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# Light absorption and hydrophobicity of a polystyrene/multiwall carbon nanotube composite with surface nanostructures

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## Abstract

This paper describes an investigation into how combined carbon nanotube doping and surface nanostructuring affects the surface properties of polystyrene. Multiwall carbon nanotubes (MWCNTs) have unique anisotropic electrical properties that can be utilized for light absorption, electromagnetic shielding and nanoscale electrostatic forces. Polystyrene was doped with 5 wt% MWCNTs and the resulting composite was wetted onto a porous anodic alumina template to form a nanostructure surface of nanotubes. Scanning electron microscopy revealed a hierarchical surface structure with the composite nanotubes bundled together as the MWCNTs increased the attractive forces between the composite nanotubes. Water droplet testing revealed that this hierarchical surface structure was superhydrophobic. Though the presence of the MWCNTs caused a direct increase in absorption, the hierarchical surface structure increased reflection. The addition of 5 wt% of the anionic surfactant Sodium Dodecyl Benzene Sulfonate to ensure MWCNT dispersal did not significantly change hydrophobicity or light absorption despite the hierarchical surface structure becoming finer. The created composite has potential use as a surface layer on an organic surface cell as it provides reduced cleaning needs and electrical disturbance but further work is required to reduce the reflection.

Keywords: light absorption, nanotube array, porous anodic alumina, nanostructured surface, hydrophobia


(Some figures may appear in colour only in the online journal)

## 1. Introduction

A superhydrophobic material with high light absorption that provides electromagnetic shielding has significant value as an integrated surface layer for an organic solar cell (OSC). In this paper we propose a composite of polystyrene (PS) doped with

multiwall carbon nanotubes (MWCNT) with a surface nanostructure that has all three of these properties. Assessment of this material is the gap in the state of the art that we fill with this paper. PS is the preferred polymer due to its resistance to chemical corrosion and light degradation. Both PS and MWCNTs have been investigated for their potential as materials for OSC [1, 2] and the combination of the two has been shown to have improved structural properties [3].

A superhydrophobic surface ensures water does not occlude the surface, that residue is not left behind and that dirt is removed by rolling water droplets [4]. In our previous work

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[5, 6] we demonstrated that using a mould to create a surface nanostructure led to superhydrophobicity and hydrophilicity with polystyrene composites. In this paper we have investigated how the doping of MWCNTs into PS changes the texture of the moulded surface nanostructure and how this in turn changes the hydrophobicity and absorption.

In a traditional photovoltaic cover glass, high transparency is wanted to ensure photons reach the photovoltaic materials. With an integrated surface layer high light absorption is wanted for improved photon capture and thus increased solar cell efficiency. Previous work [7] has demonstrated that doping PS with C60 increases absorption. As MWCNTs have a light absorbance of at least 2.8 for near ultraviolet to near infrared wavelengths [8] their inclusion will enhance photon capture.

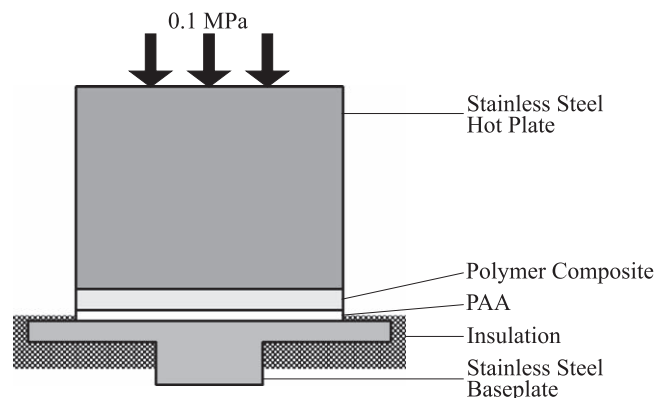
Electromagnetic shielding is important to prevent stray currents from reducing efficiency or harming the photovoltaic circuit. Huang *et al* [9] have demonstrated that a composite material made of polystyrene with carbon nanotube fillers have electrical properties with potential application for electrostatic discharge and electromagnetic shielding. This effect was also studied with MWCNT by Shrivastava and Khatua [10]. This advantage has been aptly demonstrated and is not studied further in this paper.

Previous investigations into doping PS with MWCNTs include Chipara *et al* [11] who investigated the Raman spectroscopy of PS/MWCNT nanofiber composites that were manufactured using electrospinning with a focus on how the spectral bands varied with MWCNT content. Hua *et al* [12] wetted MWCNTs into PS using esterification and copolymerization. Hatui *et al* [13] demonstrated that the addition of MWCNT to PS improves its thermo mechanical performance. These fabrication methods do not produce a hydrophobic surface nanostructure appropriate for the laminar application intended in this paper.

There is a risk that the MWCNTs might bundle together causing an uneven absorption distribution and distortion of the surface nanostructure. During manufacture of the composite films, vigorous ultrasonication was used to debundle and disperse the MWCNTs in the solvent. Zhao *et al* [14] demonstrated that the PS main chain bonds to the MWCNT surface, reducing movement of the MWCNTs to also reduce the risk of rebundling. In this paper we also added the anionic surfactant Sodium Dodecyl Benzene Sulfonate (NaDBS) as a dispersal agent [15] to promote MWCNT distribution. We were interested in what effect the presence of the surfactant would have on the surface nanostructure, in particular if its presence reduces absorption or hydrophobicity.

## 2. Materials and methods

PS was purchased from Sigma Aldrich Co Ltd with a number average molecular weight of 100600 and a polydispersity index of 1.24. MWCNTs were purchased from Bayer Material Science, with diameters of 5–20 nm and lengths of 1–10  $\mu\text{m}$ . Porous anodic alumina (PAA) templates with uniformly distributed 200 nm pores were purchased from Whatman Co



**Figure 1.** Schematic of the surface nanostructure manufacturing equipment.

Ltd UK. NaDBS, NaOH, Toluene, and Ethanol were purchased from Sigma Aldrich Co Ltd.

### 2.1. Composite film manufacture

We manufactured the PS/MWCNT composite film using solution polymerization. Three films were prepared with the following compositions:

- PS (200 mg) in toluene (5 ml).
- PS (190 mg) in toluene (5 ml) with MWCNTS (10 mg) in toluene (10 ml).
- PS (180 mg) in toluene (5 ml) with MWCNTS (10 mg) in toluene (10 ml) and NaDBS (10 mg) in toluene (10 ml).

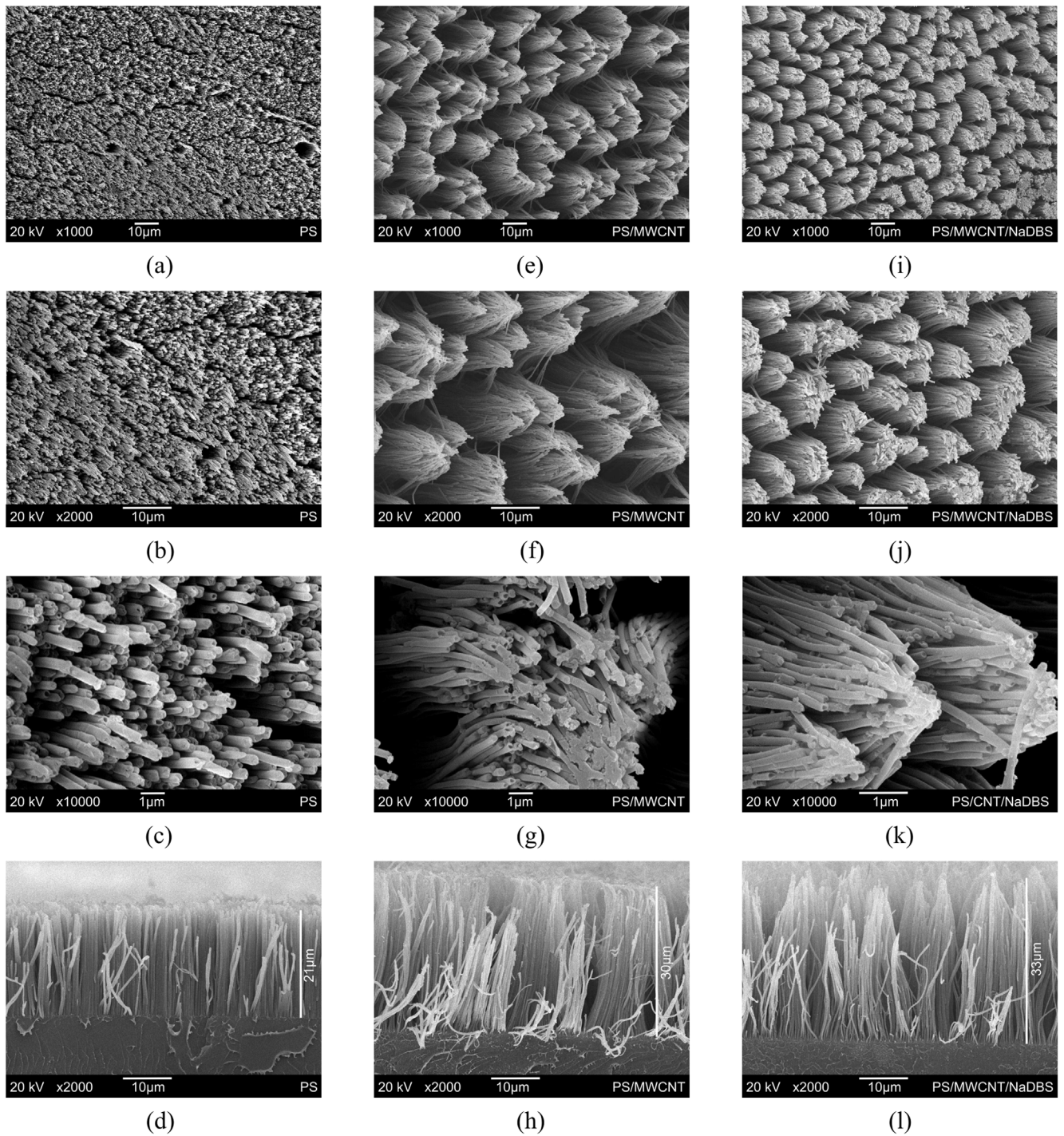
The PS and NaDBS was dissolved into the toluene under magnetic stirring and the MWCNT solutions were treated with ultrasonic vibration at 10 kHz for 60 min to ensure mixing and debundling. The MWCNT solution was mixed into the PS solution with vigorous stirring and further ultrasonic vibration at 10 kHz for 60 min. After the toluene was allowed to evaporate the resulting composites was dried at 40  $^{\circ}\text{C}$  for 2 days and then hot pressed under 1 MPa of pressure at 190  $^{\circ}\text{C}$  for 10 min to compress them into 200  $\mu\text{m}$  thick films.

### 2.2. Surface nanostructure manufacture

We manufactured the surface nanostructure by wetting the polymer composite onto PAA templates [16], using the mould shown in figure 1. The film was pressed onto the PAA template at 0.1 MPa and then heated at 170  $^{\circ}\text{C}$  for 15 min. The mould was allowed to cool naturally to ambient temperatures. The PAA template was removed in a bath of 5 wt% NaOH solution for 12 hours, after which the composite was washed with deionized water and ethanol and dried in a vacuum at room temperature for 5 hours.

### 2.3. Characterization

The surface nanostructures were characterized using a JEOL Model JSM-6490 scanning electron microscope (SEM); and a Phillips CM120 transmission electron microscope (TEM). The light absorption features were measured by UV–vis Spectrometry using an Agilent Cary 4000 which is stated by



**Figure 2.** SEM images of the surface nanostructures: PS (a)–(d), PS/MWCNT (e)–(h) and PS/MWCNT/NaDBS (i)–(l).

the manufacturer to be capable of measuring absorbance values up to 8 with values above 3 reported in the literature [17]. Reflection properties were measured using an Agilent 8453 UV–visible Spectroscopy System. Static water contact angle measurements were carried out using a Ramehart Model 250-F1 Standard Goniometer with DROPImage Advanced 2.1 at ambient room temperature. A drop of deionized water (3 μl) was placed on the surfaces using a microsyringe and then photographed. The contact angle was determined by fitting a Young–Laplace curve around the drop.

### 3. Results

Figure 2 shows the SEM images of the surface nanostructures. During manufacture the composite material has flowed down the sides of the pores of the PAA and has formed arrays of nanotubes. To avoid confusion with the MWCNT ingredient, the manufactured surface nanotubes are referred to as SNTs.

The pure PS surface nanostructure has the SNTs arranged in a unitary structure with almost no grouping. In contrast the

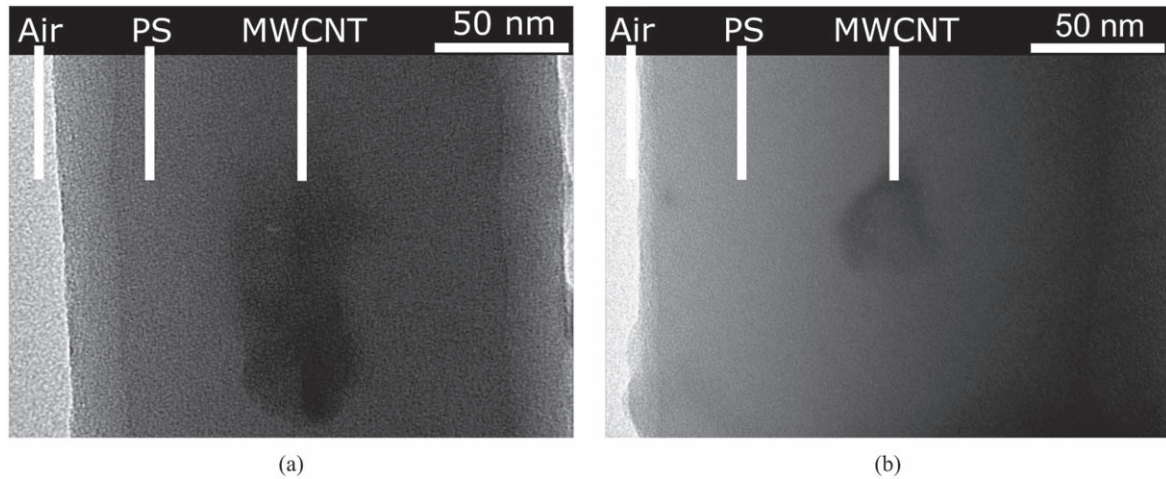


Figure 3. TEM images of (a) PS/MWCNT SNT and (b) PS/MWCNT/NaDBS SNT.

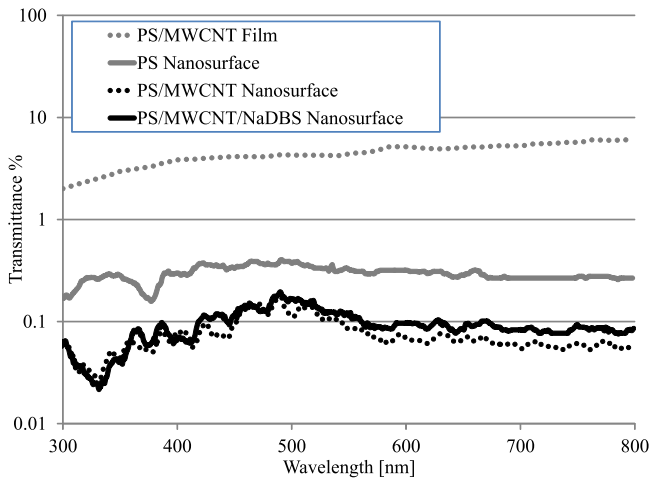


Figure 4. UV-visible light transmittance spectra for PS, PS/MWCNT and PS/MWCNT/NaDBS nanostructured surfaces.

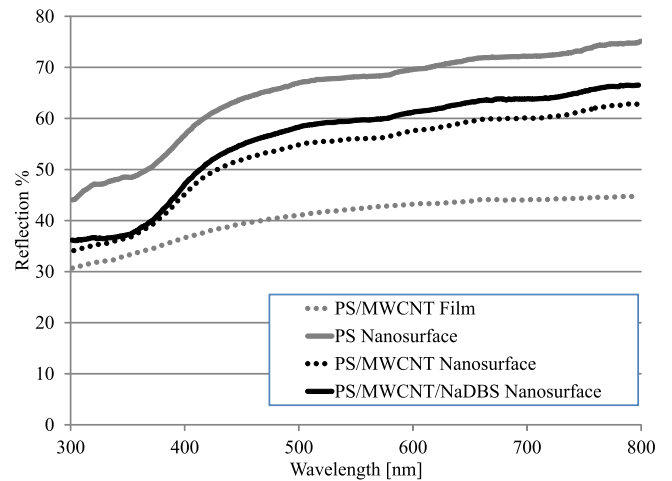


Figure 6. UV-visible light absorption spectra for PS, PS/MWCNT and PS/MWCNT/NaDBS nanostructured surfaces.

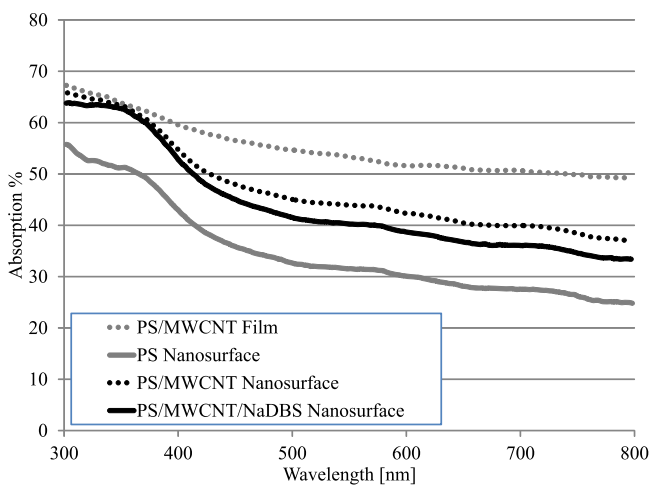


Figure 5. UV-visible light reflection spectra for PS, PS/MWCNT and PS/MWCNT/NaDBS nanostructured surfaces.

Table 1. Water contact angle.

Material	Flat surface	Nanostructured surface
PS	86°	135°
PS/MWCNT	90.5°	155°
PS/MWCNT/NaDBS	90.5°	150°

SNTs of the doped composites were almost completely bundled together creating a surface nanostructure with complex peaks separated by wide valleys. This was a hierarchical structural pattern that has both micro and nano scale features to it. The PS/MWCNT/NaDBS SNTs were gathered in groups less than half the size of the PS/MWCNT SNTs that

have less clearly define peaks. The pattern of the surface nanostructure was finer with less hierarchy.

The hierarchy of the surface nanostructure pattern was determined by the electromagnetism forces between the SNTs. The pure PS SNTs had an attractive force between them which was not enough to overcome their structural stiffness, as there were few free electrons to generate the force. The higher surface energy of MWCNTs produced a much stronger attractive force to each other resulting in large SNT bundles. The benzene ring of the NaDBS bonded to the surface of the MWCNTs, reducing electron mobility which in turn reduced the attractive force leading to smaller SNT bundles. This reduction in attractive force was how the NaDBS worked to reduce the bundling of the MWCNTs during manufacture.

The SEM results also show that the additives resulted in a greater SNTs length. This is attributed to improved flow from reduced surface tension, allowing the composite to melt further into the PAA template. The PS SNTs were approximately 21  $\mu\text{m}$  long, the PS/MWCNT SNTs were approximately 30  $\mu\text{m}$  long and the PS/MWCNT/NaDBS SNTs are approximately 34  $\mu\text{m}$  long.

Figure 3 shows two example images from a TEM survey of the SNTs taken from the side, with (a) a PS/MWCNT SNT and (b) a PS/MWCNT/NaDBS SNT. The darker area at the centre of the images were single MWCNTs within the composite SNTs. No bundling of the MWCNTs was found in either doped composite for the examined edges of the surface nanostructure.

Figures 4–6 show the transmittance, reflection, and absorption spectra for the near ultraviolet to near infrared range for the composites with surface nanostructures. The results of a PS/MWCNT composite with a flat surface are provided for comparison. As expected [2, 8] figure 6 shows that doping PS with MWCNTs results in greater light absorption.

The same cannot be said of the addition of the surface nanostructures. Though the transmittance has been reduced by an order of magnitude, the reflection data reveals that this is due to the surface nanostructures reflecting between 20% and 30% more light than the flat surface, resulting in the observed reduced absorption. This does not compare favourably with modern anti-reflective coatings which can achieve reflections of less than 5% [18].

The results show that as the surface nanostructures becomes more hierarchical there is less reflection. This is attributed to the arrangement of the SNTs. Without MWCNTs, the SNTs were arranged almost vertically (figure 2(d)) with very little exposure of the film below the SNTs. Most of the incoming light bounces off the top of the SNTs and does not penetrate deeper into the surface nanostructure where it could be absorbed. When MWCNTs are present, the gathering of the SNTs results in a massive reduction in flat surface area, exposure of the film below the SNTs, and the presence of sloped surfaces (figures 2(h) and (l)). More of the incoming light can reach deeper into the surface nanostructure and if a photon is reflected from a sloped surface it is more likely to reflect at an angle that will

bring it to another part of the surface nanostructure, increasing the chance of capture.

Though the presence of NaDBS does not effect the transmittance significantly, the finer surface nanostructure pattern presents more flat surfaces and narrower valleys which leads to an increase in reflection. The lack of effect on the absorption indicates that the NaDBS is not affecting the distribution of the MWCNTs, as clumping of the MWCNTs would result in an inconsistent absorption profile. It is thus implied that sufficient distribution of the MWCNTs was achieved by the debundling processing during manufacture. The change in reflection with greater hierarchy of the surface nanostructure implies that further increases in the hierarchy or coarseness of the pattern would further reduce reflection.

The transmittance spectra for the nanostructured composite surfaces have a lot of local minor variations, akin to a noisy signal. This is attributed to the resonant frequencies of the SNTs and signal noise that is not unexpected at these low transmittance values.

Table 1 shows that, as expected, the nanostructured surfaces have significantly increased hydrophobicity over the flat surfaces, with the composite surfaces becoming superhydrophobic due to the greater hierarchy of the nanostructure pattern and SNT length. The addition of the NaDBS resulted in only a small reduction in the hydrophobicity of the surface nanostructures, even though the surface pattern is finer compared to the PS/CNT surface nanostructures. This indicates that increasing the coarseness or SNT length of the surface nanostructures further would not yield a significant improvement in the hydrophobicity.

## 4. Conclusion

A characterization of PS, PS/MWCNTs and PS/MWCNTs/NaDBS composites with surface nanostructure fabricated by wetting the material onto a PAA template was carried out. The results show that adding 5% by weight of MWCNTs directly increased the light absorption and resulted in a hierarchical surface structure that is superhydrophobic. Unfortunately, the superhydrophobic surface reflects more light than the flat surface, resulting in a material that reflects more light than a traditional cover glass. It was shown that the addition of an anionic surfactant did not affect the distribution of the MWCNTs but instead led to a reduction in hydrophobicity and an increase in reflection. It was indicated that vigorous ultrasonication during manufacture is sufficient to disperse the MWCNTs. Increasing the hierarchy of the surface nanostructure pattern has the potential to reduce reflection losses. The resultant composite has potential as an integrated OSC surface layer that is self-cleaning with further investigation into how coarsening of the surface pattern reduces reflection.

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There are no conflicts of interest to declare.

## Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

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