

www.MaterialsViews.com



Can Metal Matrix-Hydrophobic Nanoparticle Composites **Enhance Water Condensation by Promoting the Dropwise** Mode?

Viraj G. Damle, Xiaoda Sun, and Konrad Rykaczewski*

Incorporation of condensers treated with hydrophobic modifiers that promote the efficient dropwise condensation mode can significantly enhance the performance of power generation and desalination plants. However, this approach is not used in industry because of low thermal conductivity and limited durability of the thin hydrophobic coatings. Here, it is argued that metal matrix hydrophobic nanoparticle composites can be a robust and high thermal conductivity alternative to hydrophobic polymeric and ceramic thin films. By characterizing condensation on a wide range of mimicked composite surfaces, it is demonstrated that to promote dropwise condensation the filler nanoparticles must have size and spacing significantly smaller than the few micrometer average center-to-center separation distance between closest neighboring droplets prior to onset of the coalescence dominated growth stage. Furthermore, the nanoparticle density does not have to be high enough to make the surface hydrophobic, but only sufficiently high to reduce the contact angle hysteresis, and with that pinning of droplets during coalescence and gravity assisted shedding. Using experimental results in conjunction with condensation models, it is estimated that a substantial heat transfer enhancement can be achieved via promotion of sustained dropwise mode even by using copper and aluminum matrix composites fully loaded with polytetrafluoroethylene nanoparticles if the film thickness is below ≈0.5 mm.

1. Introduction

Steam condensers are fundamental components of about 85% of electricity generation plants and 50% of desalination plants installed globally.^[1] As a consequence, finding routes to even moderately improve efficiency of the condensation process could lead to considerable economic savings as well as environmental and societal benefits. Since the 1930s, hydrophobization of metal surfaces has been known to increase heat transfer during water condensation by up to an order of magnitude,^[2] whereby this surface modification switches the condensation mode from filmwise (FWC) to dropwise (DWC). As shown in Figure 1a, promoting the latter condensation mode improves the heat transfer rate by preventing formation of a thermally

V. G. Damle, X. Sun, Prof. K. Rykaczewski School for Engineering of Transport, Matter, and Energy Arizona State University Tempe, AZ 85287, USA E-mail: konradr@asu.edu



to heat flow (see Figure 1b). Thus, in simplified terms, to increase the total heat transfer rate, thermal resistance introduced by the hydrophobic coating must be significantly smaller than that posed by the water film during filmwise condensation. Unfortunately, most hydrophobic surface modifiers have a low thermal conductivity and limited durability. For example, to withstand a steam environment within a power plant condenser during the projected lifetime of the power station (≈40 years), a polytetrafluoroethylene (PTFE) film must be at ≈20 to 30 µm thick.^[3] The thermal resistance added by this thickness of the polymeric film negates any heat transfer enhancement attained by promoting DWC, explaining why this condensation mode is not common in industry. While there are many techniques to render surfaces hydrophobic to promote DWC,^[3,4] most of the produced coatings

insulating water film. However, use of

hydrophobic coatings required to promote

DWC introduces an additional resistance

suffer from longevity issues. Recently, several alternative methods have been proposed to render surface hydrophobic including rare earth oxides,^[5] grafted polymers,^[1] and lubricant impregnated surfaces (LIS).^[6] Nevertheless, applying these materials as thin films makes them susceptible to variety of degradation issues which could include polymer oxidation at defect sites, ceramic film delamination and, for LIS, slow lubricant drainage with departing water drops.

Metal matrix composites with hydrophobic particles have been proposed as a durable alternative to thin film hydrophobic surface coatings (see Figure 1c).^[7] In particular, polished copper-graphite microparticle composites were reported to have a macroscopic water drop contact angle of ~87°.^[7] The surface of this composite has heterogeneous wetting properties consisting of microscale hydrophobic patches on a hydrophilic background. Condensation and wetting on surfaces with microscale chemical and topological heterogeneities has been studied extensively,^[6d,8] and surfaces comparable to those of the composites with microscale hydrophobic features have been demonstrated to flood during condensation.^[80] This mismatch between macroscale wetting properties and condensation mode stems from the multiscale nature of the phase change process

DOI: 10.1002/admi.201500202





Figure 1. Schematic contrasting a) filmwise condensation with b) traditional method of promoting dropwise condensation using hydrophobic coating and c) metal matrix-hydrophobic nanoparticle composites with nanoparticles with diameter *d* and pitch *P*; representative resistive heat transfer networks are also indicated with T_c , T_s , T_v , R_{film} , R_{coat} , R_{cond} , R_{comp} , and R_{cond} corresponding to bulk condenser, surface, and vapor temperatures and water film, hydrophobic coating, composite, and condensation thermal resistances, respectively; d) schematics indicating length scales relevant to the four dropwise condensation stages.

(see Figure 1d). Beysens et al.^[9] have established that condensation on smooth partially wetting substrates proceeds in four stages: (1) nucleation ($l_n \approx 1$ to 100 nm) and (2) growth of individual drops through direct vapor deposition ($l_i \approx 100 \text{ nm}$ to 5 µm) followed by (3) growth dominated by droplets' coalescence ($l_c \approx 5 \ \mu m$ to 3 mm), and for titled surfaces (4) gravityaided shedding ($l_c \approx 1$ to 3 mm). The transition between the second and third stage occurs when the average droplet diameter reaches the average center-to-center spacing between closest neighboring drops after nucleation (i.e., the drops that will coalesce with each other). While dependent on a number of variables such as supersaturation and surface chemistry/texture, the length at which this transition occurs, $l_{\rm co}$, is typically in the range of $\approx\!\!5$ to 10 $\mu m.^{[9]}$ Consequently, hydrophobic particles with size comparable or larger size than l_{co} will have no impact on growth of individual drops as well as their coalescence. In other terms, flooding of surfaces with microscale hydrophobic features occurs because droplets smaller than these features nucleate, grow, coalesce, and ultimately transition into a film on the hydrophilic background surface surrounding the hydrophobic phase.

In this work we propose that flooding of composite surfaces during condensation can be prevented by engineering



www.MaterialsViews.com

the materials on length scale greater than that of drop nuclei but significantly smaller than the average separation distance between closest neighboring microdroplet centers prior to onset of the coalescence dominated growth stage^[9] ($l_{co} \approx 5$ to 10 μ m^[10]). In particular, our hypothesis is that dispersion of hydrophobic nanoparticles with diameters, *d*, much lower than l_{co} (i.e., d below ≈ 500 nm) within the hydrophilic metal matrix will significantly disrupt individual droplet growth prior to as well as during onset of microdroplet coalescence (see schematic illustration in Figure 1c,d). As oppose to the extensively studied surfaces with microscale wetting heterogeneities, condensation on hydrophilic surfaces with nanoscale hydrophobic sites has not yet been systematically explored. To this end, we theoretically and experimentally explored how composition of metal matrix hydrophobic nanoparticle composites (MMHNPCs) affects droplet dynamics, effective thermal conductivity of the materials, and overall thermal transport during heterogeneous water condensation. To rigorously study the effect of composition of a surface with nanoscale wetting heterogeneities on condensation dynamics, we explored the topic theoretically (Section 2.1) and developed a method for fabricating surfaces with ordered arrays of nanoscale hydrophobic heterogeneities on hydrophilic background with varied wetting properties (Section 2.2). We studied how surface configuration of these mimicked composites affects their static and dynamic contact angles (Section 2.3) as well

as microscale (Section 2.4) and macroscale (Section 2.5) condensation dynamics. Last, by substituting the experimental results into DWC models, we estimated impact of MMH-NPCs composition on the overall heat transfer enhancement (Section 2.6).

2. Results and Discussion

2.1. Surface Wetting and Bulk Thermal Conductivity versus Composite Composition: Theoretical Considerations

Hydrophilic surfaces with millimeter scale hydrophobic patterns were first explored for condensation heat transfer enhancement by Tanaka and co-workers.^[11] More recent work has focused on wetting^[8a,b,e-h] and condensation^[6d,8h-u] of surfaces with both chemical and topological microscale features. The Cassie–Baxter equation is commonly used to predict the apparent contact angle of water droplets, θ_c , sitting on such surfaces.^[12] In particular, the $\cos\theta_c = \sum_{i=1}^{i_{max}} f_i \cos \theta_i$ where f_i and θ_i , are the liquid–solid interfacial area per unit plane base area and the water contact angle of individual phases present on



the surface (we use subscript s, a, and r for static, advancing, and receding contact angles and H and M for hydrophobic and matrix phases, respectively). For spherical hydrophobic particles with $\theta_{\text{Hs}} \approx 100^{\circ}$ (e.g., PTFE or ceria^[5]) with diameter (d) distributed uniformly on corners of a cubic lattice with a center-to-center pitch (P), a hydrophobic composite is achieved for a P/d (nanoparticle volume fraction) of 1.15 (0.34) and 1.35 (0.2) for copper and aluminum matrices with $\theta_{Ms} \approx 60^{\circ}$ and 80° , respectively (our contact angle measurements for thoroughly cleaned mirror polished metal surfaces are in good agreement with literature^[13]). The corresponding nondimensional effective thermal conductivities $(k_{\rm eff}/k_{\rm M})$ calculated using Maxwell's formula are 0.56 and 0.71. We note that this formula neglects nanoscale effects and is used here only to obtain a rough estimate of the effective conductivities.^[14] For copper, this corresponds to $k_{\text{eff}} \approx 180 \text{ W mK}^{-1}$, which is dramatically higher than that of PTFE (≈ 0.25 W mK⁻¹) or ceria (≈ 17 W mK⁻¹) and comparable to pure aluminum (≈200 W mK⁻¹). Thus, according to these calculations MMHNPC could provide the highly desired high thermal conductivity hydrophobic materials for improved condensation (for calculation details see discussion in the Supporting Information and Figures S1 and S2).

Nevertheless, the predictions of thermodynamic models of composite surfaces' static contact angles often do not correspond to condensation behavior. For example, macroscopically superhydrophobic surfaces can be easily flooded by water condensate and careful nanoengineering is required to promote DWC on those surfaces.^[8q,10,15] Furthermore, Anand et al.^[6b] and Rykaczewski et al.^[6c] recently demonstrated DWC of water

FULL PAPER

and wide array of low surface tension liquids with static contact angles significantly below 90°, but with very low contact angle hysteresis (the CAH is the difference between advancing and receding contact angles). Consequently, low CAH not necessarily hydrophobicity of surface ($\theta_{cs} > 90^{\circ}$), is a better criterion for predicting whether a material is suitable to promote DWC. The volume fraction of hydrophobic nanoparticles within metal matrix required to reduce the CAH sufficiently to promote DWC might be different from the values predicted using static contact angle calculations. Unfortunately, quantitative theoretical prediction of dynamic wetting properties of heterogeneous surfaces can be quite challenging,^[8f,12b,16] hence we explored this topic experimentally. Since fabrication of metal matrix composites can be quite complex and the resulting particle distribution across the metal matrix is random,^[7,17] below we studied condensation on surfaces with well-defined ordered nanoscale heterogeneities that mimic those of MMHNPCs.

2.2. Mimicked Composite Morphology

We mimicked the heterogeneous surfaces of the composites by fabricating ordered arrays of PTFE nanospheres on silicon substrates using a modification of the procedure given by Park et al.^[18] (see **Figure 2a**). Specifically, after fabrication of the nanospheres via directed dewetting of liquid PTFE precursor using soft lithography and thermal annealing (steps i–iii), we removed residual PTFE thin film using oxygen plasma etching (step iv), and adjusted the wetting property of the



Figure 2. a) Schematic of the mimicked composite fabrication procedure with inset images showing corresponding static water contact angles with silicon, PTFE, and ODMCS indicated with gray, blue, and green colors, respectively; the inset in iii shows example AFM image of a PDMS soft stamp surface; b–e) SEM images of PTFE nanosphere arrays fabricated with different grating pitch soft stamps; we note that morphology of the grounding metal thin film required for high quality imaging is also visible in-between spheres.

ADVANCED MATERIALS INTERFACES www.advmatinterfaces.de

Table 1. Geometrical parameters of PTFE nanosphere array fabricated with soft stamps made from gratings with indicated line spacing (ls). "*a-b*", $d_{A_{fcr}}$, and A_{fm} stand for the average values of rectangular grid sides, PTFE nanosphere diameter, and calculated and measured area fractions, respectively.

ls [nm]	830			560			420			280		
Parameter	а	Ь	d	а	Ь	d	а	b	d	а	Ь	d
	$\textbf{328} \pm \textbf{129}$	664 ± 42	135 ± 53	420 ± 108	603 ± 35	190 ± 31	209 ± 61	451 ± 41	120 ± 13	258 ± 72	319 ± 28	158 ± 27
A _{fc}	0.065 ± 0.058			0.11 ± 0.047			0.12 ± 0.04			0.24 ± 0.11		
A _{fm}	0.088			0.12			0.13			0.17		

silicon background using vapor phase deposition of octyldimethylchlorosilane (ODMCS) (step v). The images of static water contact angle corresponding to different fabrication steps clearly illustrate the alteration of effective wetting properties of the composites induced by changes of the contact angle of the background surface (from $\theta_{\rm Ms} \approx 100^\circ$ for PTFE to $\theta_{\rm Ms} < 10^{\circ}$ for clean Si to $\theta_{\rm Ms} \approx 60^{\circ}$ to 80° for different ODMCS modification). We tailored the ODMCS deposition procedure to achieve background (i.e., measured on flat silane modified wafer without nanospheres) static water contact angles of 65° $\pm~4^\circ$ and $77^\circ~\pm~3^\circ$ to fabricate samples that mimic surfaces of composites with "Cu-like" ($\theta_{Ms} \approx 60^\circ$) and "Al-like" ($\theta_{Ms} \approx 80^\circ$) matrix, respectively. To mimic different volumetric fractions of the hydrophobic nanoparticles, PTFE nanosphere arrays with varied pitch were fabricated by tuning the geometry of the polydimethylsiloxane (PDMS) soft stamps. In particular, stamps with parallel nanogrooves with line spacing (ls) of ≈ 280 , ≈ 420 , \approx 560, and \approx 830 nm were fabricated by spin-coating uncured elastomer on optical gratings having corresponding ls (inset in Figure 2a-iii shows example atomic force microscopy (AFM) image of a stamp). The scanning electron microscopy (SEM) images in Figure 2b-e show typical PTFE nanosphere arrays resulting from thermal curing of spin-coated liquid PTFE precursor pressed by these four types of parallel groove PDMS stamps. The fabricated PTFE nanospheres have diameters in the range of ≈120 to ≈190 nm and are not arranged on a perfectly square grid. However, all average grid dimension values presented in Table 1 are below ≈650 nm, being at or below the upper bound of the length scale regime we want to study. Based on direct image analysis of SEM and AFM data, the samples fabricated with ≈280, ≈420, ≈560, and ≈830 nm line spacing gratings had PTFE area fractions of ≈0.09, ≈0.12, ≈0.13, and ≈0.17, respectively (see the Supporting Information for calculation details). As shown in Table 1, the area fractions calculated based on average diameters and grid dimensions (rectangle with side dimensions a and b) are in close agreement with the directly measured area fractions. We note that the AFM analysis revealed that oxygen plasma treatment flattened the nanospheres to a thickness of \approx 20–50 nm (for consistency we continue referring to these discs as spheres). Importantly, the produced PTFE particle arrays uniformly covered entire ≈1 cm² sample area and could be reproduced with high repeatability. In all, we studied wetting properties and condensation dynamics on samples with four different PTFE nanosphere distributions with Cu-like and Al-like background and, as reference, bare and PTFE as well as silane modified silicon (see the Experimental Section for further details). We note that besides rigorous cleaning of the samples with every use, precautions such as

checking of wetting properties prior to and after experiments were taken to ensure that samples' wetting properties were not altered due to hydrocarbon contamination.

2.3. Wetting Properties of Mimicked Composites

The presence of the nanosphere arrays on the ODMCS modified samples did not appreciably alter the static contact angle of water drops but had a major effect on their contact angle hysteresis. Specifically, the plot in **Figure 3**a shows that for all



Figure 3. a) Static contact angles and b) contact angle hysteresis (CAH) of the mimicked composites.



www.MaterialsViews.com

mimicked Cu-like and Al-like composites the measured static contact angles were within $\approx 5^{\circ}$ of $\approx 65^{\circ}$ and $\approx 80^{\circ}$, respectively. This observation is not surprising if we take into account the area fraction of the PTFE nanospheres is at most 0.2. The plots in Figures S1 and S2 of the Supporting Information show that for such area fraction (whether of hemispheres or circles) the Cassie-Baxter equation predicts a static contact angle increase below 5° for θ_{Ms} equal or greater than $\approx 40^{\circ}$. On the contrary to the static contact angles, the CAH was found to decrease significantly with increasing density of the hydrophobic phase. The plot in Figure 3b shows that the CAH was reduced by $\approx 10^{\circ}$ (≈33% to 42% reduction) with addition of the highest density of PTFE particles (fabricated with grating with line spacing of 280 nm corresponding to $A_{\rm f} \approx 0.2$) compared to the bare ODMCS modified wafer. In particular, the CAH is reduced from $\approx 25^{\circ}$ to $\approx 15^{\circ}$ for $\theta_{\rm Ms}$ \approx 77° and from $\approx 30^{\circ}$ to $\approx 20^{\circ}$ for $\theta_{\rm Ms} \approx 65^{\circ}$. This decrease is more substantial than predicted by area fraction based Cassie-Baxter arguments (below 5°, see Table S1, Supporting Information), but it could be explained by considering the effect of the hydrophobic phase on motion of the solid-liquid-air contact line around the perimeter of the drops.^[8f,19] In this perspective, the contribution of the hydrophobic phase in Cassie-Baxter equation is evaluated per unit length of the drop perimeter not per unit base area. For the disk-like PTFE patches, we can quantify the fraction of the total length of three phase contact line over hydrophobic phase as $fl_{\rm H} \approx d/P$. We note that this expression for $fl_{\rm H}$ is quite crude as it neglects any possible effects of bending of the contact line and effects of three dimensional drop surface distortions. Because the per base area arguments scale with $f_{\rm H} \approx 0.25 \pi (d/P)^2$, the hydrophobic phase contribution is much more substantial when dynamic contact angles are evaluated using per contact line arguments (see discussion in the Supporting Information). Substituting the $f_{\rm H}$ and $f_{\rm H}$ and advancing and receding contact angle values for PTFE and ODMCS into Cassie-Baxter relation we can estimate a CAH change obtained from adding the densest distribution of PTFE discs (280 nm line spacing). Using the per base area and per contact line arguments we estimate a CAH decrease of $\approx 4^{\circ}$ to $\approx 5^{\circ}$ and $\approx 9^{\circ}$ to $\approx 12^{\circ}$, respectively (see Table S1, Supporting Information, for all values). Thus, we assert that even a small addition of ≈ 0.2 area fraction of nanoscale hydrophobic patches onto a hydrophilic matrix can substantially reduce the CAH of macroscale water drops by altering the contact line motion dynamics. Next we explore whether the use of nanoscale hydrophobic particles can also enable the alteration of microscopic drop dynamics and condensation mode.

2.4. Microscale Condensation Dynamics

Onset of the second growth stage occurs when droplet diameters become comparable to the average separation distance between closest neighboring droplet centers (i.e., $l_{co} \approx 5$ to 10 µm).^[9b,c,10,20] To image the details of water condensation on this length scale occurring on the sample set described in Section 2.2, we used a custom humidity chamber coupled to a high speed camera mounted onto a high magnification optical microscope. A water-chilled Peltier element was used to decrease the

temperature of the samples to achieve a large subcooling of ≈20 K (for further details see the Experimental Section). To provide perspective, we illustrate droplet dynamics on bare plasma cleaned (Figure 4a) and PTFE coated (Figure 4b) silicon wafers. These two cases can be referred to as the bounding cases of rapid DWC-to-FWC mode and sustained DWC mode, respectively. Because the first sample has a receding contact angle below 5°, the outer part of the water droplets' contact line does not move after a coalescence event. This leads to rapid formation of highly distorted puddles (perimeter circularity, $p_c \ll 1$) that eventually merge into a continuous film. In contrast, microdrops formed by coalescence on the PTFE coated silicon recoil into equilibrium spherical cap shape with circular perimeter within $\approx 0.1 \text{ ms}$ ($p_c \approx 0.9$). On macroscale, this sample has a high receding contact angle ($\approx 110^{\circ}$) and very low CAH ($\approx 10^{\circ}$). The rest of the images in Figure 4 shows that on both Cu-like and Al-like samples increasing contact line fraction ($f_{\rm H} \approx d/P$) of the PTFE nanospheres from 0.27 to 0.55 (fabricated with gratings with line spacing of 830 to 280 nm) significantly reduces contact line pinning. Specifically, images in Figure 4c,e show that, after merging, drops on composites with $f_{\rm H} \approx 0.27$ are highly deformed and essentially cover the outline of precoalescence drops (the compound drops in bottom images of Figure 4c,e have $p_c \approx 0.6$ to 0.7). In contrast, images in Figure 4d,f show that within 0.4 ms after droplets merging on composites with $f_{\rm H} \approx 0.55$, contact line retracts to form drops with high circularity ($p_c \approx 0.8$ to 0.9). Thus, by increasing the amount of nanoscale hydrophobic patches on our composite samples, we not only significantly decrease macroscopic CAH but also amend microdroplet coalescence dynamics to nearly resemble those occurring during sustained DWC mode on the fully PTFE coated sample. We note that in agreement with literature, the l_{co} for all the composite samples was about 10 µm.

2.5. Macroscale Condensation Dynamics

The heat transfer rate during sustained DWC increases with decreasing drop departure radius.^[3] To quantify how surface configuration of our mimicked composites impacts the drop departure radius, we conducted steady state condensation experiments on vertically mounted specimen. The experiments were performed in the environmental chamber with air at temperature of 298 \pm 1 K and relative humidity of 92% \pm 3%. The specimen temperature was decreased using water-chilled Peltier element to achieve subcooling of ≈20 to 25 K and supersaturation of ≈4. Figure 5a shows examples of pre- (images in left column) and post-drop departure (images in right column) drop distributions on PTFE coated silicon as well as on Al-like composite with coarse (grating line spacing of 830 nm) and dense (grating line spacing of 280 nm) PTFE nanosphere arrays. Such images captured during 1 h of continuous condensation were analyzed to determine average drop departure radius depicted in Figure 5b (average of at least six departing drops is presented). It is evident that, as the CAH, the drop departure radius decreases with increasing PTFE fraction on the surface. We observed that the specimen fully coated by PTFE had the smallest drop departure radius of ≈1 mm, while the ODMCS coated samples without any PTFE nanospheres had the largest drop departure radii of \approx 1.6 to 1.7 mm. Addition of the densest





Figure 4. Sequence of optical images showing microscale droplet dynamics during water condensation on horizontally mounted a) plasma cleaned silicon, b) PTFE coated silicon, and c–f) mimicked composites with PTFE nanospheres arrays fabricated with gratings with 830 and 280 nm line spacing (ls) on ODMCS modified silicon wafer with Cu-like ($\theta_{Ms} \approx 65^{\circ}$) and Al-like ($\theta_{Ms} \approx 77^{\circ}$) wetting properties.

PTFE nanosphere array reduced the drop departure radii to ≈1.3 mm and ≈1.45 mm for the Al-like and Cu-like composites, respectively. This change corresponds to $\approx 40\%$ of possible reduction toward the minimum reference departure radius set by drops shedding off the PTFE coated silicon. The presence of the PTFE nanosphere array made from grating with line spacing of ≈440 nm had less pronounced effect, while presence of coarse arrays (grating with line spacing of 550 nm and above) did not alter the departure radius. Furthermore, increase of hydrophobic phase density led to lower departure radius on the composite with higher static contact angle such as $\theta_{Ms} \approx 77^{\circ}$. This observation is in agreement with the absolute CAH of the Al-like composite being lower than that of the Cu-like composite. We point out that despite lack of any hydrophobic phase, the solely ODMCS modified silicon wafers also promoted sustained DWC. The reason behind this "nonfilmwise-mode" condensation might be the atomistically flat topography of the silicon wafer. In industrial setting, metal surfaces displaying a similar static contact angle have at least a microscale roughness that significantly increases CAH. To illustrate the effect of this roughness on condensation mode we conducted a control experiment on mirror polished copper with static contact angle of $64^{\circ} \pm 5^{\circ}$ and CAH of $37^{\circ} \pm 5^{\circ}$. The images in Figure S4 of the Supporting Information show that this sample rapidly transitioned into FWC mode. To summarize, the mimicked MMHNPCs promoted DWC and with a threshold density of hydrophobic phase facilitated drop shedding. In the next section we explore the interplay between heat transfer enhancement, drop dynamics, and thermal conductivity of composites with varied hydrophobic phase densities.

2.6. Estimation of Heat Transfer Enhancement during the Condensation Process

We estimated the condensation heat transfer coefficient for different composites by substituting experimentally observed contact angles and departure drop radii into DWC model developed by Kim and Kim.^[21] This model was initially developed for modeling of DWC on superhydrophobic surfaces ($\theta_c >> 90^\circ$), but was recently adapted for and experimentally validated by Rykaczewski et al.^[6c] for DWC with drops with $\theta_c < 90^\circ$. The model predicts heat transfer through a drop with radius *r* and contact angle $\theta^{[21]}$

$$q_{\rm d} = \frac{\Delta T \pi r^2 \left(1 - \frac{r_{\rm c}}{r}\right)}{\left(\frac{\delta}{\sin^2 \theta k_{\rm coat}} + \frac{r\theta}{4k_{\rm w} \sin \theta} + \frac{1}{2h_{\rm i}(1 - \cos \theta)}\right)}$$
(1)

where ΔT , r_c , h_i , δ , k_{coat} , and k_w are the surface subcooling, critical nucleation radius, interfacial liquid–vapor heat transfer coefficient, thickness of the coating, and thermal conductivities of the coating and liquid water, respectively. The overall heat transfer rate per unit area for different surface subcooling was obtained by integrating the product of q_d and drop size distribution, n(r), from r_c to the departure radius $r_d = r_{base}/\sin\theta$:





Figure 5. Sequential images captured 1 s apart of condensation on vertically mounted a) PTFE coated silicon and ODMCS modified silicon with nanosphere arrays made with Is of b) 280 nm and c) 830 nm showing sample before and after gravity assisted drop shedding; d) Plot of average departure radius for different mimicked composites as well as ODMCS and PTFE modified wafers.

$$q'' = \int_{r_c}^{r_a} q_d n(r) dr$$
⁽²⁾

The total condensation heat transfer coefficient, h, is obtained through a linear fit of the calculated heat transfer rate per unit area for modeled surface subcooling range. The effect of the hydrophobic nanoparticle filler on the overall heat transfer was incorporated using equivalent thermal conductivity of the composites calculated using the Maxwell model (δ and k_{coat}). We estimated the volumetric fraction of spherical PTFE nanoparticles corresponding to the PTFE nanosphere arrays on our mimicked composites by assuming a cuboid lattice with sides a and b (see Table 1) and height of (a + b)/2. Even the upper bound of the highest estimated volume fraction corresponding to densest PTFE nanosphere array is only 0.15. Thus, our experiments suggest that the volume fraction of hydrophobic nanoparticles required to promote DWC on MMHNPC is substantially smaller than the theoretically estimated volume fraction of nanoparticles required to make the composite surface hydrophobic (see Figure S1b, Supporting Information). Furthermore, the plot of in Figure 6a shows that 0.15 volumetric fraction of PTFE nanoparticles would only cause a minor ≈ 0.2 reduction in $k_{\text{eff}}/k_{\text{M}}$. However, as we pointed out in the previous section, metal samples will have a roughness higher than that



Figure 6. a) Ratio of effective thermal conductivity of a composite to thermal conductivity of matrix metal as a function of different volume fractions of hydrophobic PTFE nanoparticles. Volume fractions corresponding to different nanosphere line spacing (Is) of the mimicked composites are indicated; and b) modeled heat transfer coefficient for different thickness hydrophobic coatings consisting of PTFE film (red continuous), ceria film (red dashed), and different composition AI-PTFE NP (blue), Cu-PTFE NP (orange), and Ni-PTFE NP (green) composites with volume fraction between 0.03 to 0.45 (3% to 45%). For reference, lines indicating heat transfer coefficient for filmwise condensation occurring on bare copper and twice that value are also shown.

www.advmatinterfaces.de

of the nearly perfectly smooth silicon wafers. Consequently, a larger volumetric fraction of hydrophobic particles will likely be needed to promote DWC using these composites. To account for this possibility, we also model heat transfer on composites with volumetric fraction of hydrophobic particles three times higher than the upper bound set by our experiments (i.e., 0.45).

The calculated heat transfer coefficients for different thicknesses of aluminum, copper, and nickel (another common condenser material with $k_{\rm M} \approx 91$ W mK⁻¹) matrix composites with PTFE nanoparticle filler with volume fraction between 0.03 and 0.45 are shown in Figure 6b. The heat transfer coefficients for DWC occurring on a PTFE and ceria films (departure radius of $\approx 1.35 \text{ mm}^{[5]}$) with different thicknesses are also plotted. For reference, lines indicating heat transfer coefficient for filmwise condensation of water occurring in same conditions calculated using the Nusselt model and twice this value are also indicated.^[6c,22] In agreement with literature,^[3] this theoretical analysis predicts that benefits of enhancing DWC using a low thermal conductivity polymer such as PTFE are annulled when the film is thicker than $\approx 6 \mu m$. In turn, a sixfold and a twofold heat transfer enhancement over FWC can be achieved by using higher thermal conductivity ceria film even with a thickness of ≈ 10 and $\approx 100 \ \mu\text{m}$, respectively. However, the mismatch of thermomechanical properties of metals commonly used in condensers and ceria would likely lead to delamination of the ceramic film. Such failure mode might be avoided with use of MMHPCs. Our heat transfer analysis suggests that the fivefold heat transfer enhancement over FWC achieved by using these materials can be sustained even with composite thicknesses of 100 to 200 µm. Furthermore, about a twofold heat transfer enhancement can be obtained with essentially bulk-like composites with thickness of 1 mm or more. Most importantly, the condensation heat transfer enhancement achieved by use of the composites with thicknesses below ≈ 1 mm is nearly independent of the volume fraction of hydrophobic nanoparticles (within the modeled 0.03 to 0.45 range). This result highlights the benefit of using metal matrices with high thermal conductivity. Even when reduced by half of the matrix material's conductivity by presence of hydrophobic nanoparticles, Cu and Al based composites have thermal conductivities much greater than that of ceria and PTFE ($k_{Cu0.45PTFE}\approx$ 177 W mK^{-1} and $k_{Al0.45PTFE} \approx 105 \text{ W mK}^{-1} \text{ versus } k_{ceria} \approx 17 \text{ W mK}^{-1} \text{ for ceria}$. Consequently, even if it turns out that a higher content of hydrophobic nanoparticles than projected by our experiments is required to promote DWC on metal matrices with industrial surface finish (i.e., not perfectly flat), this is unlikely to significantly reduce achieved heat transfer enhancement.

Our heat transfer modeling results can also be used to roughly quantify a threshold thermal resistance posed by DWC promoter coating, $R'_i \approx L/k$, that negates the advantages of DWC and reduces the net heat transfer rate to level attained by FWC without any coating (i.e., when in the modeled saturation conditions $h_{\rm DWC}/h_{\rm FWC} \approx 1$). Specifically, for both PTFE and ceria $R'_i \approx 2.5 \times 10^{-5}$ K W⁻¹ ($R'_i \approx 6 \times 10^{-6}/0.25 \approx 4.8 \times 10^{-4}/17 \approx 2.5 \times 10^{-5}$ K W⁻¹). For a promoter material with given thermal conductivity, this value of threshold thermal resistance can be used to quickly estimate threshold thickness of the coating ($L_t \approx R'_i k$) when $h_{\rm DWC}/h_{\rm FWC} \approx 1$. From the industrial point of view, it can be assumed that at least a twofold heat



transfer enhancement should be attained by promoting DWC ($h_{\rm DWC}/h_{\rm FWC} \approx 2$) in order to justify cost of the DWC promoter coating. For both PTFE and ceria films, $h_{\rm DWC}/h_{\rm FWC} \approx 2$ is attained when $L \approx L_t/3$ (i.e., $R'' \approx R''_i/3$). Using these simple arguments, we estimate that copper and aluminum matrix composites fully loaded with PTFE nanoparticles (experimental limit of $\approx 0.64^{[23]}$) can be used to promote DWC and at least double heat transfer rate over FWC if they are thinner than 800 and 500 µm, respectively.

3. Conclusion

In this work we argued that metal matrix composites with hydrophobic nanoparticles could provide an attractive alternative to hydrophobic thin film materials for enhancing water condensation rate by promoting the dropwise mode. The key findings of our experimental and theoretical investigation are:

- (i) To alter condensation mode from FWC to DWC hydrophobic nanoparticles need to have diameters and spacing much smaller than average center-to-center spacing in-between closest neighboring drops prior to coalescence dominated growth stage (e.g., diameters of ≈100 to 200 nm as in our experiments).
- (ii) To promote DWC of water, surfaces do not necessarily have to have static contact angle greater than 90° (i.e., be hydrophobic), but rather need to have a low CAH.
- (iii) Our experiments suggest that the desired low CAH can be attained with significantly lower hydrophobic nanoparticle density than that required to make the surface hydrophobic. The likely explanation for this observation is that the hydrophobic phase on the surface facilitates movement of the drop contact line during coalescing and gravity assisted shedding.
- (iv) Our calculations show that a substantial heat transfer enhancement (twofold and higher) can be achieved even by using copper and aluminum matrix composites fully loaded with PTFE nanoparticles (maximum volume fraction ≈0.64) to promote DWC if their thickness is below ≈0.5 mm. The maximum volumetric fraction is four times higher than the upper bound of volumetric fraction needed to facilitate droplet shedding in our experiments. Use of a higher nanoparticle density might be needed to reduce the CAH of rough surface composites (in contrast to flat silicon wafer used as base for our mimicked composites). However, we provided arguments showing that using much higher nanoparticle density will not annul the heat transfer enhancement attained via DWC.

Hydrophobic composites could be fabricated according to the proposed composition guidelines in scalable routes and consist of cost-effective materials such as copper or aluminum matrices with PTFE or ceria nanoparticles. Illustrating feasibility of this approach, fabrication of bulk steel and cerium oxide microparticle composites has been reported as early as the 1970s,^[24] while a variety of metal composites coatings with high volume fraction of PTFE nanoparticles (up to ~0.5) have been fabricated using low-temperature coelectrodeposition.^[25,26] Some of the metal matrix PTFE nanoparticle composites were even found to have hydrophobic surface properties.^[26b] Naturally, a variety



of thermomechanical issues common to composites^[17] could affect the durability of MMHPCs as DWC promoters. Our work provides the motivation to explore use of the various composites for this application and, if proven to be successful, further research addressing potential durability issues.

4. Experimental Section

Sample Preparation: Surfaces of the metal matrix hydrophobic nanoparticle composites were mimicked by fabricating ordered arrays of PTFE nanospheres on silicon substrates using modification of the method described by Park et al.^[18] that included oxygen plasma treatment and vapor phase deposition of ODMCS. Two types of specimens were made to mimic the composites having Cu-like and Al-like wetting properties with static contact angles of ~65° and ~77°, respectively. Details of fabrication steps illustrated in Figure 2a are described below.

PDMS Soft Patterns: PDMS soft patterns with parallel grooves of different pitches (\approx 280, \approx 440, \approx 560, and \approx 830 nm) were made by spincoating (using SCK model a, Instras Scientific spin coater) mixed and degassed mixture of PDMS elastomer base and curing agent (Sylguard 184, Dow Corning) (10:1 by mass) on glass gratings (Thorlabs) having corresponding groove pattern. After spin coating, PDMS was allowed to settle and deaerated for 20 min. This procedure was followed by thermal curing on hotplate (Cimarec, Thermo Scientific) at 85 °C for 115 min. The stamps were later cautiously removed off the glass gratings and used in the further fabrication process.

PTFE Nanosphere Templating: 1 \times 1 cm silicon wafer (University Wafers) pieces were washed using water and ethanol and cleaned using oxygen plasma in a plasma reactor (Blue Lantern from Integrated) Surface Technologies) for 1 min at pressure of 250 mTorr and power of 150 W. PTFE precursor solution (AF1600, DuPont) was diluted in FC-40 (Sigma-Aldrich) in the ratio 1:4.25 by mass. The solution was mixed in ultrasonicator for 10 s and heated at 75 °C for a short period (a few seconds). Subsequently, the mixture was spin-coated on cleaned silicon substrate at 4500 \pm 60 rpm for 1 min. Immediately after spin-coating, the PDMS soft patterns were brought into contact with the PTFE solution covered silicon substrate and pressed using a 200 g weight. The whole assembly was thermally cured on the hotplate at 120 $^\circ$ C for 1 h. After completion of the curing process, the weight and PDMS patterns were carefully removed off the substrate. As fabricated, the samples with PTFE nanospheres had static contact angles above 100°, indicating presence of a residual PTFE film.

Octyldimethylchlorosilane Treatment of the Specimens: The samples fabricated using the procedure described in Section 4.1.2 were subjected to oxygen plasma at 250 mTorr and 150 W for three subsequent 10 min intervals with 1 min breaks. Post plasma etching, the static water contact angles of the samples were around 30° , confirming that the residual PTFE film in-between the spheres was removed. The etched specimens along with the beaker containing silane solution (ODMCS, Sigma-Aldrich) were transferred to desiccator placed in the environmental chamber (model 5518, ETS) set at 25 °C and 15% relative humidity. The desiccator was then evacuated for 15 min using a roughing vacuum pump (Edwards RX-5). We found that the total ODMCS exposure duration and the amount of ODMCS used during the experiment could be used to tune the resulting contact angle of the modified silicon wafer with PTFE nanospheres. To produce Al-like samples, the etched specimens were exposed to 100 μL of ODMCS solution for 4 h. In turn, the Cu-like samples were produced by exposure of the etched specimens to 10 μL ODMCS solution for 30 min. The static contact angles of the bare silicon treated with these protocols were found to be $77^\circ\pm1^\circ$ and $65^{\circ} \pm 4^{\circ}$, respectively. We found that samples could be produced with high repeatability using the outlined procedure. We also conducted control experiments to ensure that silane was preferentially deposited on the exposed silicon, not the PTFE nanospheres. In particular, a fully PTFE-coated wafer was exposed to the silane using the described procedure. We confirmed that the static contact angle of this sample

previous orientation. We found that the orientation did not affect the CAH value significantly $(17^{\circ} \pm 1^{\circ} \text{ vs } 15^{\circ} \pm 4^{\circ})$. Experimental Procedures: Static and Dynamic Contact Angle Measurements: A home-built goniometer composed of a stage 3D printed using Makerbot Replicator 2×, a CCD camera (Imaging Source DFK23U618) with high magnification lens (Navitar 6232A), a syringe pump (New Era Pump System NE-1000), and a diffuse light source (Dolan-Jenner MH-100), was used to measure the static and dynamic contact angles of water on all the fabricated specimens. For calculating the static contact angle, a 2 µL water drop was placed using a micropipette (Capp Bravo) on the sample. For each sample, six different drops were dispensed, images were captured and analyzed to calculate the average static contact angle. Corresponding uncertainty values were calculated using a two-tailed T-student's distribution with 95% confidence interval. To measure the contact angle hysteresis, the liquid was gradually dispensed and retracted from tip of a syringe using the syringe pump. The specimen was kept on the stage and illuminated from the back via the diffused light source. Images captured during

the experiment were stored and analyzed using ImageJ software.^[27] Specifically, separate images were chosen to calculate six advancing $(\theta_{a1}, \theta_{a2}, ..., \theta_{a6})$ and six receding $(\theta_{r1}, \theta_{r2}, ..., \theta_{r6})$ contact angles. Average advancing and receding contact angle, θ_a and θ_r respectively, were calculated using these values. The uncertainty values in θ_a $(\sigma\theta_a)$ and θ_r $(\sigma\theta_r)$ were calculated considering a two-tailed T-student's distribution with 90% confidence interval. Average contact angle hysteresis was later computed as CAH = $\theta_a - \theta_r$ with $\sigma_{CAH} = ((\sigma\theta_a)^2 + (\sigma\theta_r)^2)^{1/2}$.

High Speed Imaging of Microscopic Condensation Dynamics: To observe the microscopic coalescence dynamics, condensation experiments were performed under the optical microscope (Zeiss Axio-Zoom V16) and images were recorded using high speed camera (Photron Fastcam Mini UX-100) at 5000 fps. The experimental setup consisted of a glass humidity box with a custom acrylic top. Flow of nitrogen saturated with water was used to control the humidity around \approx 75% ± 2%. The samples were cooled using a water-cooled Peltier element (Analog Technologies). The surface temperature was measured using a K-type thermocouple connected to data logger and was controlled by adjusting input current for the Peltier element. Temperature, relative humidity, and air velocity inside the box were recorded using (EK-H5 Sensirion) and (Accusense UAS Sensor (UAS1100PC), Degree Controls, Inc), respectively. Images captured using high speed camera were postprocessed using PFA (v1.2.0.0) software.

Imaging of Steady-State Condensation Dynamics on Vertically Mounted Samples: The Peltier element cooled with flow of cold water supplied by circulating chiller (AP28R-30-V11B, VWR) was held vertically using the 3D printed mount in the environmental chamber set at 25 \pm 1 $^\circ\text{C}$ and 92% \pm 3%. The specimens were attached to the Peltier element using thermal grease (TG-2, Thermaltake). To determine the droplet departure radii we conducted steady-state condensation experiments for at least 1 h for each sample. The sample temperature was monitored and controlled in same way as described in Section 4.2.2. The surface subcooling was adjusted to \approx 20 to 25 K. Images of the condensation process were captured with 1 s interval using DFK 23UP031 camera (ImagingSource) with 3.5-10.5 mm lens (Computar). The droplet departure radius was calculated by analyzing the captured images using ImageJ software. Specifically, six predrop departure images were chosen to measure the departure diameter of the liquid droplet. In the event of multiple droplets with diameter d_1 , d_2 ..., d_n , having volume v_1 , v_2 ... v_n , merging to form a bigger shedding drop, volume of the departed drop was set to $v_1 + v_2 + ... + v_n$. The diameter of the detached drop was then calculated from using this volume assuming a spherical cap geometry

with $\nu = \frac{\pi (R/\cos\theta)^3}{3} (1-\cos\theta)^2 (2+\cos\theta)$ as given by Whyman et al.

(where θ is the static contact angle *R* is the base radius of the liquid droplet).^[28]



Sample Characterization and Postprocessing of Images: The fabricated samples were characterized using SEM (FEI XL-30 with field emission gun) and AFM (Bruker Dimension). Specifically, AFM images were recorded for each sample over the area $5 \times 5 \ \mu m$ and $10 \times 10 \ \mu\text{m}$. The captured images were analyzed using Nanoscope Analysis v1.40 (Bruker Corporation) to quantify the diameters and the spacing of the nanospheres. In particular, ≈30 measurements of the interspherical center-to-center distance along the row of nanospheres (a), the distance between neighboring spheres in the parallel rows (b), and the diameter of the spheres (d) were recorded. Based on these 30 data points, average values a_{avg} , b_{avg} , d_{avg} with corresponding the standard deviations $\sigma_{\rm a},\,\sigma_{\rm b}$, and $\sigma_{\rm d}$ were calculated. The "b" parameter is roughly governed by the Thorlabs master gratings spacing whereas the "a" distance is determined by the dynamics of dewetting induced by heating the thin film of PTFE precursor solution spin coated on the silicon wafer above the glass-transition temperature. Using these three parameters, surface fraction of nanospheres was translated into volume fraction (vf) of the mimicked MMC using $\frac{4}{3}\pi \left(\frac{d}{2}\right)^2 /ab\frac{a+b}{2}$. In turn,

the corresponding uncertainty of the volume fraction was calculated

as $\sigma_{\rm vf} = \sqrt{\left(\frac{\partial vf}{\partial a}\sigma_a\right)^2 + \left(\frac{\partial vf}{\partial b}\sigma_b\right)^2 + \left(\frac{\partial vf}{\partial d}\sigma_d\right)^2}$. In addition to the AFM

characterization, SEM images were captured to confirm the uniform fabrication of the nanospheres across the entire 1 cm² substrate area.

Supporting Information

www.advmatinterfaces.de

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

This work was funded by Ira A. Fulton Schools of Engineering at Arizona State University. Authors gratefully acknowledge the use of facilities with the LeRoy Eyring Center for Solid State Science at Arizona State University. The authors also thank Dr. Soojin Park and Hyungmin Park for help with nanosphere fabrication procedure. Additionally, authors would also like to extend their sincere gratitude to Dr. Marlon Walker from NIST for his suggestion in silane treatment optimization and Dr. Sushant Anand from MIT for his thoughtful suggestions in the preparation of this article.

> Received: April 22, 2015 Revised: June 18, 2015 Published online:

- A. T. Paxson, J. L. Yague, K. K. Gleason, K. K. Varanasi, Adv. Mater. 2014, 26, 418.
- [2] E. Schmidt, W. Schurig, W. Sellschopp, Forsch. Ingenieurwes. 1930, 1, 53.
- [3] J. W. Rose, Proc. Inst. Mech. Eng. A 2002, 216, 115.
- [4] a) H. Müller-Steinhagen, Q. Zhao, Chem. Eng. Sci. 1997, 52, 3321;
 b) Z. Qi, Z. Dongchang, L. Jifang, Int. J. Heat Mass Transfer 1991, 34, 2833; c) M. H. Rausch, A. P. Fröba, A. Leipertz, Int. J. Heat Mass Transfer 2008, 51, 1061; d) M. H. Rausch, A. Leipertz, A. P. Fröba, Int. J. Heat Mass Transfer 2010, 53, 423; e) A. Bani Kananeh, M. H. Rausch, A. P. Fröba, A. Leipertz, Int. J. Heat Mass Transfer 2006, 49, 5018; f) L. C. F. Blackman, M. J. S. Dewar, H. Hampson, J. Appl. Chem. 1957, 7, 160; g) K. P. Perkins, DTIC Document 1979; h) D. W. Woodruff, J. Westwater, Int. J. Heat Mass Transfer 1979, 22, 629; i) G. A. O'neill, J. Westwater, Int. J. Heat Mass Transfer 1984, 27, 1539; j) P. Marto, D. Looney, J. Rose, A. Wanniarachchi, Int. J. Heat Mass Transfer 1986, 29, 1109.



www.MaterialsViews.com

- [5] G. Azimi, R. Dhiman, H. M. Kwon, A. T. Paxson, K. K. Varanasi, Nat. Mater. 2013, 12, 315.
- [6] a) S. Anand, K. Rykaczewski, S. B. Subramanyam, D. Beysens, K. K. Varanasi, Soft Matter 2015, 11, 69; b) S. Anand, A. T. Paxson, R. Dhiman, J. D. Smith, K. K. Varanasi, ACS Nano 2012, 6, 10122; c) K. Rykaczewski, A. T. Paxson, M. Staymates, M. L. Walker, X. Sun, S. Anand, S. Srinivasan, G. H. McKinley, J. Chinn, J. H. J. Scott, K. K. Varanasi, Sci. Rep. 2014, 4, 4158; d) R. Xiao, N. Miljkovic, R. Enright, E. N. Wang, Sci. Rep. 2013, 3, 1988.
- [7] M. Nosonovsky, V. Hejazi, A. E. Nyong, P. K. Rohatgi, *Langmuir* 2011, 27, 14419.
- [8] a) J. Drelich, J. D. Miller, A. Kumar, G. M. Whitesides, Colloids Surf., A 1994, 93, 1; b) J. Drelich, J. L. Wilbur, J. D. Miller, G. M. Whitesides, Langmuir 1996, 12, 1913; c) G. Lopez, H. Biebuyck, C. Frisbie, G. Whitesides, Science 1993, 260, 647; d) A. Kumar, G. M. Whitesides, Science 1994, 263, 60; e) M. Morita, T. Koga, H. Otsuka, A. Takahara, Langmuir 2005, 21, 911; f) R. Raj, R. Enright, Y. Zhu, S. Adera, E. N. Wang, Langmuir 2012, 28, 15777; g) A. R. Parker, C. R. Lawrence, Nature 2001, 414, 33; h) L. Zhai, M. C. Berg, F. C. Cebeci, Y. Kim, J. M. Milwid, M. F. Rubner, R. E. Cohen, Nano Lett. 2006, 6, 1213; i) K. K. Varanasi, M. Hsu, N. Bhate, W. Yang, T. Deng, Appl. Phys. Lett. 2009, 95, 094101; j) L. Mishchenko, B. Hatton, V. Bahadur, J. A. Taylor, T. Krupenkin, J. Aizenberg, ACS Nano 2010, 4, 7699; k) L. Mishchenko, M. Khan, J. Aizenberg, B. D. Hatton, Adv. Funct. Mater. 2013, 23, 4577; I) M. He, X. Zhou, X. Zeng, D. Cui, Q. Zhang, J. Chen, H. Li, J. Wang, Z. Cao, Y. Song, L. Jiang, Soft Matter 2012, 8, 2680; m) D. M. Anderson, M. K. Gupta, A. A. Voevodin, C. N. Hunter, S. A. Putnam, V. V. Tsukruk, A. G. Fedorov, ACS Nano 2012, 6, 3262; n) C. Yao, T. Garvin, J. Alvarado, A. Jacobi, B. Jones, C. Marsh, Appl. Phys. Lett. 2012, 101, 111605; o) L. Vonna, H. Haidara, Soft Matter 2013, 9, 765; p) X. Chen, R. Ma, H. Zhou, X. Zhou, L. Che, S. Yao, Z. Wang, Sci. Rep. 2013, 3, 2515; q) X. Chen, J. Wu, R. Ma, M. Hua, N. Koratkar, S. Yao, Z. Wang, Adv. Funct. Mater. 2011, 21, 4617; r) A. Ghosh, S. Beaini, B. J. Zhang, R. Ganguly, C. M. Megaridis, Langmuir 2014, 30, 13103; s) Y. Hou, M. Yu, X. Chen, Z. Wang, S. Yao, ACS Nano 2015, 9, 71; t) H. Zhao, D. Beysens, Langmuir 1995, 11, 627; u) M.-G. Medici, A. Mongruel, L. Royon, D. Beysens, Phys. Rev. E 2014, 90, 062403.
- [9] a) D. Beysens, C. R. Phys. 2006, 7, 1082; b) D. Beysens, Atmos.Res.
 1995, 39, 215; c) D. Beysens, C. M. Knobler, Phys. Rev. Lett. 1986, 57, 1433; d) D. Beysens, C. M. Knobler, H. Schaffar, Phys. Rev. B 1990, 41, 9814.
- [10] R. Enright, N. Miljkovic, A. Al-Obeidi, C. V. Thompson, E. N. Wang, Langmuir 2012, 28, 14424.
- [11] S. Kumagai, S. Tanaka, H. Katsuda, R. Shimada, Exp. Heat Transfer 1991, 4, 71.
- [12] a) A. B. D. Cassie, S. Baxter, Trans. Faraday Soc. 1944, 40, 546;
 b) P.-G. de Gennes, F. Brochard-Wyart, D. Quéré, Capillarity and Wetting Phenomena: Drops, Bubbles, Pearls, Waves, Springer, NY, USA 2003.
- [13] J. D. Bernardin, I. Mudawar, C. B. Walsh, E. I. Franses, Int. J. Heat Mass Transfer 1997, 40, 1017.
- [14] a) A. Minnich, G. Chen, Appl. Phys. Lett. 2007, 91, 073105;
 b) C.-W. Nan, R. Birringer, D. R. Clarke, H. Gleiter, J. Appl. Phys. 1997, 81, 6692.
- [15] a) R. D. Narhe, D. A. Beysens, Phys. Rev. Lett. 2004, 93, 076103;
 b) C. H. Chen, Q. J. Cai, C. L. Tsai, C. L. Chen, G. Y. Xiong, Y. Yu, Z. F. Ren, Appl. Phys. Lett. 2007, 90, 173108; c) Y. C. Jung, B. Bhushan, J. Microsc. 2008, 229, 127; d) J. B. Boreyko, C. H. Chen, Phys. Rev. Lett. 2009, 103, 184501; e) Y. M. Zheng, D. Han, J. Zhai, L. Jiang, Appl. Phys. Lett. 2008, 92, 084106; f) N. A. Patankar, Soft Matter 2010, 6, 1613; g) K. Rykaczewski, J. H. J. Scott, A. G. Fedorov, Appl. Phys. Lett. 2011, 98, 093106; h) K. Rykaczewski, J. H. J. Scott, S. Rajauria,



www.advmatinterfaces.de



- J. Chinn, A. M. Chinn, W. Jones, Soft Matter 2011, 7, 8749;
 j) K. Rykaczewski, W. A. Osborn, J. Chinn, M. L. Walker,
 J. H. J. Scott, A. M. Chinn, W. Jones, C. Hao, S. Yao, Z. Wang, Soft Matter 2012, 8, 8786; k) K. Rykaczewski, Langmuir 2012, 28, 7720;
 l) N. Miljkovic, R. Enright, E. Wang, ACS Nano 2012, 6, 1776;
 m) N. Miljkovic, R. Enright, Y. Nam, K. Lopez, N. Dou, J. Sack,
 E. N. Wang, Nano Lett. 2012, 13, 179; n) K. A. Wier, T. J. McCarthy, Langmuir 2006, 22, 2433; o) C. Dorrer, J. Rühe, Langmuir 2007, 23, 3820; p) B. Mockenhaupt, H.-J. Ensikat, M. Spaeth, W. Barthlott, Langmuir 2008, 24, 13591; q) D. Torresin, M. K. Tiwari, D. Del Col,
 D. Poulikakos, Langmuir 2012, 29, 840.
- [16] a) J. F. Joanny, P. G. de Gennes, J. Chem. Phys. 1984, 81, 552;
 b) B. He, J. Lee, N. A. Patankar, Colloids Surf., A 2004, 248, 101;
 c) N. A. Patankar, Langmuir 2010, 26, 7498.
- [17] N. Chawla, K. K. Chawla, Metal Matrix Composites, Springer, New York 2006.
- [18] H. Park, T. P. Russell, S. Park, J. Colloid Interface Sci. 2010, 348, 416.
- [19] a) L. Gao, T. J. McCarthy, *Langmuir* 2007, *23*, 3762; b) C. W. Extrand, *Langmuir* 2003, *19*, 3793; c) A. T. Paxson, K. K. Varanasi, *Nat. Commun.* 2013, *4*, 1492.

- [20] a) J. L. Viovy, D. Beysens, C. M. Knobler, *Phys. Rev. A* **1988**, *37*, 4965; b) R. Narhe, D. Beysens, V. S. Nikolayev, *Langmuir* **2004**, *20*, 1213.
- [21] S. Kim, K. J. Kim, J. Heat Transfer **2011**, 133, 081502.
- [22] F. P. Incropera, D. P. DeWitt, Fundamentals of Heat and Mass Transfer, John Wiley & Sons, New York 2002.
- [23] C. Song, P. Wang, H. A. Makse, Nature 2008, 453, 629.
- [24] P. K. Rohatgi, R. Asthana, A. Das, Int. Met. Rev. 1986, 31, 115.
- [25] a) Y. Wan, Y. Wang, H. Tao, G. Cheng, X. Dong, J. Mater. Sci. Lett. 1998, 17, 1251; b) R. Balaji, M. Pushpavanam, K. Y. Kumar, K. Subramanian, Surf. Coat. Technol. 2006, 201, 3205.
- [26] a) P. Drasnar, J. Kudlacek, V. Kreibich, V. Kracmar, M. Vales, MM Sci. J. 2011, 248, 1803; b) Y.-H. You, C.-D. Gu, X.-L. Wang, J.-P. Tu, Int. J. Electrochem. Sci. 2012, 7, 12440; c) V. Stankovic, M. Gojo, Surf. Coat. Technol. 1996, 81, 225.
- [27] W. S. Rasband, ImageJ, U. S. National Institutes of Health, Bethesda, Maryland, USA 1997.
- [28] G. Whyman, E. Bormashenko, T. Stein, Chem. Phys. Lett. 2008, 450, 355.