An amorphous layer surrounding TiO_2 particles (Aeroxide P25, 21 nm) was detected *via* scanning transmission electron microscopy (S-TEM) after coating with PDMS, as seen in Fig. 2e. This exterior polymeric coating was measured to be of approximately 7 ± 2 nm thickness and energy dispersive X-ray spectroscopy (EDS) was used to highlight a high density of titanium, silicon and oxygen atoms in areas where particles were present.

The thickness of the polymer coating surrounding nanoparticles was seen to impact the resultant hydrophobicity of coatings; an inadequate mass of PDMS led to incomplete particle encapsulation, showing varied hydrophobicity throughout the film due to partial exposure of semiconductor material. Conversely, an excess of polymer resulted in decreasing surface roughness and subsequently a loss in hydrophobicity, as a result of limiting surface porosity. Therefore, an optimal ratio between nanoparticle and PDMS exists, whereby the greatest WCA's were attained from ensuring complete particle coverage while maintaining a roughened surface morphology. The critical mass of PDMS was established to be approximately 30–40 wt% (see ESI†) and found to form a polymer layer sufficiently thick for suppressing photodegradation. This result is in close agreement with Qing *et al.* who reported a critical mass of 30 wt% PDMS.[27] The primary interaction between TiO_2 and PDMS has been speculated to be hydrogen bonding between the surface adsorbed hydroxyl groups of TiO_2 and backbone oxygen atoms of PDMS. Siloxanes are a class of polymers that have highly flexible backbones. Therefore, a combination of high surface coverage through extensive intermolecular interactions, excellent backbone flexibility and an optimal ratio enabled PDMS to suppress the photo-degradation caused by TiO_2 particles.[34]

To generate films with UV resilience of the highest order, we fabricated and subject CeO_2-PDMS films to the same conditions. A minimal change in WCA from 165° ± 1 (CAH =

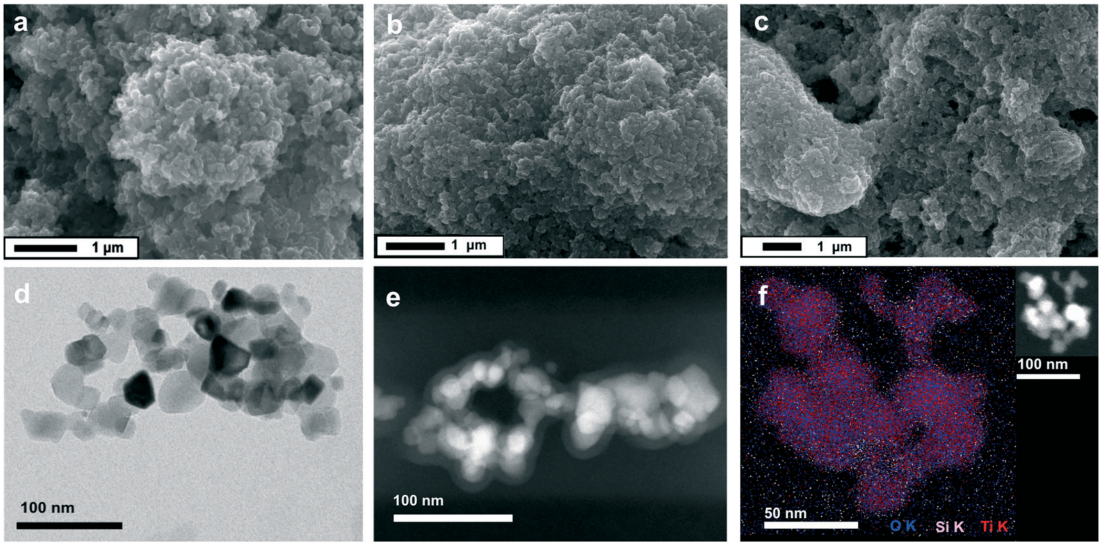

Fig. 2 SEM micrographs showing the morphology of (a) TiO_2-PDMS; (b) CeO2-PDMS; and (c) 1 : 10-PDMS. (d) TEM image of P25 TiO_2 (80 : 20 anatase : rutile). (e) S-TEM image of PDMS coated TiO_2 particles. (f) EDS map of PDMS coated TiO_2 particles. Scale bars shown.

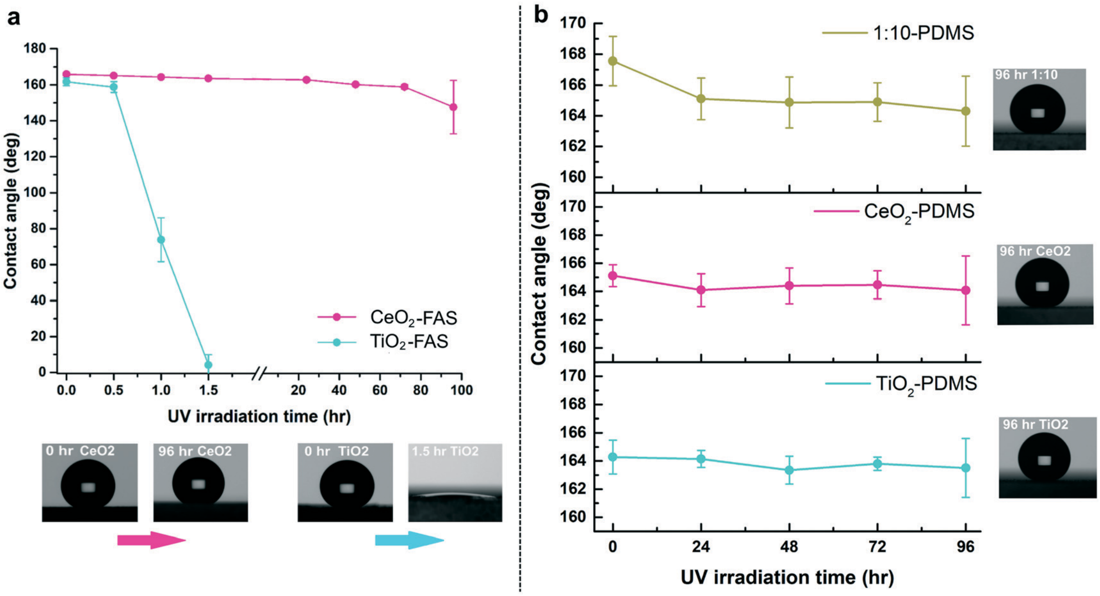

Fig. 3 Plots to show the variation in WCA of (a) TiO_2-FAS and CeO_2-FAS and (b) TiO_2-PDMS, CeO_2-PDMS and 1:10-PDMS when subject to 96 hours of UV irradiation (365 nm). Inset photos show a single water droplet on the surface of each coating at noted time intervals.

2°) to 164° ± 2 (CAH = 2°) was observed, clearly highlighting the positive impact of using polymeric coatings to obtain durable superhydrophobic pigmented coatings. In an attempt to improve the white pigmentation of CeO_2 nanostructured coatings, without compromising the UV stability of films, TiO_2 and CeO_2 nanoparticles were blended in a 1:10 mass ratio (1:10-PDMS). UV-vis diffuse reflectance was used to confirm an enhancement in the white pigmentation of these coatings (see ESI†), while degradation tests showed a change in WCA from 168° ± 2 (CAH = 2°) to 164° ± 2 (CAH = 2.5°) after 96 hours of irradiation. Greater WCA's were observed initially for 1:10-PDMS as a result of the difference in reported diameters of nanoparticles (TiO_2 24 ± 7 nm and CeO_2 27 ± 14 nm). All three polymer based coatings displayed significantly more UV resilience in comparison to molecular based FAS coatings (Fig. 3) and were seen to remain highly functional as self-cleaning surfaces when tested with the removal of simulated dirt particles (see ESI†).

Additionally, extended studies were carried out whereby films were exposed to a maximum of 250 h intense irradiation. This resulted in a WCA of ~160° and ~162° for TiO_2-PDMS and CeO_2-PDMS, respectively, further evidence that CeO_2 based coatings have reduced photocatalytic activity and can aid the durability of coatings. Furthermore, films were observed to remain superhydrophobic after 100 days of storage under ambient conditions, emphasizing the real-world applicability of these coatings.

4. Conclusions

This research demonstrates how the inclusion of CeO_2 nanoparticles into superhydrophobic formulations can be hugely beneficial in extending the life-time (with respect to UV durability) of self-cleaning pigmented coatings. Furthermore, we elaborate on how silicone elastomer coatings can be used to further suppress photo-degradation. The reported technique is a facile spray coating process which is highly compatible with a wide range of substrates. Hence, this technology is highly pertinent to any application that requires contamination-free surfaces and is compatible with superhydrophobic self-cleaning mechanisms (*e.g.* external coatings that can be cleaned by falling rainwater). There is also additional relevance to industries where aesthetics is an important factor, provided the use of common pigments as surface roughening agents.

Conflicts of interest

There are no conflicts of interest to declare.

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References

1 A. Chabas, T. Lombardo, H. Cachier, M. H. Pertuisot, K. Oikonomou, R. Falcone, M. Verità and F. Geotti-Bianchini, *Build. Environ.*, 2008, **43**, 2124–2131.
2 W. Shen, C. Zhang, Q. Li, W. Zhang, L. Cao and J. Ye, *J. Cleaner Prod.*, 2015, **87**, 762–765.
3 A. Bozzi, T. Yuranova and J. Kiwi, *J. Photochem. Photobiol., A*, 2005, **172**, 27–34.

4 F. Liu, S. Wang, M. Zhang, M. Ma, C. Wang and J. Li, *Appl. Surf. Sci.*, 2013, **280**, 686–692.

5 S. S. Latthe, P. Sudhagar, A. Devadoss, A. M. Kumar, S. Liu, C. Terashima, K. Nakata and A. Fujishima, *J. Mater. Chem. A*, 2015, **3**, 14263–14271.

6 S. P. Dalawai, M. A. S. Aly, S. S. Latthe, R. Xing, R. S. Sutar, S. Nagappan, C.-S. Ha, K. K. Sadasivuni and S. Liu, *Prog. Org. Coat.*, 2020, **138**, 105381.

7 W. Barthlott and C. Neinhuis, *Planta*, 1997, **202**, 1–8.

8 Y. A. Mehanna, R. L. Upton and C. R. Crick, *J. Mater. Chem. A*, 2019, **7**, 7333–7337.

9 X.-M. Li, D. Reinhoudt and M. Crego-Calama, *Chem. Soc. Rev.*, 2007, **36**, 1350–1368.

10 L. Xu, R. G. Karunakaran, J. Guo and S. Yang, *ACS Appl. Mater. Interfaces*, 2012, **4**, 1118–1125.

11 R. L. Upton, Z. Davies-Manifold, M. Marcello, K. Arnold and C. R. Crick, *Mol. Syst. Des. Eng.*, 2020, **5**, 477–483.

12 M. Pelaez, N. T. Nolan, S. C. Pillai, M. K. Seery, P. Falaras, A. G. Kontos, P. S. M. Dunlop, J. W. J. Hamilton, J. A. Byrne, K. O'Shea, M. H. Entezari and D. D. Dionysiou, *Appl. Catal., B*, 2012, **125**, 331–349.

13 Y. Zhu, G. C. Allen, J. M. Adams, D. Gittins, P. J. Heard and D. R. Skuse, *Compos. Struct.*, 2010, **92**, 2203–2207.

14 J. H. Braun, A. Baidins and R. E. Marganski, *Prog. Org. Coat.*, 1992, **20**, 105–138.

15 R. Xing, S. S. Latthe, A. K. Bhosale, R. Li, A. M. Kumar and S. Liu, *J. Mol. Liq.*, 2017, **247**, 366–373.

16 T. He, H. Zhao, Y. Liu, C. Zhao, L. Wang, H. Wang, Y. Zhao and H. Wang, *Colloids Surf., A*, 2020, **585**, 124080.

17 B. Jalvo, M. Faraldos, A. Bahamonde and R. Rosal, *J. Hazard. Mater.*, 2017, **340**, 160–170.

18 Y. Qing, C. Yang, N. Yu, Y. Shang, Y. Sun, L. Wang and C. Liu, *Chem. Eng. J.*, 2016, **290**, 37–44.

19 Q. F. Xu, Y. Liu, F.-J. Lin, B. Mondal and A. M. Lyons, *ACS Appl. Mater. Interfaces*, 2013, **5**, 8915–8924.

20 X. Zhang, M. Jin, Z. Liu, D. A. Tryk, S. Nishimoto, T. Murakami and A. Fujishima, *J. Phys. Chem. C*, 2007, **111**, 14521–14529.

21 S. Nishimoto, A. Kubo, K. Nohara, X. Zhang, N. Taneichi, T. Okui, Z. Liu, K. Nakata, H. Sakai and T. Murakami, *Appl. Surf. Sci.*, 2009, **255**, 6221–6225.

22 Y. Lai, Y. Tang, J. Gong, D. Gong, L. Chi, C. Lin and Z. Chen, *J. Mater. Chem.*, 2012, **22**, 7420–7426.

23 X. Zhang, Y. Guo, Z. Zhang and P. Zhang, *Appl. Surf. Sci.*, 2013, **284**, 319–323.

24 S. Li, J. Huang, M. Ge, C. Cao, S. Deng, S. Zhang, G. Chen, K. Zhang, S. S. Al-Deyab and Y. Lai, *Adv. Mater. Interfaces*, 2015, **2**, 1500220.

25 Y. Lu, S. Sathasivam, J. Song, C. R. Crick, C. J. Carmalt and I. P. Parkin, *Science*, 2015, **347**, 1132–1135.

26 S. Nishimoto, M. Becchaku, Y. Kameshima, Y. Shirosaki, S. Hayakawa, A. Osaka and M. Miyake, *Thin Solid Films*, 2014, **558**, 221–226.

27 Y. Qing, C. Yang, Y. Sun, Y. Zheng, X. Wang, Y. Shang, L. Wang and C. Liu, *Colloids Surf., A*, 2015, **484**, 471–477.

28 X. Ding, S. Zhou, G. Gu and L. Wu, *J. Mater. Chem.*, 2011, **21**, 6161–6164.

29 G. Azimi, R. Dhiman, H.-M. Kwon, A. T. Paxson and K. K. Varanasi, *Nat. Mater.*, 2013, **12**, 315.

30 N. M. Zholobak, V. K. Ivanov, A. B. Shcherbakov, A. S. Shaporev, O. S. Polezhaeva, A. Y. Baranchikov, N. Y. Spivak and Y. D. Tretyakov, *J. Photochem. Photobiol., B*, 2011, **102**, 32–38.

31 A. Rafieepour, F. Ghamari, A. Mohammadbeigi and M. Asghari, *Ann. Med. Health Sci. Res.*, 2015, **5**, 129–133.

32 A. Mills and S. Le Hunte, *J. Photochem. Photobiol., A*, 1997, **108**, 1–35.

33 A. L. Linsebigler, G. Lu and J. T. Yates, *Chem. Rev.*, 1995, **95**, 735–758.

34 P. Klonos, G. Dapei, I. Y. Sulym, S. Zidropoulos, D. Sternik, A. Deryło-Marczewska, M. V. Borysenko, V. M. Gun'ko, A. Kyritsis and P. Pissis, *Eur. Polym. J.*, 2016, **74**, 64–80.