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Recent advances in fluorine-free functionalized nanomaterials for low-wettability applications

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The reduction in wettability afforded by applying superhydrophobic coatings onto substrate materials imbues many useful properties. This review presents recent research advancements of superhydrophobic surfaces formed from functionalised nanoparticles in some of their most promising applications. Silica and metal oxide nanoparticles can be readily functionalised with commercially available hydrophobic compounds to lower their surface energy and can be easily applied to materials with complicated forms and topographies using methods such as spraying or dipping, thus making the coating process adaptable to many situations. Advances in these coatings for imbuing icephobicity, corrosion resistance, self-cleaning, oil-in-water separation, and anti-biofouling behaviour are presented in this short review.

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Introduction

Due to changes in legislation regarding the use of fluorocarbons [1,2] and wider awareness of their toxicological impact [3], there has been significant progress in the last five years in the use of non-fluorinated materials for low-wettability applications. Here we review some of the recent advancements in the area of superhydrophobic nanoparticles functionalized by non-fluorinated low surface energy compounds. These compounds possess alkyl as opposed to perfluoroalkyl groups and consequently have lower toxicological and environmental impact. The purpose of this review is to showcase some of the most impressive advancements in this area and provide an informed opinion about the direction that the research is likely to take. Currently, research efforts are directed towards attempting to reduce the use of fluorinated compounds wherever possible with the aim of devising a non-toxic, mass producible coating that has the smallest amount of environmental impact. Notably, this review is distinct from the article written in 2022 by Sharma et al., which communicated the research progress of superhydrophobic silica nanoparticle coatings [4]. This review aims to highlight the advancements of superhydrophobic nanoparticle coatings towards potential applications more comprehensively for systems involving both silica and metal oxide nanoparticles and provide an opinion on the suitability of the systems for the different applications.

Superhydrophobic surfaces have undergone significant research in the last several decades. In recent years, the definition of what it takes to make a surface superhydrophobic has become more stringent because of the large amount of study in the area. It is now defined as a surface that shows an apparent receding water contact angle that is greater than 150°, as this parameter has a profound influence on its droplet roll-off angle. Previously, they had been defined as surfaces that show apparent water contact angles greater than 150° and sliding angles less than 10° [5]' and debate often continues about how this behaviour should be defined. The generation of these low-wettability surfaces has relied significantly upon biomimicry to inspire methodologies that possess nanoscale topographies suitable to affect the desired Cassie-Baxter wetting states [6]. Inspired heavily by structures found on the surfaces of animals and plants, substantial research interest has led to the design of smart and functional materials that are both highly repellent towards water and also show a range of other desirable applications [6]. A large number of studies have shown that these surfaces possess a range of properties, including drag reduction, anti-reflection behaviour, anti-fouling behaviour, the ability to separate oils from water, and the ability to protect metals from corrosion, amongst a range of others [7,8]. Due to the large breadth of the field, this paper will only seek to review some of the more active areas of the current research into superhydrophobic surfaces by focussing on coatings formed from functionalised nanoparticles, a promising methodology for fabricating water-repellent surfaces. Commercially available nanoparticles are relatively inexpensive and can be readily functionalised with a range of reagents to lower their surface energy under mild synthetic conditions. They can also be suspended in liquids with low environmental impact, such as alcohols, to enable them to be applied onto substrates of interest by widely used methods like dipping and spraying to create coatings that show superhydrophobic behaviour. Methodologies that have been widely utilised to functionalise nanoparticles are discussed in section Nanoparticle functionalization of this paper, in addition to methods used to improve coating durability, whilst potential applications for the methodology are discussed in section Applications of superhydrophobic nanoparticle coatings. Finally, the evaluation of the coatings in their applications are discussed in section Conclusions and outlook, along with directions that we feel that this emerging research should take in the future.

Nanoparticle functionalization

The term "functionalization" is often coined in surface science to communicate that solid interfaces have adsorbed molecules with chemical groups that influence surface energy. The nature of the adsorption can be physical, whereby molecules interact through relatively weak intermolecular forces, such as Van der Waals interactions etc, or chemical, whereby new covalent bonds are created between the adsorbing molecule and surface atoms. It is the latter that is the case when the term is used to describe the adsorption of molecules onto nanoparticles to prepare them for incorporation in low wettability coatings, whereby strong covalent interactions are generated that ensure that the molecules are not removed from the particles' surface because of factors such as abrasion.

The native surfaces of the nanoparticles studied are largely oxidic and contain variable amounts of hydroxyl groups, thus making them hydrophilic by nature [9,10]. Functionalization of molecules bearing alkyl substituents lowers their surface energy, providing these groups are organized such that they point away from the surface [11]. Consideration of the interfacial energy is key when designing liquid-repellent surfaces. A study of the fundamental theory relating to wettability reveals that for a surface to show a contact angle of 90° and be classed as "hydrophobic", the surface free energy of the solid must be a quarter of the surface tension of the liquid in question [11]. Surfaces bearing CH_3 terminated alkyl groups show surface energies of approximately 22−24 mN/m and thus show hydrophobic contact angles towards water (surface tension = 72.8 mNm^{-1}) [8,12]. This wettability can be further lowered by the surface roughness created by the nanoparticle film as described in Conclusions and outlook. By comparison, the wettability of these surfaces is high towards lower surface tension liquids like oils and alcohols which possess surface tensions lower than about 30 mNm^{-1}. Repellency of these liquids requires surface terminal groups with even lower free energy and surfaces that possess topographies containing what have been so-called "re-entrant" surface structures [13], the discussion of which is beyond the scope of this short review. Fluoroalkyl compounds are the only materials in existence that show surface energies low enough to reduce the wettability of oils and low surface tension organic solvents [11]. However, their toxicity and environmental impact haas led to research into other strategies for creating oleophobic surfaces utilising lubricant or "lubricant-like" layers that are immiscible with the fouling liquids [14,15]. Despite their efficacy, surface oiling is not always practical for the application in question and can become depleted, which restricts the use of the methodology. Consequently, substrate coating with alkyl-terminated nanoparticles is an attractive methodology when hydrophobicity is the only requirement. The rest of this section will focus on highlighting the main synthetic protocols used for functionalising nanoparticles to lower their interfacial energy.

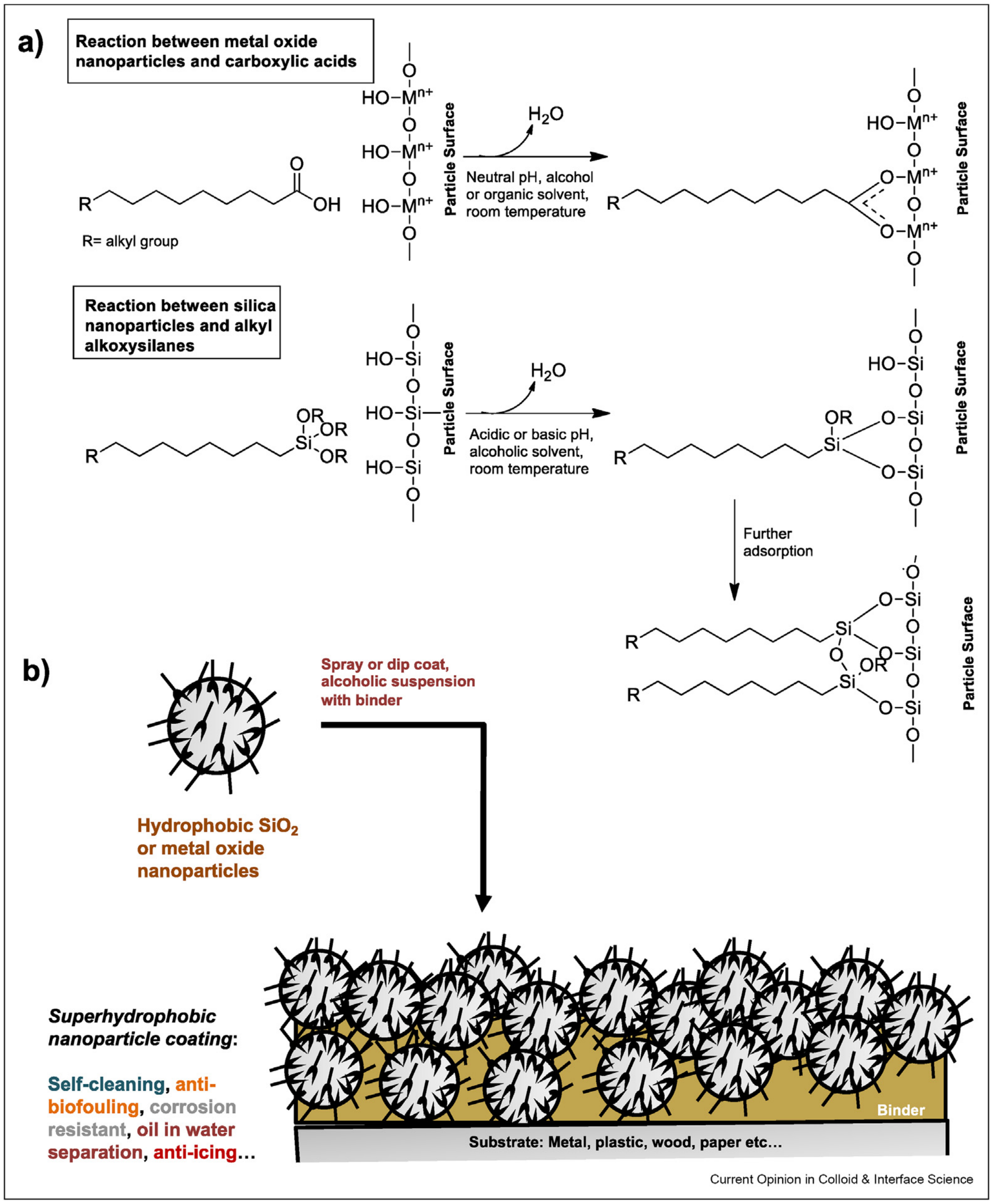
Silica nanoparticles have been widely utilised in the literature to fabricate low wettability nanoparticle coatings through sol−gel condensation chemistry using alkyl alkoxysilanes, which have the structure $SiR(OR')_3$, where R and R' are alkyl moieties [16]. More commonly, commercially available silica nanoparticles are utilised for hydrophobization in the functionalization reactions with these reagents, although some groups have chosen to synthesise and functionalize silica nanoparticles in one step by using a mixture of tetraethoxysilicate and an alkyl alkoxysilane in one step via the Stober reaction [17].

The Stober reaction typically proceeds by adding this mixture of alkoxysilanes to an ethanolic solution that contains water and ammonia [17]. Polycondensation of the alkoxysilanes occurs in a sol−gel manner, whereby base-catalysed hydrolysis of the alkoxy groups generates reactive silanols that attack the Si atoms of other alkoxysilanes/silanols to create oligomers and then polymers [16]. These species can then react further in the same manner to form larger particles [17]. Termination of the growth occurs when all the pendant groups bound to the Si atoms are alkyl as opposed to alkoxy or silanol, and there are thus no sites for further condensation [16]. The size of the particles generated in the process is influenced by the concentrations of all the reagents, making it a process that can be difficult to control [18]. Park et al. employed this process recently to produce superhydrophobic silica nanoparticles terminated with hexadecyl groups. Films of the particles showed water contact angles of 165° and sliding angles of less than 2° [17].

By comparison, the functionalization of preformed commercially available silica nanoparticles takes place via the addition of the alkyl alkoxysilane to an alcoholic, typically ethanolic, suspension containing the particles (Figure 1(a)) [19]. Sol–gel condensation then similarly takes place to the above under acidic or basic conditions, whereby hydrolysis of the alkoxysilanes occurs to generate silanols that react with surface hydroxyl groups to functionalize the surface (Figure 1(a)) [16]. Since each Si atom of the alkyl alkoxysilane has three alkoxy groups this can mean that the chemisorbed species can then react further with neighbouring adsorbed alkyl alkoxysilanes providing they still possess reactive groups, thus creating a rigid crosslinked network (Figure 1(a)) [20].

Metal oxide nanoparticles have also been utilised to create superhydrophobic surfaces after functionalisation with carboxylic acids [6]. Chemical adsorption of carboxylic acids, as carboxylates, has been observed to

Figure 1



(a) Schematic diagrams depicting the functionalization of metal oxide nanoparticles with carboxylic acids and silica with alkyl alkoxysilanes. **(b)** Schematic diagram showing the fabrication of functionalized nanoparticle/binder superhydrophobic coatings.

occur onto the hydroxylated surfaces of aluminium oxide [21–23], magnesium oxide [20], zinc oxide [24,25], and magnetite [22], amongst others. To our knowledge, carboxylate formation has not been observed to occur on silica surfaces, indicating that the metal cation also plays a role in the reaction. The mechanism leading to adsorption has been described in the literature as an acid–base reaction [20]. However, it is also possible that it might be more akin to a conventional esterification process performed in synthetic organic chemistry. Despite the ambiguity, carboxylate adsorption onto the metal oxides has been observed largely in the bridging coordination mode, as elucidated using infrared spectroscopy, where both O atoms of the carboxylic acid interact with two different metal sites (Figure 1(a)) [21,22].

Nanoparticle functionalisation has most commonly proceeded with carboxylic acids and alkoxysilanes, largely because of the low cost of the reagents and the gentle synthesis conditions. However, the creation of superhydrophobic surfaces using nanoparticles is not only limited to these reagents. Any molecule bearing a suitably hydrophobic group that is capable of chemically adsorbing onto a reactive surface with the necessary level of surface roughness is a worthy candidate for lowering the wettability to the desired level. For example, *Li* et al. utilised the strong covalent interaction of the S anion when they chemically adsorbed octadecyl thiol onto textiles decorated with Ag and Fe, Co, Ni and Cu oxide nanoparticles [26]. The functionalised textiles were observed to be highly water-repellent and displayed tilting angles as low as 2° for water droplets [26].

Morphology and durability of superhydrophobic functionalised nanoparticle films

Superhydrophobic wetting states are observed because of a combination of surface energy and roughness. It is observed that the maximum contact angle of what is regarded as a "smooth" PTFE surface is less than 120° [27]. For a hydrocarbon-terminated surface, this value is lower because of the higher surface energy alkyl groups versus perfluoroalkyl groups [28]. Increasing the contact angle of these materials further is only possible through roughening the surface, as described by Cassie and Baxter in their fundamental theory that was communicated in 1944 [29]. Detailed discussion of how surface topography affects the wettability are beyond the scope of this short application-focussed review. Briefly, roughening the surface creates a state where the water droplet sits on top of the surface features, since it is thermodynamically unfavourable for it to penetrate between them. This results in a low contact area between the droplet and underlying surface, with air pockets existing between the surface features, a state defined as Cassie-Baxter wetting [30]. Due to its low contact area, the droplet sitting at the composite (solid-liquid-gas) interface is weakly adherent to the solid and can readily roll off if the surface is tilted or if energy is transferred so that it can overcome the frictional force [30]. In nature, many examples of surfaces like these are observed in order to confer organisms with biological advantages. Water striders, for example, utilise superhydrophobic surfaces on their legs for their mobility [31]. Creating superhydrophobic nanoparticle coatings requires composite surfaces of this nature to be created. This can be achieved using nano-sized particles alone, or so-called coatings with "hierarchical" roughness that are formed from both micron- and nano-sized particles [30]. Coatings with these dual-length scales have been studied because of their similarity with the hierarchical roughness that is observed on superhydrophobic surfaces observed in the natural world, such as on the lotus leaf for instance [30].

It has been shown that micron-scale topographies are sufficient for creating Cassie-Baxter states, whereby the contact angles are greater than 150° and droplets show sliding behaviour during tilting angle measurements [32,33]. For example, this behaviour has been observed in studies that have investigated the topography of hydrophobic micropillar arrays [32,33]. However, droplets in Cassie-Baxter states are less stable to transition to the Wenzel state during evaporation of these surfaces [32]. For hydrophobic coatings that show a random topography, such as those formed from functionalized nanoparticles, a greater level of nanoscale roughness substantially reduces the contact angle hysteresis and thus adhesion that water droplets experience with the underlying surface [21].

Without any additives, the forces acting between the particles and the underlying substrate are relatively weak and comprise physisorption alone. This means that the surface structures of the coating are quite delicate and thus susceptible to most forms of abrasion. This presents a challenge when considering applications for these coatings since damage would most likely result in an increase in their wettability and lead to the environmental release of particles. Consequently, research has been directed towards increasing the durability of nanoparticle coatings through embedding particles in adhesive resins [22,34,35], or naturally sticky materials such as waxes [36]. (Figure 1(b)) presents a schematic diagram of the fabrication process for functionalized nanoparticle/binder superhydrophobic coatings.

It has been shown that durable superhydrophobic coatings can be created by either applying the particles onto a substrate that had been pre-coated with adhesive [34] or adding the adhesive directly into the nanoparticle coating suspension [22]. Surface fouling of the particles by the adhesive, leading to a covering of hydrophobic groups, also takes place to an extent. This means that the relative proportions of the particles and adhesive need to be optimised to ensure the superhydrophobic effect remains [22]. The addition of adhesive or binder into the coating mixture allows a more durable composite material to be created, which can show resistance to damaging types of mechanical wear such as that caused by sandpaper abrasion [34]. The low wettability of the coatings is maintained since any coating material lost through abrasion exposes underlying layers of nanoparticles [28,37].

The roughness created by the nanoparticles in the coatings leads to them scattering visible light, and so far, no research has shown that these coatings can be made to be entirely optically transparent. However, progress has been made recently using small silica nanoparticles (<7 nm), where it has been shown that light scattering can be limited when the surface roughness is kept below 100 nm, resulting in films that show high levels of optical transparency [38].

Particle functionalization methodologies are robust and widely established. As a result, it is perhaps not surprising that significant further research has not been conducted in recent years. Table 1 summarises what we feel are the advantages and disadvantages of the nanoparticles that have been studied heavily over the last several years and highlights applications where we feel they might show the most promise.

Attention instead has focussed on developing the coating processes to achieve strong and reliable adhesion onto desired substrates, or so the films can achieve certain properties, such as being antireflective or resistant to bacterial adhesion. Methods involving adhesives/binders have become established since they can readily and effectively produce durable coatings and consequently are still widely used in current research reports. However, other methodologies such as grafting particles onto the adhesives directly or embedding particles in porous films have been studied in recent years to prepare coatings for certain applications. Our evaluation of the utility of some selected examples of recently developed coating methodologies are displayed in Table 2 and compared to the more traditional “particles and adhesive” strategies.

Applications of superhydrophobic nanoparticle coatings

The ultra-low adhesion experienced by water droplets on superhydrophobic surfaces means that coatings that show this extremely low wettability could be utilised for a wealth of different applications. In this section, we discuss applications that nanoparticle coatings of this nature might be particularly suitable for because of their inherent properties, for the particular applications in mind.

Self-cleaning applications

The ease of spraying coupled with the compatibility of the particles with binders and adhesives makes functionalised nanoparticles potential candidates for coating onto substrates that are not required to be optically transparent. As discussed, the poor abrasion resistance of the coatings without a binder makes them highly vulnerable to environmental release. Consequently, robust behaviours, self-cleaning or otherwise, can only be achieved by additives included in the film to increase durability. Self-cleaning behaviour of a variety of materials from the food and beverage, textile, and manufacturing industries, alongside environmental contaminants, has been demonstrated for superhydrophobic nanoparticle coatings. This section

Table 1

Evaluation of nanoparticles that have been utilised recently to create non-fluorinated superhydrophobic coatings.

Particles	Advantages	Disadvantages	Promising Applications
SiO_2	Coatings often show high levels of optical transparency	Basic conditions often required during functionalisation.	Building [38] facades
Ferrous oxides	Magnetic properties could be exploited for mobility during application Reactivity with alkyl alkoxysilanes and carboxylic acids	Magnetic properties make them difficult to disperse Coatings are often coloured and opaque	Oil in water separation [35]
Aluminium oxide	Widespread compatibility with many engineering materials Reactivity with alkyl alkoxysilanes and carboxylic acids	Coatings are often milky	Oil in water separation [23]
Cerium o xide	Reactivity with widely used silicone oil reported	CeO_2 NPs can exhibit toxic effects on living organisms.	Antibiofouling [39]

Table 2

Different types of coating methodologies are used to fabricate superhydrophobic non-fluorinated nanoparticle coatings.

Coating methodology	Description	Advantages	Disadvantages	Applications
“Spray onto” method	Substrate material is coated with adhesive or binder material.	Less control of particle and binder proportions required to create a non-wetting state.	Two-step process, more difficult to scale and utilise as a commercial product.	Self-cleaning [34]
	Particles are coated onto the binder as a separate step.	Can utilise commercial adhesives and natural binders such as waxes.		Icephobicity [19]
“One pot” spray method	Particles and binder are sprayed onto substrate from one suspension.	Single step process, more easily to implement on a production line.	Studies are required to optimise the coating in terms of its wettability and durability.	Self cleaning [37]
		Greater homogeneity of coating/binder film.	Greater possibility of surface fouling by the binder and subsequent loss of wettability	Oil in water separation [35]
Coupling of particles onto binder	One-pot spray utilising particles, binder and coupling agent.	Covalent interactions between binder and particles resulting in strong adhesion.	Coupling agents studied have inherent toxicity.	Oil in water separation [40]
Particle embedding in porous coatings	Pores are created in coatings.	Coatings produced have been shown to be highly optically transparent.	Likely loss of hydrophobicity because of less particles present at the surface.	Antireflective coatings [41]
	Pore-creating agents are subsequently degraded by annealing and particles are applied to fill the pores.		Energy costs associated with heat treatment.	
Adsorption of low surface energy compounds onto particles following film formation	Rare earth oxide nanoparticle deposition on pre-cast polydimethylsiloxane through flame spray pyrolysis.	Silicone oil is widely available and regarded as non-toxic. It is currently utilised in a range of applications.	Film durability studies have not yet been performed.	Anti-biofouling [39]
	Hydrophobization achieved through vapour deposition of silicone oil onto particles.		Hydrophobization methodology using silicone oil not observed on silica nanoparticles, so method may show low versatility.	

highlights some of the most impressive self-cleaning behaviours demonstrated over the last several years.

In 2022 Yu et al. reported a straightforward approach to fabricate superhydrophobic composite films prepared from a mixture of zinc oxide nanoparticles and the shrimp-derived biopolymer chitosan, using layer-by-layer assembly [24]. Post-film modification using stearic acid was used to lower the surface energy that imbued the surface with superhydrophobic properties [24]. It was observed that the tensile strength of the films increased after both nanoparticle incorporation and functionalisation, indicating the compatibility of the particles with the biomaterial [24]. The composite surfaces were observed to show self-cleaning behaviour when water was applied to films that had been contaminated with carbon black, confirming their potential utility [24]. This study shows an advancement in the field since it presents positive synergistic behaviour between nanoparticles and naturally derived polymers.

Similarly, Gong et al. showed that superhydrophobic surfaces prepared using SiO_2 nanoparticles functionalised by vinyl and methyl-terminated alkoxysilanes showed self-cleaning ability when contaminated with carbon powder [34]. Interestingly, the short C2 and C1 of the hydrophobic agents were able to create surfaces that displayed contact angles of approximately 160° and sliding angles of less than 6°, which showed that the functionalising molecule didn’t need to possess a long alkyl chain [34]. Furthermore, the surfaces retained their superhydrophobic behaviour after being coated with epoxy resin [34]. The adhesive was observed to increase the durability of the vinyl-terminated nanoparticle coating, as demonstrated by retaining its low wettability after sixty cycles of sandpaper abrasion [34]. Notably, its high durability was significantly greater than other silica-derived superhydrophobic coatings, indicating its prospective utility [34].

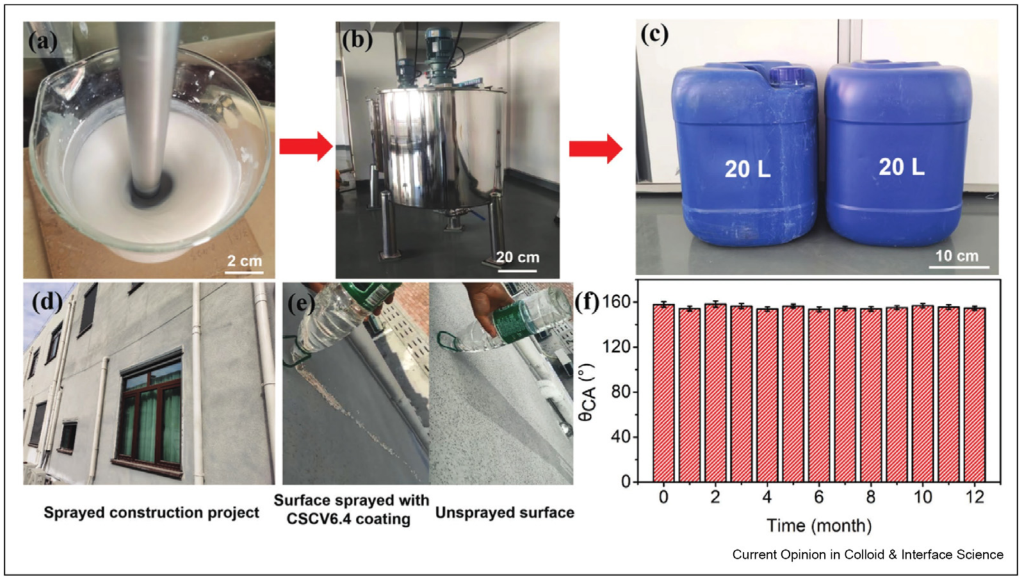
Furthermore, it has been shown recently that self-cleaning examples of superhydrophobic SiO_2 nanoparticle/binder coatings can be readily applied in outdoor environments [37]. It was demonstrated that the fractal, nanoscale coral-like structures formed from combining commercially available hydrophobic SiO_2 particles and varnish-containing acrylic acid and dodecanol ester could be readily applied to building facades to generate highly robust water-repellent surfaces (Figure 2) [37]. The low temperature required to affect curing of the varnish facilitates its usage for external applications at scale, since other binders that have been widely used in the literature (epoxy resins etc) have generally been cured at 80−100 °C [37]. Water applied to the coating was shown to readily remove contaminants such as sand, and the coatings were resistant to fouling with common liquids such as ink, coffee and brine. The coated building façade was shown to retain its superhydrophobicity after one year, indicating the coating's resistance to external weathering (Figure 2(f)).

Oil in water separation

The preferential wetting of oil droplets onto hydrocarbon-terminated superhydrophobic surfaces has meant that these coatings can be readily applied onto porous substrates to create materials that effectively separate oils and lower viscosity organic liquids from water and emulsions. Differences in the Laplace pressure of the two liquids on these surfaces lead to selective diffusion of the oil or organic liquid through the pores, thus leading to effective separation [42]. This methodology has been most widely studied using gravity-fed separation apparatus [35,42,43]. However, several different protocols have also been developed. More recently, the buoyant properties of the superhydrophobic coatings are being utilised to fabricate boats that can collect oils from the aqueous phase [35,42].

Yu et al. fabricated an impressive coating for cotton fabric by combining SiO_2 nanoparticles, polyethylene imine, 3-(trimethoxysilyl)propyl acrylate, and a dodecyl alkoxysilane as the hydrophobic agent [42]. Michael addition of the amine groups of polyethylene imine onto the acrylate's double bond of the α,β-unsaturated ester and condensation of its alkoxy groups with the surface OH groups present on the silica particles created a cross-linked network, with the hydrophobic silane chemically adsorbing onto the particles' vacant sites [42]. The network was observed to show superhydrophobic wetting behaviour, which imbued self-cleaning abilities, and was shown to be abrasion resistant as a result of the high degree of hydrogen bonding taking place between the N−H groups of polyethylene imine and the OH groups present on cotton fabric [42].

Figure 2



Large-scale preparation and application of CSCV-6.4 coating: **(a)** laboratory preparation; **(b)** large-scale production; CSCV-6.4 coating suspension; **(d)** outdoor exposure building project; **(e)** wetting performance comparison; **(f)** weather resistance. Reproduced with permission from reference 38. Copyright 2024 John Wiley and Sons.

The authors utilised the composite coating on fabric for oil in water separation for different organic solvent/water mixtures, where the joint superoleophilic/superhydrophobic properties of the surface allowed complete wetting of the surface by the organic liquids but not by water [42]. The coated fabric was observed to show robust separation of greater than 99.5 %, which was only observed to diminish slightly after eighteen cycles [42]. Interestingly, the authors were able to observe that they were able to make boats out of the coated fabric that were capable of floating on the water when the pieces were bent over copper mesh [42]. These boats were able to remove oils from the water phase through adsorption followed by diffusion of the organics through the porous fabric into the inside of the vessels, suggesting that this methodology could be employed to clean up oil spills [42].

Nguyen et al. also utilised a silica nanoparticle coating with a cross-linked low surface energy polymer to fabricate a sponge capable of performing oil recovery from aqueous environments [43]. Taking advantage of boroxine chemistry, the authors prepared supramolecular crosslinked polymers through dehydrating monomers formed from aminated polydimethylsiloxane and 2-formylphenylboronic acid [43]. These monomers self-adsorbed onto spiky SiO_2 nanoparticles to generate highly effective superhydrophobic coating material [43]. The coating showed extremely low wettability (WCAs $>165°$) and was highly optically transparent when applied to glass substrates [43]. Interestingly, the coatings were observed to show robust self-healing abilities, as evidenced by their hydrophobic recovery, after being subjected to O_2 plasma cleaning [43]. This behaviour was ascribed to the burying of nascent hydrophilic groups, formed from oxidation by the plasma, through the surface energy lowering reorganization of the polymer backbone [43]. Applying the coating onto a sponge made an efficient oil-in-water separation material that could remove chloroform droplets from aqueous suspensions [43]. In addition, the authors also demonstrated that the coated sponge was able to robustly separate dichloromethane from water and showed a separation efficiency of 97 % after twenty cycles [43].

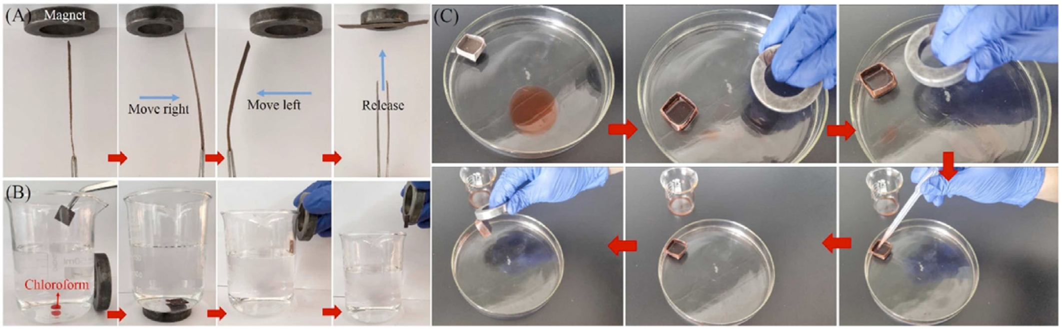
Liu et al. extended the utilisation of this methodology through demonstrating that it was possible for superhydrophobic nanoparticle coatings to successfully remove a variety of micro and nano nano-sized plastic particles from aqueous solutions containing small amounts of hexane [23]. The authors utilised a one-pot particles and adhesive approach to deposit coatings formed from carboxylate functionalised Al_2O_3 nanoparticles and polydimethylsiloxane onto sponges through dip coating [23]. Hydrophobic interactions led to the preferential wetting of the organic solvent onto the plastic particles, which in turn wetted the superhydrophobic sponges as a result of its oleophilicity, leading to the pick-up of the particles onto the sponge [23]. Their coated sponges also showed a robust capacity for adsorbing organic liquids from water mixtures (50 g/g for chloroform) and for removing oil droplets from emulsions [23]. Furthermore, the coated sponges also maintained separation efficiencies of over 90 % for chloroform and n-hexane after ten cycles in the more well-studied gravity-fed oil-in-water separation experiments, providing more evidence for the utility of the coating [23].

Li et al. showed that it was also possible to have control over the movement of a porous substrate coated with superhydrophobic nanoparticles during oil recovery operations [32]. The authors fabricated a coating that contained PDMS functionalised silica and Fe_3O_4 nanoparticles that were bound onto paper using epoxy resin [35]. The coating was observed to be able to separate a variety of organic liquids and high-viscosity oils from the aqueous phase (toluene, dichloromethane, diesel etc) using gravity-fed separation and also to remove chloroform from water in oil emulsions [35]. Interestingly, the authors were able to utilise the ferrimagnetic properties of the Fe_3O_4 to drive a paper boat with the coating, which they defined as EP@PDMS@Fe_3O_4@SiO_2@PP, which floated on the water as a result of its superhydrophobic properties, across the water to an area contaminated with n-hexane, where it absorbed the organic liquid (Figure 3) [35]. Following this, the boat was magnetically moved to another area where the oil could be recovered (Figure 3(c)) [35]. This shows a further level of control that can be imbued onto coatings of this nature because of exploiting magnetic nanoparticles in this application.

Icephobicity

Ice accumulation on structures in cold regions can negatively impact society and infrastructure. It can impact power transmission, and communication systems, and cause accidents during transportation [44]. Consequently, mechanisms that lower ice adhesion and delay the freezing time of water could offer tangible benefits. As discussed, the small contact area observed when water droplets are placed onto a surface that shows Cassie-Baxter wetting is responsible for their extremely low adhesion onto the surfaces. During freezing, it is not believed that the volume expansion of the droplets that occurs is sufficient to cause significant penetration of the frozen water into areas between the surface features [45]. As a result, these surfaces have been described as “icephobic” since the adhesion of frozen water onto them is low because of the small contact area, and the term “icephobicity” was coined. In addition, the reduced thermal conduction taking place as a result of the trapped air pockets on the surface increases the freezing time of water droplets meaning that surfaces can be exposed in cold environments for longer without experiencing ice build-up [45]. Notably however, the Cassie-Baxter state is only effective for imbuing this

Figure 3



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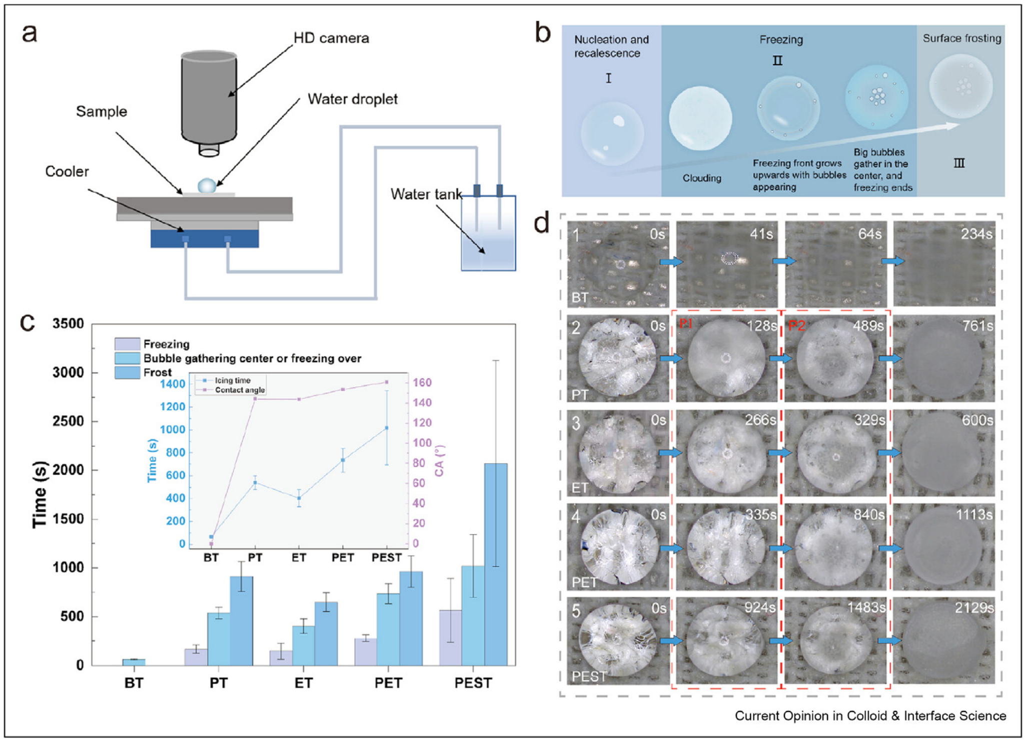
Optical images demonstrating magnetic response of EP@PDMS@Fe_3O_4@SiO_2@PP **(a)**. Optical images showing the process of selective heavy oil adsorption from oily water by EP@PDMS@Fe_3O_4@SiO_2@PP using a magnet **(b)**. Optical images showing the process of selective light oil absorption, collection, transportation and recovery from oil-polluted water region by a small paper boat made from EP@PDMS@Fe_3O_4@SiO_2@PP driven using a magnet **(c)**. Reproduced with permission from reference 36. Copyright 2024 Elsevier.

behaviour for droplets impacting the surfaces with low-to-moderate Weber numbers, a parameter used to define the ratio of a droplet's inertia to its surface tension. It has been studied that droplets can transition to the Wenzel state on superhydrophobic surfaces when they impact with high velocities, thereby inhibiting the icephobic behaviour imbued by the surface's topography [46]. Despite this, superhydrophobic nanoparticle coatings might be quite suitable for reducing ice build-up in situations where this does not need to be considered since they can be readily sprayed onto structures in outdoor environments and thus help reduce some of the negative effects of freezing weather. This might not be in the context of aircraft where the relative speed of droplets can reach ten metres per second or terminal velocity raindrops. Rather, the coatings could find the most effective application in cold, dry environments where ice accumulation stems from droplet accumulation from water vapour in the air.

Recently, Allahdini et al. showed that a superhydrophobic anti-icing coating can be prepared using fumed silica nanoparticles, methyl trimethoxysilane and an alkoxysilane binder [19]. The coating was subjected to ice push off and centrifuge tests to study the adhesion of ice onto the aluminium, where it was observed that the coating reduced the adhesion strength by an order of magnitude from 650 kPa to just 13 kPa in the push-off tests [19]. Furthermore, it was observed that the low adhesion could be maintained for 15 cycles without increasing significantly. The authors also studied the freezing delay of water droplets as a function of temperature. As expected, the rate was observed to be temperature-dependent. However, the largest differences between the coated and uncoated samples were observed at the lower temperatures studied. For example, at -10 °C the freezing delay was 3294 s for the superhydrophobic surface, whereas it was less than 250 s for the uncoated aluminium [19].

Qin et al. adopted a similar approach when they demonstrated that a highly durable superhydrophobic coating could be readily sprayed onto textiles from an ethanolic suspension containing silica nanoparticles, polydimethylsiloxane, epoxy resin, and the alkyl-amine bearing alkoxysilane 3-aminopropyltriethoxysilane, as a cross-linking agent [47]. This coating, which the authors termed PEST, was observed to show a contact angle of greater than 160° (Figure 4(c)) and displayed a contact angle hysteresis of only 2° [47]. The coating formed on the textile's fibres was found to be highly robust towards mechanical abrasion as a result of cross-linking between the siloxane and the epoxy resin and was observed to possess water contact angles of greater than 150° after more than 1200 abrasion cycles [47]. Studies observing the freezing of water droplets on the nano-silica coated surface revealed that it took droplets 1019 ± 324 s to freeze, which was substantially longer than the untreated fabric (64 ± 5 s), indicating the utility of the coating for imbuing delayed icing behaviour [47]. The authors observed the freezing of individual droplets using a high-definition camera and where they were able to observe the freezing fronts advancing from the outside to the inside of the droplets (Figure 4). Textile samples coated with either the siloxane or epoxy resin, which showed contact angles between 143 and 145°, presumably because of the roughness of the textile fibres, were observed to display droplet freezing times of between 400 and 550 s (Figure 4(c) PT and ET sample), whereas samples coated with a combination thereof showed a contact angle of 153° and a freezing temperature of 735 ± 103 s (Figure 4(c) PET sample) [47].

Figure 4



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(a) Schematic diagram of icing delay equipment. **(b)** Schematic diagram of the freezing process of the droplet on a hydrophobic surface. **(c)** Time at various stages of different surfaces (inset is the time when droplet freezing ends on different surfaces). **(d)** Top observation of ice formation on (1) BT, (2) PT, (3) ET, (4) PET, and (5) PEST surfaces at −8 °C with delay times. P1 and P2: the different stages of ice growth. Reproduced with permission from the American Chemical Society.

These results strongly support the assertion that freezing behaviour of a water droplet on a rough surface is intimately linked to its contact angle.

Wu et al. synthesised an acrylate copolymer using free radical polymerisation for use as an adhesive in a superhydrophobic coating with hydrophobic 7 nm silica particles [38]. The copolymer contained pendant alkoxysilyl groups that cross-linked with each other and the particles in the presence of moisture to create a highly durable abrasion-resistant coating [38]. Using this methodology, it was possible to create surfaces that showed water contact angles of greater than 160° and sliding angles of less than 2° [38]. The coatings also retained high optical transparency when applied to glass substrates (>89 % in the visible region), possibly because of the small size of the nanoparticle used [38]. The authors subjected their coatings to simulated freezing rain in sub-zero conditions and observed negligible ice formation because of the coating's self-cleaning behaviour [38]. They also studied the freezing behaviour of water droplets on the coating's surface where they observed a twenty-three-fold increase of droplet solidification of 1140 s compared to uncoated glass and similarly observed that the freezing time is likely to be a function of the amount of hydrophobic material in the coatings [38]. The authors also observed a substantial reduction in the adhesion of ice on the coated surface with respect to the as-received glass (632 vs 31 kPa), in line with the related reports [38].

Jian et al. fabricated a hierarchical two-tiered superhydrophobic surface composed of acid-etched aluminium alloy and methyl-terminated fumed silica nanoparticles [48]. The acid etching created a micron-stepped surface onto which the functionalised nanoparticles were deposited via dip coating [49]. Despite the absence of a binder, the coating was able to withstand over 100 g of sand hitting its surface in impact tests, without losing its superhydrophobic properties [49]. It's possible that the abrasion resistance could be in part linked to the micron-scale topography, which could provide roughness to hold the nanoparticles in place when they suffer impact. Impressively, water droplets on this surface took over 4970 s to freeze at −20 °C and the coating was able to maintain its superhydrophobicity after multiple icing and de-icing cycles [49]. Although the authors did not speculate, it is plausible that this behaviour might be due to even lower levels of thermal conduction through a superhydrophobic coating with hierarchical micro- and nano-surface roughness. Notably, this is the longest onset of the freezing time on superhydrophobic nanoparticle films that we have found from articles published in the last two to three years. However, a study reported by Eberle et al. in 2014 showed that a nanostructured surface displayed a freezing delay of over 24 h because of a quasiliquid layer preventing ice nucleation [48]. The two orders of magnitude difference between this surface and those constructed using functionalized nanoparticles indicates that although these coatings are attractive because of their ease of fabrication, there are some limitations in terms of performance.

An interesting phenomenon that has been observed on superhydrophobic surfaces in freezing environments is a behaviour that has been described as “jumping droplet condensation”. This is where the surface energy that is released when subcooled condensate droplets coalesce is sufficient for them to spontaneously eject from the surfaces [50]. This behaviour prevents ice nucleation across the bulk of the surface, thereby reducing the rate of frost formation. However, frost formation has still been observed to occur on these surfaces through a mechanism described as inter-droplet “ice bridging” at so-called “edge defects”. This is where vapour formed during the evaporation of the condensate droplets deposits onto freezing droplets and contributes to the formation of ice bridges that connect and freeze adjacent droplets and lead to frost propagation across the substrate [50]. We believe that this behaviour is likely to occur across all superhydrophobic surfaces and is one reason why we believe that it will never be possible to design surfaces that remain completely frost-free using these topographies.

Corrosion resistance

Superhydrophobic nanoparticles can enhance corrosion resistance by forming a protective barrier on metal surfaces to moisture and corrosive ions (Cl^- etc). Furthermore, the high mobility of water droplets on these surfaces, which could contain corrosive ions, limits the contact time in which a corrosive attack could occur. By providing a barrier against moisture and corrosive substances, superhydrophobic nanoparticles help to prolong the lifespan of metal structures, equipment, and components in various industries, including construction, transportation, and marine applications. Studies into the corrosion resistance provided by superhydrophobic coatings applied onto metallic substrates are assessed largely through electrochemical methods such as potentiodynamic measurements and electrochemical impedance spectroscopy (EIS) [51,52]. These are often conducted in tandem with salt spray tests to visually assess the extent of corrosion [53].

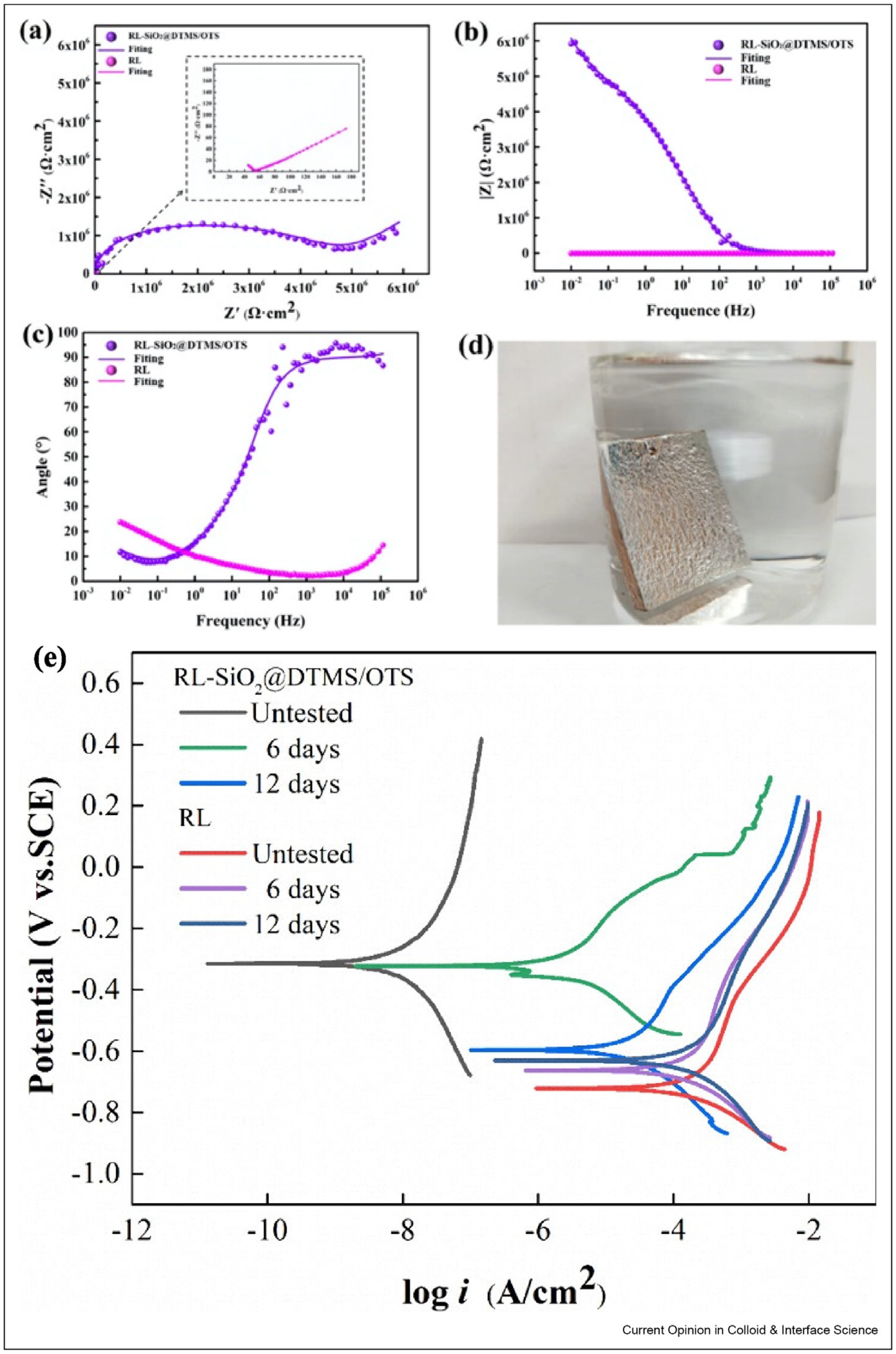
Doganci et al. recently used aluminium oxide nanoparticles hydrophobized by treatment with octylsilane coated onto galvanized steel and skin-passed galvanized steel substrates to prepare coatings that showed contact angles greater than 160° [54]. The coatings were observed to show self-cleaning behaviour towards several common liquids, including tea, cherry juice and milk [54]. Epoxy resin was also added to the spraying suspension to enhance the coating’s durability. It was observed that the amount of red rust observed after salt spray tests on the galvanized and skin-passed galvanized steel surfaces was dependent on the number of hydrophobic nanoparticles in the coatings, indicating that the corrosion behaviour might be related to the self-cleaning behaviour of the coatings [54].

Sun et al. used sol–gel chemistry to deposit a silica nanoparticle layer onto preformed rust layers created on weathering steel [55]. The purpose of the study was to investigate the corrosion behaviour of the hydrophobically coated rust film, which they termed RL-SiO_2@DTMS/OTS, compared to the hydrophilic rust film (RL), in order to create a coating that could be applied to the rust layer of weathering steels to combat some of the environmental problems associated with their rust “runoff” [55]. The coating was hydrophobized using a mixture of dodecyl- and octadecyltrimethoxysilane [55]. Interestingly, the authors observed that the nanoparticle film was present throughout the rough structure of the FeOOH phase present in the rust layer, as elucidated using SEM and tape-peeling experiments [42]. Although not superhydrophobic, the hydrophobic structure (water contact angle = 143°) created by the nanoparticle coating adsorbed an effective barrier layer of air into its porous structure that blocked the flow of water and ions to its surface. EIS measurements (Figure 5 (a)-(c)) revealed that the nanoparticle coating had significantly higher polarisation resistance, indicating that the film was providing a robust barrier to corrosion by increasing the complexity of ionic paths through the coating layer [55]. In addition, the authors also observed that the corrosion potential of the substrate moved to a more positive potential when the nanosilica coating was applied during twelve days of cyclic wet-dry corrosion tests and observed a drop in corrosion current by four orders of magnitude, which corresponded to a corrosion inhibition efficiency of 99.9 % (Figure 5(e)) [55]. The authors did observe using SEM and contact angle measurements that some of the particles would fall off the surface during the twelve of cyclic corrosion testing. However, the surface remained highly hydrophobic and maintained a corrosion inhibition efficiency of over 90 %, indicating that the methodology had significant longevity [55].

Anti-biofouling

The self-cleaning behaviour of superhydrophobic surfaces combats bacterial growth since microorganisms are largely contained within water droplets. In addition,

Figure 5



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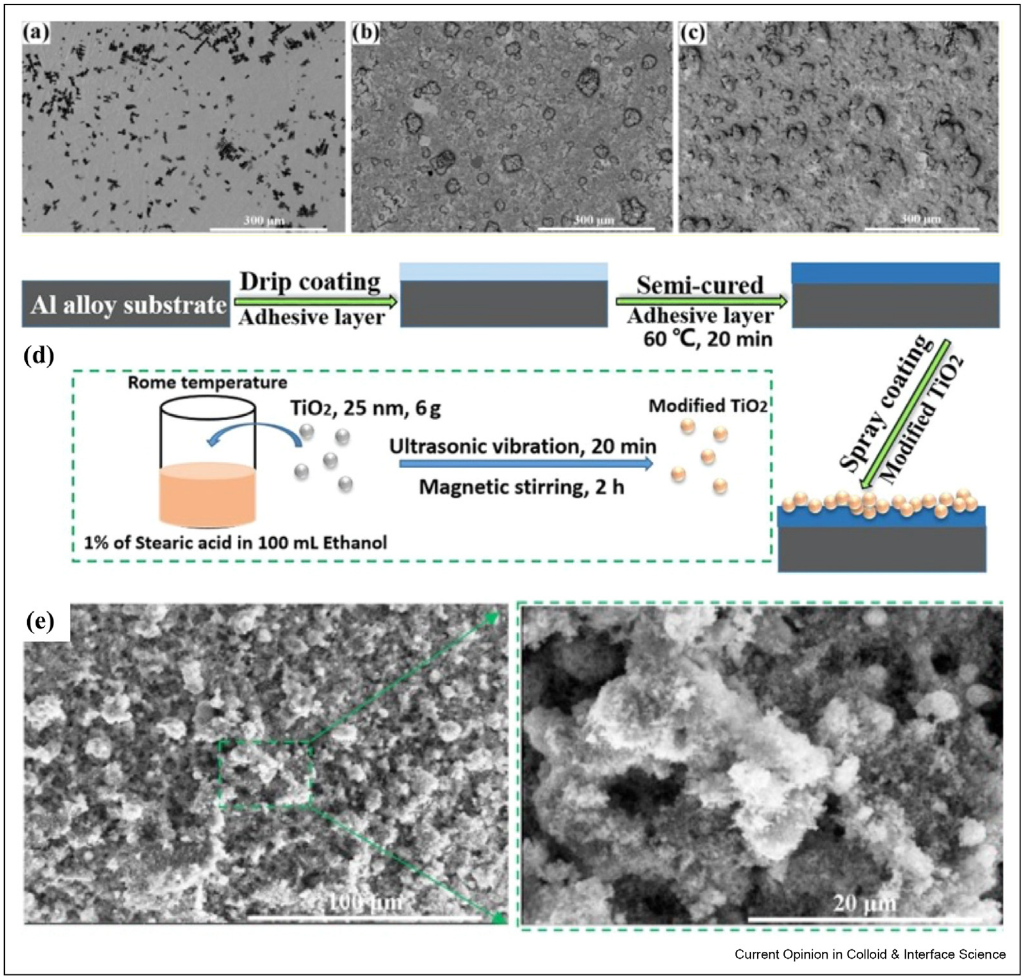
Nyquist plots of RL and RL-SiO_2@DTMS/OTS samples **(a)**, bode plots of RL and RL-SiO_2@DTMS/OTS samples **(b, c)**, the silver mirror phenomenon of RL-SiO_2@DTMS/OTS sample immersed in water **(d)**, and polarization curves of different samples after the wet−dry cyclic corrosion test. **(e)**. Reprinted with permission from 56. Copyright 2024 American Chemical Society.

bacterial attachment onto surfaces with rough micro- and nanoscale topographies can lead to cell wall deformation and lysis [56]. By repelling water, these surfaces create an inhospitable environment for microorganisms to colonize, thereby reducing the risk of biofouling. Biofouling is particularly pertinent in marine and maritime environments where fouling of boat hulls by algae and marine organisms increases mass and has a significant effect on fuel consumption [57]. Deployment of superhydrophobic coatings formed from functionalised nanoparticles onto these surfaces could contribute to environmental sustainability by reducing the need for the biocidal paints that are currently in use, some of which may still contain harmful heavy metals [58]. Significant research has been undertaken to examine the anti-biofouling properties of superhydrophobic surfaces. The reports discussed herein on surfaces prepared using functionalised nanoparticles represent some of the most recent studies in this area.

Li et al. utilised the photocatalytic behaviour of TiO_2 particles embedded in a semi-cured epoxy resin on an aluminium alloy to reduce the content of stearic acid required for a superhydrophobic coating (Figure 6 (d) and (e)) [59]. The authors studied droplet impingement at various velocities (0.43—3.43 m/s) to show that their coating had robust impalement resistance. Most significantly, the surface's superhydrophobicity combined with its photocatalytic ability was found to prominently improve the coating's anti-biofouling ability. Figure 6 (a)—(c) shows images of *E. coli* on the Al alloy substrate the superhydrophobic coating in the dark, and the superhydrophobic coating under UV irradiation. The quantity of *E. coli* on the superhydrophobic coating under dark or UV light is significantly lower than that on the Al alloy substrate, confirming the effectiveness of the low wettability surface for removing bacteria [59]. As expected, the coating that had been exposed to UV light showed the lowest amount of *E. coli* cells, which is

Figure 6



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SEM images of the *E. coli* on the **(a)** *Al* alloy substrate, **(b)** superhydrophobic coating in the dark **(b)**, **(c)** superhydrophobic coating under UV after cultivating for 1 day **(c)**, schematic showing the materials and coating method onto the Al alloy substrate **(d)**, SEM images showing the nanoscale structures in the coating. Reproduced from reference 60. Copyright 2024 Elsevier.

ascribed to the photocatalytic behaviour of the titania, whereby absorption of UV photons generates holes and free radicals that are highly effective at degrading organic materials like bacteria. Interestingly, the photocatalytic behaviour was not observed to degrade the carboxylic acid, at least significantly, since the surface retained its superhydrophobic properties after UV irradiation [59].

Dietl et al. have used nanoparticle coatings of CeO_2 which were deposited directly by FSP onto catheter-mimicking surfaces (30 μm thick PDMS-coated Si substrates 5 × 5 mm) [39]. Subsequent vapour phase deposition of silicone oil was performed to render the coatings superhydrophobic [39]. After confirming their superhydrophobic nature, their antibiofilm capabilities were tested against a clinically relevant strain of uropathogenic *E. coli* isolated from a patient with a urinary tract infection, which can form biofilms on silicone urinary catheters. The bare Si substrate shows slightly lower biofilm formation compared with the PDMS-coated substrate, possibly because of its lower surface roughness [39]. Whereas the superhydrophobic CeO_2 coating showed a clear inhibition of biofilm formation, with a greater than one log reduction of bacterial growth compared with the PDMS-coated substrate control [39]. This study achieved a growth reduction of the bacterial biofilm load of more than 90 % without toxic anti-fouling agents, thus demonstrating the significant impact lowering the wettability can have alone [39].

Conclusions and outlook

The wide breadth of the study presented here shows that superhydrophobic nanoparticle coatings could be utilised in many different applications. As discussed, the extremely low wettability of these coatings, and the relative ease at which they can be applied to a variety of substrate materials, imbues additional advantages that could positively impact society leading to environmental and infrastructural benefits. Furthermore, the compatibility of the particles with binders and adhesives to enhance durability opens the door to more diverse applications where previously the harmful implications of particle release had been a problem.

However, despite these advancements in the field, we feel that the cytotoxic effects observed when exposing nanoparticles towards a range of cell types make them unlikely candidates for incorporation in coatings where skin contact or some route of ingestion is likely to occur. This might include applications for these self-cleaning coatings in the food and beverage sector, or for medical devices where bacterial build-up might result in infection. We believe even the most robustly bound particle/binder coating would face a substantial uphill struggle to overcome the legislation surrounding nanomaterials in these areas. An in-depth discussion of the nature of the types of cytotoxic effects that have been observed in the field of nanotoxicology is beyond the scope of this article. However, we invite readers to investigate these cited reviews for more information [60,61]. On the other hand, strongly adherent systems might have less resistance for application as self-cleaning coatings where human contact is less frequent. In this review, we have discussed how the high optical transparency of some of these coatings could mean that they would be useful for the design of self-cleaning windows, or for building facades. These surfaces generally suffer far less human contact, which could mean that there is an opportunity for applying materials of this nature, providing suitable diligence is taken to assess whether significant environmental release of particles is likely to occur.

Oil-in-water separation could also be a promising application for the coatings. As presented herein, the separation efficiencies, and the ability of these coatings to remove oils and lower viscosity organic liquids from the aqueous phase, provide compelling evidence that these coatings could be useful for clearing up oil spills. However, for this to occur, further research needs to be carried out into developing this coating for methods that could efficiently capture oil at scales like those observed in oil spills. This methodology could perhaps take the form of pilot scale trials applying coatings onto different adsorbent materials and quantifying their efficacy over larger scales than those studied in the laboratory experiments that have been done previously. It might also be advantageous to do more studies in sea/wastewater where surface fouling from compounds present in these environments may impact efficacy.

Although the delays in ice formation on these superhydrophobic surfaces are impressive, we feel that these coatings could only find limited application in this area since, despite this and the lower adhesion strength, freezing of water droplets on these surfaces always happens eventually. Consequently, this type of coating would be best applied onto surfaces that are only exposed to icy conditions for a limited time. This may be as coatings for vehicles or for things like sports equipment, skis etc. Investigation of the longevity of the icephobic effect in real-world situations are important studies that need to be conducted to understand whether the coating research in this area is possible to produce a coating that sustains useful efficacy. Application of the coatings to imbue materials with corrosion resistance or resistance to bacterial fouling might find more widespread use because of the ease that they can be spray coated onto different substrates, which lends itself to incorporation into manufacturing processes. Furthermore, the high levels of optical transparency reported by many of the coatings in the literature also make it more attractive since the appearance of the surfaces would suffer less alteration.

Studies into the preparation of superhydrophobic materials is a field that has become highly developed in recent years because of the considerable efforts of the researchers, which is largely driven by the tangible potential to develop the methodology for these applications. Because of this, many of the challenges relating to factors relating to considerations such as durability, material selection and fabrication, and optical properties have been overcome. Consequently, it is becoming harder for researchers to present novelty in research reports. In our view, one useful avenue of development would be studying to what extent the fluorocarbon content can be lowered in oleophobic coatings since it is not possible to repel oils using hydrocarbon-terminated surfaces. Our group has already begun some research to this end [62], alongside others [63], however, to our knowledge, this is a topic that remains largely unexplored. This research could be particularly pertinent now because of the strides in coating durability that have been made, which could greatly limit the environmental release of any fluorinated material and thus greatly reduce some of the environmental considerations.

Looking ahead, research in this area could also greatly benefit from life cycle assessment to gain an understanding of what would happen if nanoparticle release did occur. This would have to expand the nature of the work to involve greater multi- and interdisciplinary collaboration, which would take the research beyond synthetic chemistry/materials science laboratories. These studies might be largely theoretical and assess where superhydrophobic nanoparticles could end up in the environment and food chains considering their prospective applications and would provide important information on whether their expected benefits would justify their impact. Although broad investigations of this nature have been made previously [64], further study is needed to specifically understand how the non-wetting nature of this material affects its behaviour when it is released into the environment. To complement these investigations, it would be useful to quantify the number of particles being removed from the surfaces during durability experiments.Authors are keen to report that the wettability of their surfaces are robust during these experiments, but so far, to our knowledge, there has been no effort to quantify the amount of nanomaterial that has been released. In our view, the lack of understanding in this area is one of the factors holding back this methodology from more widespread application.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

No data was used for the research described in the article.

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* of special interest
* * of outstanding interest

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This study has advanced the field of superhydrophobic nanoparticle coatings because not only does the durable nanoparticle coating show robust separation with a wide variety of viscosity oils and organic liquids, it also shows that the coated structure can be magnetically controlled to clean up oil spills. This study is a significant advancement because adds a new level of control to the methodology that could be potentially utilised for oil cleanup activities.

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This study indicates that it is possible to apply a robust superhydrophobic nanoparticle coating at scale onto building facades that can function without losing its wettability as result of weathering or other environmental factors. Furthermore, the low curing temperature of the binder that they use could mean that it could readily deployed at scale onto many structures without further treatment.

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