

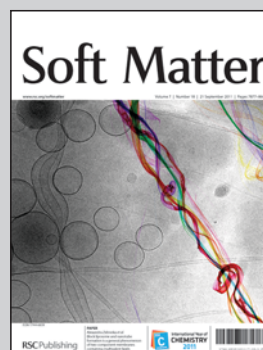


Showcasing joint research results from a recent collaboration between the Italian Institute of Technology and the University of Illinois.

Title: Solvent resistant superhydrophobic films from self emulsifying carnauba wax-alcohol emulsions

This work describes a simple and easily scalable emulsion based technique to fabricate all-organic self cleaning superhydrophobic films. Natural carnauba wax can self emulsify with alcohols such as ethanol or isopropyl alcohol. No surfactants or emulsifiers are required. These emulsions can be used to suspend hydrophobic polymeric nanoparticles such as Teflon. Spraying these emulsions on surfaces creates microporous wax-polymer composite films. Annealing these films above the melting point of wax, transforms the porous structure into a self cleaning superhydrophobic morphology.

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Solvent resistant superhydrophobic films from self-emulsifying carnauba wax–alcohol emulsions

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By dispersing molten carnauba wax in warm isopropyl alcohol or ethanol with subsequent mild ultrasonic mixing, highly stable surfactant-free natural wax-in-alcohol emulsions were prepared for the first time. These emulsions can easily suspend hydrophobic colloidal organics or solids. We demonstrate fabrication of superhydrophobic films from sub-micron polytetrafluoroethylene (PTFE) particle-dispersed emulsions by a simple drop and/or spray casting procedure and subsequent thermal annealing above the melting point of carnauba wax. We investigate effect of wax and Teflon concentration and thermal annealing on the degree of superhydrophobicity. Moreover, the films display superior resistance to solvent etching against aggressive solvents such as chloroform, toluene, acetone and alcohols upon immersion into such solvent baths for one hour. Composite films remain superhydrophobic after solvents evaporate from their surfaces following their removal from the solvent baths. Moreover, detailed contact angle hysteresis measurements revealed that solvent bath immersion does not downgrade “self-cleaning” superhydrophobicity to “sticky” superhydrophobicity.

Carnauba wax is an ester wax of natural origin, which is extracted from the leaves of carnauba palm *Copernicia prunifera* in Brazil. It is a multi-component wax comprising aliphatic esters, uncombined alcohols, *n*-hydroxy esters, *p*-methoxycinnamic aliphatic and *p*-hydroxycinnamic aliphatic diesters having several chain lengths, in which C₂₆ acids and C₃₂ alcohols predominate.^{1,2} It melts around 82.0–85.5 °C. Due to its high melting point, it has been extensively used in various industrial applications such as protective and polishing agents, glazing for paper, coating of pharmaceuticals, and food additives.² It has been also successfully used for encapsulation and controlled release of hydrophobic drugs.^{3,4} The most common form of carnauba wax is in an aqueous emulsion.⁵ Preparation of wax-in-water emulsions generally requires melting of wax and mixing with warm water with suitable dispersants such as morpholine, oleic acid, triethanolamine, or various silicone oils under shear mixing.^{5,6} These wax emulsions are generally used for the coating of papers, fibers, wood or ceramic products or admixed to an aqueous emulsion of

cement, paint or other materials in industry.⁷ Moreover, there is a great interest towards designing stable multifunctional wax emulsion systems in aqueous or environmentally friendly liquids.⁸ The main objective of the application of such an emulsion is to provide the material with waterproof properties after evaporation of water. However, since natural and synthetic waxes are highly hydrophobic in nature, the process of dispersing and emulsifying the wax is in conflict with this inherent property. In order to obtain a stable emulsion, a large quantity amounting to more than 10% of an emulsifier must be added. The water repellent or waterproof property of wax is considerably reduced as the quantity of the emulsifier is increased, which may result in failure to attain the desired functionality.

Oil-in-alcohol emulsions are rarely reported in literature. In certain oil-in-water emulsions addition of alcohols can influence Ostwald ripening and enable self-emulsification.⁹ Self-emulsification of certain oil/water mixtures with alcohols is known as the “ouzo” effect (relating to the Greek alcoholic beverage ouzo which attains an opaque whitish color upon mixing with water).¹⁰ According to some recent studies, for instance, vegetable/animal oil-in-alcohol emulsions have been evaluated as effective clean fuel substitutes for diesel engines.¹¹ In particular, animal fats self-emulsify with alcohols like ethanol and methanol reducing the cost of the emulsification process. Vegetable oil-in-alcohol emulsions, in general, require emulsifiers for stability; however, the primary advantage of vegetable oil–ethanol emulsions over conventional water–oil emulsions is that they enable the incorporation of water- and oil-insoluble or poorly soluble functional compounds and/or drugs into the emulsions.¹² In the present study, we show that molten carnauba wax can easily self-emulsify with isopropyl alcohol or ethanol without using additional emulsifiers. These emulsions are highly stable and can be used in numerous applications such as forming water proof wax coatings and films with faster drying rates compared to water based emulsions, as additives in various environmentally friendly coating formulations to impart water repellency, and to suspend hydrophobic colloids for the fabrication of functional biomaterials and bionanocomposites. Herein, we show that sub-micron PTFE particles can be easily suspended in these emulsions without the use of any surfactants. Furthermore, upon drop or spray casting and subsequent thermal annealing of the suspensions, highly water repellent all-organic carnauba wax–PTFE composite films can be prepared. The films require no post-surface treatment with hydrophobic macromolecules such as fluorsilanes, a common method used to obtain

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superhydrophobicity.¹³ The films also display superior resistance to solvent etching against aggressive solvents such as chloroform, acetone, toluene and alcohols. Indeed, upon immersion of the composites in different solvent baths and subsequent removal and solvent evaporation, their surfaces remain superhydrophobic with no change in contact angle hysteresis.

In a typical procedure, 30 ml isopropyl alcohol or ethanol was brought to boiling on a hot plate at 85 °C. To this 0.3 g of carnauba wax flakes were added slowly and within 5 minutes the mixture turned into a pale yellow clear solution after complete melting of the wax. The boiling solution was then transferred to an ultrasonic processor containing warm water and sonicated for 20 minutes and slowly cooled to room temperature. Varying amounts of PTFE particles (Sigma Aldrich, USA) were then added in order to form PTFE/wax composite films with mass fractions ranging from 0 to 1.5 and the mixtures were sonicated for 20 minutes more at room temperature. The submicron PTFE particles are spherical and on average are 150 nm in size.¹⁴ Thick films (150 μm) were prepared on 1 mm thick microscope glass slides from PTFE suspended emulsions by drop or spray casting. An internal mix air brush (Paasche VL, USA) was used for spraying the emulsions on substrates. The emulsions were sprayed from a distance of approximately 10 cm. Thinner films (10–20 μm) were prepared on thin glass slides (~0.3 mm) for atomic force microscope (AFM) measurements. The films, however, do not become superhydrophobic after complete alcohol evaporation under ambient conditions and require thermal

annealing to repel water droplets. Fig. 1a shows the optical surface micrograph of a porous carnauba wax film spray cast from an isopropyl alcohol emulsion after drying at room temperature. The film is made up of a porous network of small wax beads of 6–8 micron in size. The scanning electron microscope (SEM) in Fig. 1b shows the detailed structure of the surface roughness composed of aggregated flaky wax beads. This structure closely resembles epicuticular waxes which are commonly found on hydrophobic plant leaves.¹⁵ Epicuticular waxes on some plants such as *Aloe porphyrostachys* and *Euphorbia characias* often form similar micro-scale flaky structures for water repellency.¹⁵ Although these naturally occurring wax structures on such plant leaves are hydrophobic, they do not cause the well known “lotus effect” due to the absence of well defined protruding sub-micron morphology such as waxy nanohairs found in the lotus leaf.^{14,15} Similarly, based on detailed electron microscopy analysis, room temperature dried carnauba wax films obtained from drop or spray casting of these emulsions do not form well defined sub-micron morphological features and hence are not self-cleaning.¹⁶

When natural plant or insect waxes re-crystallize from melt, however, they tend to form solid phases with a nematic-like structure, namely a parallel array of polymethylene chains with little or no aggregation of the molecules into distinct layers.¹⁷ The optical micrograph obtained under polarized light in Fig. 1c shows the morphology of the re-crystallized porous carnauba wax film, presented in Fig. 1a, from melt. The morphology shown in Fig. 1c emerges upon cooling of the film, which had been kept on a hot plate at 110 °C for 15 minutes. The morphology is due to the formation of spherulites the borders of which impinge on the neighbor forming the mass seen in Fig. 1c. Each spherulite is composed of crystalline tubules or fibrils and amorphous regions. The texture shown in Fig. 1c can be attributed to the presence of various aliphatic and aromatic esters in natural waxes which can assemble in different direction and order compared to petroleum based paraffin waxes which assemble into more directional orderly structures due to *n*-paraffin chains.^{18,19} In Fig. 1d the X-ray diffraction (XRD) characteristics of the emulsion cast and re-crystallized carnauba wax are shown. No significant difference and no new peaks could be detected in the XRD pattern of the emulsion cast and re-crystallized carnauba wax. The two peaks at 0.415 and 0.373 nm indicate formation of orthorhombic perpendicular (O_{\perp}) sub-cell packing similar to the crystals of triacylglycerols²⁰ (commonly found in edible fats) which are generally packed in three different polymorphs (α , β' , and β) with hexagonal, O_{\perp} and triclinic parallel (T_{\parallel}) sub-cell packing.^{19–21} The XRD spectra in Fig. 1d show that β' polymorph is the dominant crystal morphology in both systems indicating that thermal annealing does not introduce morphological changes in the crystalline order of carnauba wax. Based on the XRD data of Fig. 1d percent crystallinity of the as-sprayed films (Fig. 1a) was estimated to be approximately 67%, whereas after thermal annealing (Fig. 1c), percent crystallinity was estimated to be 83%. The inset in Fig. 1d shows the optical micrograph picture of several carnauba wax spherules isolated from diluted emulsions on glass slides obtained after re-crystallization from melt. In fact, a recent study on thermo gravimetric analysis of carnauba wax indicates that the wax starts to disintegrate at 220 °C¹⁶ and annealing carnauba wax below 200 °C causes no material loss or chemical changes in wax chemistry which was verified by FTIR measurements.¹⁶

Fig. 2 shows static water contact angle and contact angle hysteresis (CAH) measurements on spray cast composite films as a function of

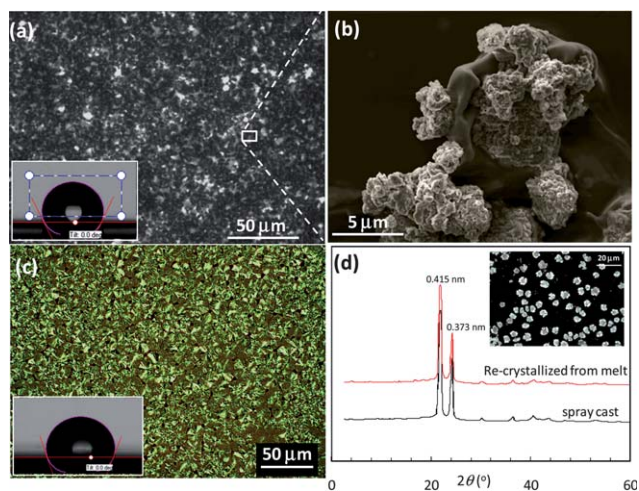


Fig. 1 (a) Optical microscope image of the surface morphology of carnauba wax film spray cast from an isopropyl alcohol emulsion upon drying at room temperature. The porous surface is made up of micron sized wax beads 6–8 μm in size on average. The surface is hydrophobic as indicated by the sessile water droplet contact angle shown in the inset. (b) Scanning electron microscope image showing morphological details of a sub-micron flaky carnauba wax bead acquired from a random surface location in (a). (c) Optical micrograph of the film in (a) under polarized light after thermal annealing at 110 °C for 15 minutes. The porosity of the original film disappears due to re-crystallization from melt. Static water contact angle of the film practically does not change as a result of annealing (inset). (d) XRD spectra of spray cast and thermally annealed films showing no change in the crystalline order after thermal annealing. The inset shows individual micron sized wax crystals isolated from a dilute emulsion after re-crystallization obtained using a polarized light optical microscope.

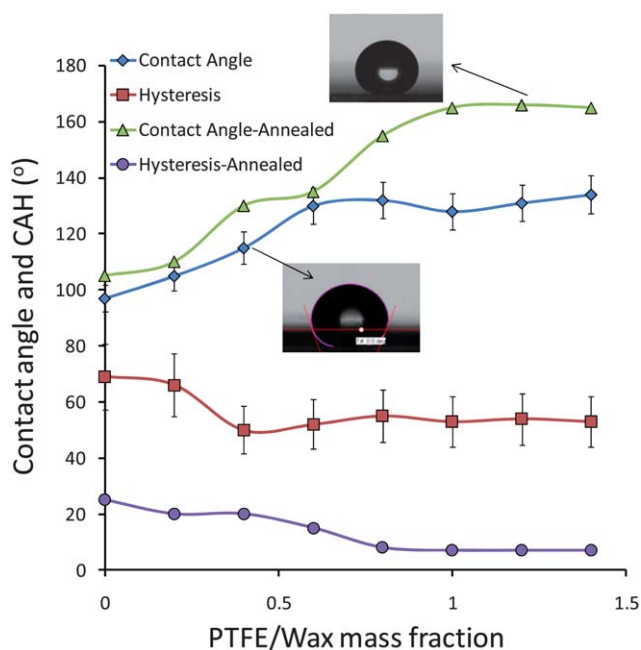


Fig. 2 Static water contact angle and CAH for PTFE/carnauba wax composite films spray cast from isopropyl alcohol emulsions before and after thermal annealing as a function of PTFE/wax mass fraction.

PTFE/wax weight fraction before and after thermal annealing. Films were spray cast from self-emulsified wax-in-isopropanol emulsions with dispersed PTFE particles on microscope glass slides. None of the PTFE/wax weight fractions studied yielded self-cleaning

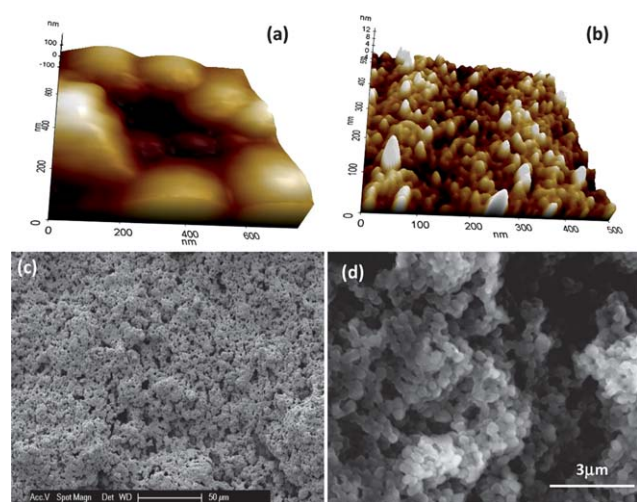


Fig. 3 (a) Three dimensional surface topology as a result of thermal annealing of a thin composite film (PTFE/wax = 0.6) at 110 °C for 15 min obtained by a non-contact mode atomic force microscopy measurement. Film thickness is approximately 10 μm. (b) Three dimensional surface topology as a result of thermal annealing of a composite film (PTFE/wax = 1) at 110 °C for 15 min obtained by a non-contact mode atomic force microscopy measurement. Film thickness is approximately 10 μm. (c) Scanning electron micrograph showing surface morphology of a self-cleaning superhydrophobic composite thick film (~150 μm) after thermal annealing at 110 °C for 15 min (PTFE/wax = 1). The scale bar is 50 μm. (d) Submicron surface roughness features of the composite film shown in (c) due to PTFE particles.

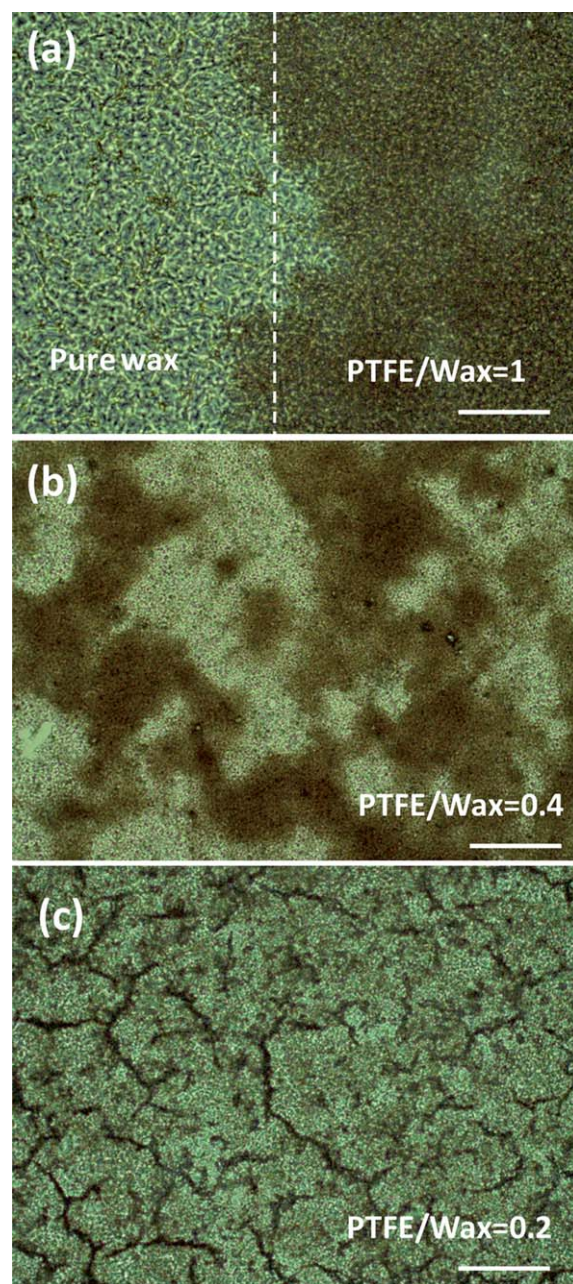


Fig. 4 (a) Optical micrograph of the border region of a glass slide coated with pure carnauba wax (left hand side of dashed line) and PTFE/wax = 1 composite film (right hand side of dashed line) captured during solidification from melt at 110 °C. Dark-brown regions/spots indicate PTFE nanoparticle aggregates on the surface. (b) Optical micrograph of a PTFE/wax = 0.4 composite film captured during solidification from melt. PTFE nanoparticle aggregates appear to be randomly distributed over the surface. (c) Optical micrograph of a PTFE/wax = 0.2 composite film captured during solidification from melt. PTFE nanoparticle aggregates are trapped at the grain boundaries. The scale bar in each image is 50 μm. Images captured under polarized light.

superhydrophobic films before annealing as indicated by the static contact angle measurements which did not exceed 135° even when PTFE/wax = 1.4. It is also seen that before thermal annealing, the films show considerable CAH including composites with PTFE/wax >1. This is consistent with the observations by Wagner *et al.*²² that

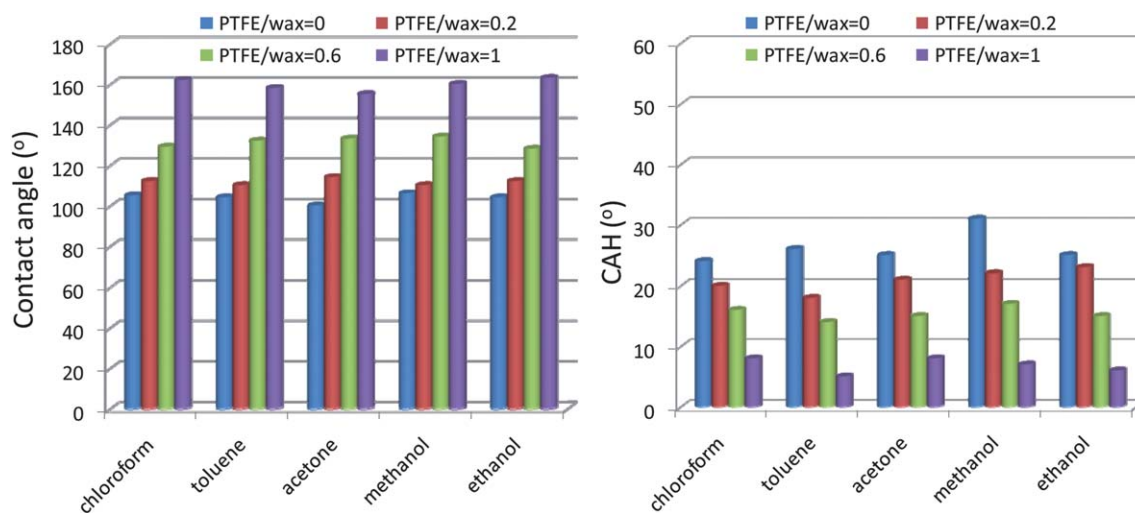


Fig. 5 Static contact angle (left) and CAH (right) measurements for four different thermally annealed composite films after immersion into different solvents for one hour. Static contact angle and CAH values before immersion into solvent baths were: PTFE/wax = 0 (106°, 24°); PTFE/wax = 0.2 (112°, 19°); PTFE/wax = 0.6 (130°, 15°); PTFE/wax = 1 (164°, 6°), respectively.

plant waxes in general are not very hydrophobic because they have many hydrophilic functional groups. However, carnauba wax surface gets more hydrophobic after re-crystallization on glass slides probably due to the rearrangement of hydrophilic groups towards the hydrophilic glass substrate. In order to test this possibility, five samples of pure wax coatings were spray cast on hydrophobic silicon wafers (water contact angle $\sim 87^\circ$) and static water contact angle and CAH measurements were recorded before and after annealing. Static water contact angles and CAH of as-sprayed coatings on hydrophobic silicon did not show significant variations compared to glass slides which fell within the experimental measurement uncertainty. This leads to the conclusion that the wettability of the spray cast films is controlled by the atomization of the emulsions. Static water contact angles of annealed films (110 °C for 15 min) on hydrophobic silicon wafers were also close to the annealed films on glass slides however CAH on hydrophobic substrates was significantly higher exceeding 87° compared to CAH on glass slides (CAH $< 25^\circ$; see Fig. 2). In general higher CAH is caused by the presence of small hydrophilic or polar groups at the coating–air interface which can increase droplet adhesion. This may not be reflected directly on the static water contact angles commonly seen in sticky-superhydrophobicity. Therefore it can be concluded that substrate hydrophobicity has a significant effect on the assembly, morphology and wettability of multi-component plant waxes. Superhydrophobic surfaces are classified as self-cleaning when the static contact angles exceed 150° with CAH being less than 10° .¹⁶ When the films were annealed at 110 °C for 15 minutes on a hot plate so that the wax can be re-crystallized from melt, static water contact angle started increasing considerably when PTFE/wax fraction of 0.6 is exceeded. Meanwhile significant reduction in CAH was measured for all the films including PTFE/wax fraction of zero (pristine wax surface) after thermal annealing as seen in Fig. 2. Up to the PTFE/wax = 0.6 composition, films display practically similar hydrophobicity before and after thermal annealing as indicated by static contact angles. However, significant reduction in CAH is apparent for the annealed films. Droplets could easily slide on the thermally annealed films when substrate tilt angle slightly increases above 30° until PTFE/wax = 0.6. For all other films where

PTFE/wax > 0.6 , droplets rolled off the surfaces when the substrate tilt angles exceeded 8° . Fig. 3a shows the typical surface roughness morphology of a PTFE/wax = 0.6 film imaged by atomic force microscopy (AFM) in non-contact mode. Although the surface is quite hydrophobic, the amount of PTFE particles is not enough to induce the required sub-micron roughness to render the composite self-cleaning. Fig. 3b, on the other hand, shows a self-cleaning superhydrophobic surface AFM morphology corresponding to films with PTFE/wax mass fraction of 1. The surface roughness structure is quite different than the case of PTFE/wax = 0.6. There appears to be many repeating protruding features on this surface which could be responsible for the self-cleaning superhydrophobicity. According to Niemietz *et al.*²³ annealing of multi-component plant waxes close to their melting points for long enough times can lead to appearance of submicron superhydrophobic roughness features due to the formation of wax tubules protruding away from the bulk surface. In the present study however, presence of PTFE submicron particles within the wax matrix can affect the formation and orientation of wax tubules significantly inducing formation of composite surface structures as a function of the amount of PTFE present within the wax matrix. Fig. 3c shows an overview scanning electron microscopy (SEM) image of the surface morphology of a thick film of PTFE/wax = 1 which is made up of randomly formed large micron and submicron roughness structures. The submicron roughness features due to PTFE particle-assembly is clearly seen in detail in the SEM image in Fig. 3d. In fact, self-cleaning superhydrophobic surfaces are always obtained starting from PTFE/wax weight ratios of 0.8 indicated by CAH being less than 10° . Fig. 4 shows optical micrographs of wax/PTFE composites captured during an intermediate stage of solidification. The micrograph in Fig. 4a is made up of two sections separated by a dashed line. The left portion corresponds to pure carnauba wax film deposited on the left half of the glass slide whereas the right side corresponds to a composite film with PTFE/wax = 1. On the right hand side submicron PTFE particle segregates are clearly seen and seem to cover most of the air–film interface. In Fig. 4b a micrograph of a PTFE/wax = 0.4 composite surface is shown just as it was solidifying. It is seen that the PTFE aggregates

form a random distribution over the surface of the composite. In the case of PTFE/wax = 0.2 as shown in Fig. 4c, PTFE aggregates appear to be trapped between the wax spherulites as they start impinging on one another during solidification from melt. Therefore it is concluded that the PTFE/wax ratio has a deterministic role in surface wettability during solidification from melt.

Melting of wax on the substrate as a result of annealing ensures that the composite films strongly adhere to the glass slide surfaces rendering them quite durable. Before thermal annealing, composite films immediately separated from the glass surfaces and started floating in the liquid surface when immersed in water or one of the solvents studied, therefore, thermal annealing was required to create a good substrate adhesion as well as superhydrophobicity. Thermal annealing of superhydrophobic lotus leaf, on the other hand, results in a significant reduction in superhydrophobicity (droplets no longer roll off).¹⁶ This is attributed to the loss of naturally occurring sub-micron roughness due to melting of wax. In the present case, when PTFE/wax > 0.6, even though carnauba wax melts the required sub-micron surface roughness is maintained by the presence of PTFE particles.

Since both carnauba wax and PTFE are highly resistant to solvents at ambient conditions, the superhydrophobic composite films are expected to be resistant to solvent etching at room temperature as well. Thermally annealed films including PTFE/wax = 0, were immersed into a number of solvents such as chloroform, toluene, acetone, methanol and ethanol for one hour at room temperature, and static contact angle and CAH were measured after the samples were dried under ambient conditions once removed from the baths. Fig. 5 shows the static water contact angle and CAH measurements for four different composite films. Comparison of the data with that of Fig. 2 indicates that wetting characteristics of the films are maintained after immersion into solvents. In particular, the surface corresponding to PTFE/wax = 1 maintains its self-cleaning ability for all the solvent systems studied. Chemical inertness of carnauba wax has proven to be quite advantageous in particular for drug release studies.^{24,25} Therefore, we argue that superhydrophobic coatings formulated using carnauba wax or other natural waxes could be highly useful for applications including microfluidic devices, biosensors which might require inertness to chemical exposure to certain fluids.

In conclusion, we demonstrated a facile technique to fabricate superhydrophobic all-organic composite films from self-emulsifying carnauba wax–alcohol emulsions for the first time. These emulsions are highly stable and can suspend micro- and nanoscale hydrophobic

colloidal particles easily. Submicron (~150 nm) PTFE particles were dispersed in these emulsions without any surfactants to fabricate superhydrophobic thin films. Large surface areas can be coated by simply spraying the emulsions. Further studies will focus on introducing additional functionalities such as electrical conductivity or magnetism by suspending other functional nanoparticles.

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