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Wettability of Nanoparticle Decorated Surfaces

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DOI:
[10.33612/diss.134698894](https://doi.org/10.33612/diss.134698894)

IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

Document Version
Publisher's PDF, also known as Version of record

Publication date:
2020

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):
Guo, J. (2020). *Wettability of Nanoparticle Decorated Surfaces*. [Thesis fully internal (DIV), University of Groningen]. University of Groningen. <https://doi.org/10.33612/diss.134698894>

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Wettability of Nanoparticle Decorated Surfaces

Weiteng Guo

PhD thesis
University of Groningen
The Netherlands

The work described in this thesis was performed in the research group Nanostructured Materials and Interfaces of the Zernike Institute for Advanced Materials at University of Groningen, the Netherlands. This work is supported by the China Scholarship Council and the Zernike Institute for Advanced Materials.

Zernike Institute for Advanced Materials PhD thesis series 2020-18
ISSN: 1570-1530

Cover design: Weiteng Guo
Printed by Gildeprint, Enschede

university of
 groningen

faculty of science
and engineering

zernike institute for
advanced materials

rijksuniversiteit
 groningen

Wettability of Nanoparticle Decorated Surfaces

PhD thesis

to obtain the degree of PhD at the
University of Groningen
on the authority of the
Rector Magnificus Prof. C. Wijmenga
and in accordance with
the decision by the College of Deans.

This thesis will be defended in public on

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To my family

Contents

1 General Introduction	1
1.1 Theories from Wetting Phenomena	2
1.1.1 Equilibrium of a Droplet on a Flat Surface	2
1.1.2 Wenzel Model and Cassie-Baxter Model	5
1.1.3 Hamaker Calculation of Van der Waals Interaction Potentials	6
1.1.4 Dynamics in Wetting	8
1.2 Wettability inspired by Nature	9
1.2.1 Lotus Effect	9
1.2.2 Rose Petal Effect	11
1.3 Effect of Roughness on Wettability	13
1.4 Wettability of Nanoparticle Decorated Surfaces	13
1.5 Effect of Airborne Hydrocarbons on Wettability	14
1.6 Motivation	14
1.7 Thesis Outline	16
References	18
2 Experimental Methods	23
2.1 Nanoparticle Deposition	24
2.1.1 GST Nanoparticle Deposition	24
2.1.2 Cu Nanoparticle Deposition	25
2.2 GST Thin Film Fabrication	27
2.3 Contact Angle Measurements	27
2.4 Transmission Electron Microscopy	30
2.5 GST NPs on Graphene	33
2.6 Atomic Force Microscopy	34
2.7 High-Pressure CO ₂ Assisted NP Engulfment	37
References	39

3 Effect of Airborne Hydrocarbons on the Wettability of Phase Change Nanoparticle Decorated Surfaces.....	41
3.1 Introduction	42
3.2 Results and Discussion	44
3.2.1 Wettability of Flat Substrate Surfaces Prior to NP Deposition	44
3.2.2 Wettability Variation in Air After Thermal Annealing and UV-O ₃ Treatments	45
3.2.3 Wettability Switch in Designed Hydrocarbon Atmosphere and UV-O ₃ Treatment	47
3.2.4 Characterization of Hydrocarbons on GST NP Decorated Surfaces	49
3.2.5 Effect on Wettability Due to Airborne Hydrocarbons.....	51
3.2.6 Beyond Wenzel Model	53
3.3 Conclusions	56
Appendix	57
References	60
4 Tunable Wettability of Polymer Films by Partial Engulfment of Nanoparticles.....	65
4.1 Introduction	66
4.2 Results and Discussion	68
4.2.1 Effect of Airborne Hydrocarbons on Surface Wettability	68
4.2.2 Wettability of PMMA Films	68
4.2.3 Effect of Cu NPs on Wettability of PMMA Films	69
4.2.4 Partial NP Engulfment in PMMA.....	70
4.2.5 Determination of Optimum NP Coverage	73
4.2.6 Wettability vs. NP Engulfment into PMMA.....	75
4.2.7 Movability of NPs on PMMA	79
4.3 Conclusions	81
Appendix	82
References	86
5 Modeling and Calculations of the Wettability of Nanoparticle Decorated Surfaces	91
5.1 Introduction	92
5.2 Results and Discussion	93
5.2.1 Influence of Nanomeniscus on Wettability	93
5.2.2 Pinning Effects of Water Drops.....	97
5.3 Conclusions	100
Appendix	102

References	105
Summary	107
Samenvatting	111
Acknowledgements	115
List of Publications	119
Curriculum Vitae	121

Chapter 1

General Introduction

Abstract

This chapter gives a general introduction about wetting research. It starts with a brief history of the development of wetting theories for describing wetting behaviors and predicting wettability of certain surfaces. Then we show cases of some special wetting behaviors of natural surfaces enjoying superior properties such as self-cleaning and water-collecting, which have inspired researchers to design surfaces with relevant wettability for various applications. Furthermore, we briefly introduce how researcher move one step further to explore how surface roughness affect the surface wettability, explaining the reason why we focused on studying the wettability of nanoparticle decorated surfaces. Subsequently, an introduction of the effect of airborne hydrocarbons on surface wettability is presented. Finally, a logic line of the motivation of the research as well as a brief introduction of later chapters are presented in the last two parts of this chapter.

1.1 Theories from Wetting Phenomena

1.1.1 Equilibrium of a Droplet on a Flat Surface

Wetting of liquids over material surfaces is a topic studied both from the fundamental and application point of view, where chemistry, physics, and engineering intersect. Explorations of the origins of wetting can be traced back hundreds of years. Much of the early work attempted to explain the seemingly spontaneous rise of liquids in small diameter “capillary” tubes. Consequently, still to this day, wetting phenomena between liquids and solids are often referred to as capillary action or capillarity. Some of the first careful observations were reported by Hauksbee in 1706.¹ He noted that liquids rise higher in smaller-diameter tubes and that vacuum has no influence. A decade later, Jurin showed that the final rise height is inversely proportional to the tube diameter. In 1752, Segner established the surface tension as an intrinsic property of a liquid that causes its surface to behave as if it were an elastic membrane.²

Figure 1.1 Schematic to explain of the Young equation.

At the beginning of the 19th century, Young observed that the angle of contact between a given liquid and a solid is independent of geometry, which ultimately led him to the conclusion that “all the phenomena of capillary action may be accurately explained and mathematically demonstrated from the general law of equable tension of the surface of the fluid, together with the consideration of the angle of contact appropriate to every combination of a fluid with a solid.”³ Young avoided mathematical symbols and equations in his writings. Instead, he gave verbal descriptions of various wetting phenomena as well as to his now famous Young equation

$$\gamma_{sv} = \gamma_{sl} + \gamma_{lv} \cos \theta_Y, \quad (1.1)$$

where γ_{sv} , γ_{sl} and γ_{lv} are the surface energies of solid-air, solid-liquid, and liquid-air, respectively, and θ_Y represents the SCA of the liquid on the flat solid surface. When $\gamma_{sv} - \gamma_{sl} < 0$, one obtains $\theta_Y > 90^\circ$ and the surface is termed as hydrophobic, while $\gamma_{sv} - \gamma_{sl} > 0$, one obtains $\theta_Y < 90^\circ$ and the surface is termed as hydrophilic.

Another approach to the description of wetting of smooth homogeneous surfaces was proposed by Derjaguin and Frumkin.⁴ They developed a theory of wetting⁴ which makes it possible to relate the macroscopic contact angle θ_0 (see Figure 1.2a) to the disjoining pressure isotherm $\Pi(h)$, which characterizes the dependence of the interaction forces between phases 1 and 2 that confine the wetting/adsorption film of liquid 3, on the film thickness h

$$\cos \theta = 1 + \frac{1}{\gamma} \int_{h_e}^{\infty} dh \Pi(h) + \frac{h_e}{\gamma} \Pi(h_0). \quad (1.2)$$

In Eq. (1.2), h_e is the equilibrium thickness of the wetting film at the disjoining pressure equal to the capillary pressure in the drop. The concept of disjoining pressure was introduced by Derjaguin in 1936 as the difference between the pressure in a region of a phase adjacent to a surface confining it, and the pressure in the bulk of this phase.⁴ In general, the disjoining pressure includes several interactions due to dispersion forces, electrostatic forces between charged surfaces, interactions due to layers of neutral molecules adsorbed on the two surfaces, and structural effects of the solvent.⁴ The radii of curvature of the meniscus and drops used for experimental measurements of contact angles usually lie between 1 and 20 mm, which corresponds to the capillary and disjoining pressures of at most 1 mPa. In this case, the h_e value is almost equal to the film thickness h_0 corresponding to the zero-disjoining-pressure point in the isotherm (see Figure 1.2b).

Figure 1.2 Schematics for Derjaguin and Frumkin's theory. **a** A droplet on a smooth hydrophilic substrate **b** Types of disjoining pressure isotherms.⁵

More efforts were paid in understanding of the relationship between wettability and surface morphology. Using the concept “work of adhesion” introduced by Dupré,⁶ and taking the air-liquid interface on a solid as a one-dimensional system, Pease⁷ emphasized that the SCA is the result of an equilibrium position that the three-phase contact line (TPL) could reach. Then the dynamic wettability including the advancing contact angle (ACA) and the receding contact angle (RCA) were also expressed in terms of the work of adhesion.^{8,9} It was shown that wetting depends on the shape of the disjoining pressure isotherms (see Figure 1.2b), which in turn are determined by the nature of the surface forces acting in the system as it was shown Boinovich.¹⁰ In particular, for type 1 isotherms the integral in Eq. (1.2) is positive. Such isotherms characterize three-phase systems in which complete wetting with the zero contact angle occurs. In these systems, a liquid droplet placed on a substrate will spread in a saturated vapor atmosphere with the formation of a macroscopically thick film with the zero contact angle. Meanwhile, the 2 and type 3 isotherms correspond to partial wetting, and a basic difference between systems characterized by type 2 and type 3 isotherms is related to specific features of wetting, which characterize the three-phase equilibrium. In systems with type 2 isotherm a “sessile” liquid drop is in equilibrium with the “dry” substrate not covered with liquid molecules, whereas systems with type 3 (S-shaped)

disjoining pressure isotherm are characterized by the equilibrium between the drop and the substrate covered with the wetting/adsorption film of finite thickness. In addition, the integral in Eq. (1.2) for the systems with type 2 isotherm is always negative, which is why the contact angle differs from zero. The contact angle in the system depends on the ratio of the area under the disjoining pressure isotherm to the surface tension of the liquid. In systems with type 3 isotherm, complete wetting is possible if the integral in Eq. (1.2) is positive; otherwise, partial wetting occurs. Formally, large water contact angles on hydrophobic and superhydrophobic surfaces can be attained in systems that are characterized by both type 2 and type 3 isotherms. Here, the action of rather strong attractive (*e.g.*, structural) forces in the system is prerequisite. Eqs. (1.1) and (1.2) were derived for the equilibrium contact angles, but they can also be used to determine the quasi-equilibrium receding and advancing angles. Here, one should only take into account the thickness difference between the wetting films in Eq. (1.2) that are in quasi-equilibrium with the receding or advancing fronts of the liquid. Analysis of numerous experimental data on the determination of contact angles on smooth surfaces showed that the hydrophobic properties of the surface layer can be improved only slightly by varying the chemical composition of this layer.⁵

1.1.2 Wenzel Model and Cassie-Baxter Model

Since smooth homogeneous surfaces are rare in practice the applicability of Eqs. (1.1) and (1.2) for calculations of the contact angles on real surfaces is rather limited. The roughness of a surface is a major reason for the deviation of the measured contact angle from the contact angle on smooth surface. Rough surfaces are characterized by one of the two types of wetting (Wenzel state and Cassie-Baxter state). In homogeneous wetting,¹¹ the liquid contacts the whole surface of a solid and completely fills all the grooves (see Figure 1.3a). For homogeneous wetting the effective contact angle on a rough substrate is calculated using the Wenzel relation¹¹

$$\cos\theta_w = r\cos\theta_Y, \quad (1.3)$$

where r is the roughness factor. The latter is given by $r = A_r/A_p$ where A_r is the actual rough surface area, and A_p is the projected surface area on the average surface plane. Since $r > 1$ the absolute value of $\cos\theta_w$ is increased, indicating consistency in wettability so that the hydrophilic/hydrophobic surfaces would become more hydrophilic/hydrophobic with increasing surface roughness.

The effect of the surface heterogeneity of the surface on the measured contact angle can be included based on the relationship proposed by Cassie¹²

$$\cos\theta_c = \sum_i f_i \cos\theta_{iy}. \quad (1.4)$$

Eq. (1.4) can be used if the size of surface inhomogeneities is much smaller than the diameter of the contact area between the liquid drop and the substrate. From Eq. (1.4) it follows that contact angle on a smooth heterogeneous surface varies in an interval that is characteristic of each surface

type depending on the ratio of the surface areas of fragments of different chemical composition. As it is shown in Figure 1.3b, if a liquid drop is placed on a heterogeneous substrate with a smooth surface with deep pores, two types of equilibrium are possible. One of them occurs if pores are not filled with the liquid (pores in which the liquid contacts the air-vapor phase) while the other occurs when pores are filled with the liquid. Taking into account the fact that in the former case the contact angle on the surface of pores (liquid/air-vapor phase interface) is 180° , Eq. (1.4) for the smooth surface with unfilled pores is reduced to

$$\cos\theta_{CB} = f\cos\theta_y + (f - 1), \quad (1.5)$$

where f is the proportion of the surface area occupied by the matrix material, which was first derived by Cassie and Baxter.¹³

Figure 1.3 Schematics of the two models that describe the relationship between wettability and roughness: **a** Wenzel model, and **b** Cassie-Baxter model.

1.1.3 Hamaker Calculation of Van der Waals Interaction Potentials

The wetting behavior of a liquid on a solid substrate is determined by the difference between the cohesive interactions holding the liquid together and the adhesive interactions between the liquid and the solid. In principle, the equilibrium properties can thus be related to the molecular interaction potentials of the Lennard-Jones form with a short-range repulsion¹⁴

$$w(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]. \quad (1.6)$$

Although the algebraic $1/r^6$ tail of the Lennard-Jones form adequately describes the London dispersion energy between nonpolar molecules, the Debye energy between dipolar and nonpolar molecules, as well as the Keesom energy between freely rotating dipolar molecules, there are other forces (*e.g.*, hydrogen bonding, hydration forces, *etc.*) which are very short ranged and

which lead to exponentially decaying forces between interfaces rather than algebraic ones. Sharma *et. al.*¹⁵ have referred to these short- ranged forces as “polar” and to the Lifshitz–van der Waals forces (arising from $1/r^6$ potentials) as “apolar.” In a first step toward a systematic study of the interplay (or competition) between these short-ranged polar surface forces and the apolar ones, they adopted the simplifying assumption that the apolar spreading coefficient is simply proportional to the amplitude of the tail of the net apolar interaction between interfaces. Using the Young-Laplace and Navier-Stokes equations they related the stability properties of a thin adsorbed film to macroscopic parameters of wetting such as the contact angle.

One quantifies the net effect of the interaction potentials on the wetting behavior by considering a liquid film of thickness l on a solid substrate. If, for instance, the adhesive solid-liquid interactions are strong, the system can lower its free energy by increasing the distance between the two surfaces. This leads to a net repulsive force per unit area between the solid-liquid and liquid-vapor interfaces, which is called the disjoining pressure^{16,17} and can be measured experimentally. Theoretically, it can be derived from the so-called effective interface potential $V(l)$ through¹⁸

$$\Pi(l) = -dV(l)/dl, \quad (1.7)$$

where

$$\gamma_{sv}(l) = \gamma_{lv} + \gamma_{sl} + V(l) \quad (1.8)$$

is the excess free energy per unit area of the liquid film, where γ_{sv} , γ_{lv} , and γ_{sl} are the same items defined in Eq. (1.1), the and $V(\infty) \equiv 0$. Surface excess free energies are well defined thermodynamically and can be calculated using statistical mechanics¹⁸

If the disjoining pressure is known, the equilibrium wetting state can be predicted, but a calculation based on first principles is difficult. Starting from the Lennard-Jones potentials, density functional theory DFT in principle provides a means of calculating the equilibrium wetting state.¹⁹ DFT is based directly on microscopically specified molecular interactions. Within mean-field theory, one attempts to find the free energy of the system as a functional of the density profile $\rho(r)$ alone. This is, however, difficult owing to the slow decay of, *e.g.*, the Lennard-Jones potential, the Lennard-Jones potential $\rho(r)$. Thus, either some simplifications have to be made or the problem has to be solved numerically. Quantitative predictions based on numerical solutions of the full DFT that have been verified by experiment are so far limited to the wetting behavior of simple atoms or molecules (*e.g.*, He) on simple substrates (*e.g.*, Cs) at zero temperature.²⁰ Considering only the $1/r^6$ van der Waals attractive tail of $w(r)$, the disjoining pressure for large distances can be calculated explicitly. If in addition the spreading coefficient is known (for instance, from the phenomenological Cahn-Landau theory), the wetting behavior can be predicted.

The subtleties and strengths of an approach based on DFT are illustrated by derivations of an effective Hamiltonian for liquid-vapor interfaces.²¹ Taking into account only bulk fluctuations,

first an intrinsic density profile is obtained, and in the next step undulations of the inter- face position are described by a statistical theory for capillary waves on all length scales. The result is a non-local and non-Gaussian functional of the interface con- figuration. From this the usually postulated (local) Helfrich Hamiltonian can be deduced by a gradient expansion, which, however, features divergent coefficients for all but strictly finite-range interactions. If one expands, as is usually done, the Fourier transform of the Helfrich Hamiltonian in powers of the transverse momentum q , one obtains an approximate wavevector- dependent interfacial tension $\gamma(q)$. However, the Gaussian approximation to the nonlocal interface Hamiltonian derived by Mecke *et al.*²¹ leads to a form for $\gamma(q)$ that is qualitatively different in the long capillary wavelength limit and agrees better with experiments on liquids with intermolecular dispersion forces.²²

The van der Waals interaction potential W between two particles with atomic number density q was derived by Hamaker to be of the form²³

$$W = - \int dv_1 \int dv_2 \frac{q^2 \lambda}{r^6}, \quad (1.9)$$

where dv_1 , and dv_2 refer to volume elements of the two particles, respectively, and λ is the London-van der Waals constant. The van der Waals interaction $1/r^6$ includes all intermolecular dipole-dipole, dipole-induced dipole, and induced dipole-induced dipole interactions.

Using Eq. (1.9) by integrating the specific volume, the van der Waals interaction potential in some situations were also calculated by Hamaker, *i.e.*, the potential W_a between an atom and a spherical particle with atomic number density of q is given by²³

$$W_a = - \int_{R-R_0}^{R+R_0} \frac{\lambda q}{r^6} \pi \frac{r}{R} [R_0^2 - (R - r^2)] dr, \quad (1.10)$$

where R is the distance between the atom and the center of the particle, R_0 is the radius of the particle, and r is the distance between the atom and a specific atom in the particle. Furthermore, the van der Waals interaction potential W_a between two spherical particles with radii of R_1 and R_2 with atomic number density q is given by²³

$$W_a = -\pi^2 q^2 \frac{1}{6} \left[\frac{2R_1 R_2}{C^2 - (R_1 + R_2)^2} + \frac{2R_1 R_2}{C^2 - (R_1 - R_2)^2} + \ln \frac{C^2 - (R_1 + R_2)^2}{C^2 - (R_1 - R_2)^2} \right], \quad (1.11)$$

where C is the distance between the centers of the two particles.

1.1.4 Dynamics in Wetting

There are mainly two aspects in the wettability of a surface. One is the equilibrium state of liquids deposited on a solid or another liquid which is often characterized by static contact angle (SCA). The other is the dynamic problem which is often measured by the advancing and receding contact angles (ACA / RCA) and the contact angle hysteresis θ_H (CAH), which is defined as the difference between ACA (θ_A) and RCA (θ_R) with $\theta_H = \theta_A - \theta_R$.²⁴ CAH shows up when the

strength of the defect is above a certain threshold. Therefore, compared with SCA which shows a equilibrium state, CAH is more sensitive to the heterogeneity of the tested surfaces. For instance, the models based on the description of CAH tend to give better prediction to surfaces with rose petal-like wettability²⁵. On the other hand, CAH is an important parameter of wettability for evaluating the wetting property in practical applications, *e.g.*, a low CAH of lotus leaf-like surfaces usually implies superior self-clean ability. Therefore, wetting dynamics is an important aspect in study of the effect of roughness on wettability.

Wetting is a subject in which disorder plays an important role in practice, and even under idealized laboratory conditions, for both the static and dynamic aspects. On one hand, impurities may lead to frustration, so that the true equilibrium state is never reached. In this case a small droplet is often observed to rest on an inclined surface. On the other hand, the resulting roughness of the contact line leads to complicated dynamics, which is still poorly understood. The close connections to other dynamical problems involving many length scales, such as domain walls, imbibition fronts, or vortex lattices, have made this an extremely active field.

1.2 Wettability inspired by Nature

It has been widely accepted that the surface morphology plays an important role in surface wettability, and various types of roughness have been created to control the wettability. With the development of nanoscience and micro/nanotechnology, several micro/nanostructured surfaces were created to mimic surface structures occurring in nature. And the two most discussed candidates are the lotus leaf and the rose petal, where the effects named after themselves, as the lotus effect²⁶ and the rose petal effect.²⁷ With more diverse wettability in nature, more and more natural surfaces, *e.g.*, Gecko's feet,²⁸ fly eyes,²⁹ and rice leaf^{30–32} are inspiring researchers to create surfaces with certain wettability.

1.2.1 Lotus Effect

The lotus leaf has been extensively studied for its self-cleaning property, and the phenomenon that a surface shows high SCA (larger than 150° which is defined as the threshold of superhydrophobicity), and low CAH is defined as the lotus effect²⁶. With characterization of the microstructure of this self-clean surface (see Figure 1.4), a combination of a hierarchical micro/nanostructure and low surface-energy have been revealed as the fundamental mechanism of this phenomenon.^{33,34} Moreover, superhydrophobic and self-cleaning plant surfaces are always correlated with the presence of three-dimensional waxes, but both properties are optimized in surfaces of hierarchical surface structures with multiple-length-scale roughness. Water on such a surface forms a spherical droplet, and both the contact area and the adhesion to the surface are dramatically reduced.

Figure 1.4 SEM micrographs (shown at three magnifications) of the Lotus (*Nelumbo nucifera*) leaf surface, which consists of **a** The low-magnification SEM image of the microstructure formed by papillose epidermal cells covered with epicuticular wax tubules on surface. **b** The SEM image of a papilla. **c** The SEM image of the detailed morphology of a papilla.³⁵

Figure 1.5 SEM images of PMNCF prepared from a 7 wt % PS/DMF solution. **a** 3D network structure of PMNCF. **b** Surface nanostructure of a single porous microsphere. **c** Water droplet on PMNCF.³⁶

Using electrohydrodynamic techniques, Lei Jiang et. al.³⁶ created a stable superhydrophobic EHD film with two-hierarchy microstructure composed from porous microparticles and uniform fibers which realized superhydrophobicity with $CA=160.4^\circ$ (see Figure 1.5). Continuing mimicking the lotus leaf, surfaces with various materials as well as morphology were prepared for applications such as self-cleaning,^{37,38} anti-fogging,^{39,40} and anti-bacteria.⁴¹

1.2.2 Rose Petal Effect

Figure 1.6 **a, b** SEM images of the surface of a red rose petal, showing a periodic array of micropapillae and nanofolds on each papillae top. **c** Shape of the water drop on the surface of the rose petal indicating its superhydrophobicity with a contact angle of 152.4°. **d** Shape of the water drop on the surface of the rose petal when it is turned upside down.²⁷

Unlike the lotus leaf, some rose petals²⁷, scallions, and garlic exhibit superhydrophobicity with high CAH,^{27,42,43} inspiring applications in fields such as droplet transportation⁴⁴ and energy harvesting.⁴⁵ also water harvesting By imaging a rose petal using SEM, a periodic array of micropapillae with an average diameter of 16 μm and height of 7 μm with cuticular folds in the nanometer scale was revealed by Feng *et al.*²⁷ It is known that the hydrophobicity of a surface can be enhanced by being textured with different scale structures. In nature, the surface of the lotus leaf is famous for its self-cleaning property, which is induced by the roughness at two length scales amplifying the intrinsic hydrophobicity. Similar to this effect, the surface of the rose also exhibits superhydrophobicity with a contact angle of about 152.4° (see Figure 1.6c) owing to its surface micro- and nanostructures. However, the diverse design in the surface microstructures

and the different sizes of the lotus leaf and the red petal result in different dynamic wetting. That is, water droplets with the same volume can effortlessly roll off the surface of a lotus leaf, while they stay pinned to the surface of a red rose petal. Water droplets on the petal's surface maintain the sphere shape when the surface is facing up or even when it is turned upside down (see Figure 1.6d)

Though extensive experiments and characterization, Bhushan *et al.*⁴³ revealed that for a microstructure with a large pitch value and small peak-to-base height and a nanostructure with low density, the water could impregnate between the microstructures. However, it is still not completely wet into the nanostructure, resulting in high adhesion while maintaining high static contact angle. However, high density of the nanostructure even for a larger pitch value may prevent the transition from the Cassie-Baxter to Wenzel regime, and may lead to an increased propensity of air pocket formation between micro- and nanostructures with low adhesion (see Figure 1.7).

Figure 1.7 Schematic illustrations of droplets on the hierarchical structure with two nanostructures. As an example, the mass of n-hexatriacontane changes the density of the nanostructure. The latter play an important role in contact formation between water and the underlying substrate.⁴³

1.3 Effect of Roughness on Wettability

Learning from nature, the major strategy to control surface wettability is a combination of surface roughening with additional alteration of the surface chemistry. Although micro/nanoscale surface roughness can lead even to superhydrophobicity, the control of wettability via control of the nanostructure of surfaces is far from trivial. Although the two well-known models have enabled the explanation of the wettability of surfaces with various types of morphology, several other studies^{7,46,8,25,47} have demonstrated complex cases of surface wettability, where both the Wenzel and the Cassie-Baxter models could not explain the experimental data. Therefore, more efforts were devoted to understanding of the relationship between wettability and surface morphology. Using the concept “work of adhesion” introduced by Dupré,⁶ and taking the air-liquid interface on a solid as a one-dimensional system, Pease⁷ emphasized that the SCA is the result of an equilibrium position that the three-phase contact line (TPL) could reach. Then the dynamic wettability including advancing contact angle (ACA) and receding contact angle (RCA) were also expressed in terms of the work of adhesion.^{8,9} Wang et al.⁴⁸ argued that the 90° CA could not be used as the mathematical wetting threshold between the hydrophobicity and hydrophilicity in nanostructured surfaces through the results on nanofibrous membranes. Derjaguin^{4,49} discovered that a solid surface is pre-wetted by a wetting film when in contact with a liquid droplet and described the film with the concept of the disjoining pressure. Furthermore, Boinovich et al.⁵⁰ evaluated the wettability of curved surfaces on the basis of the isotherms of the disjoining pressure. In addition, more and more surfaces with various morphologies have been created with micro/nanotechnology, showing that the relationship between roughness and wettability might be more complex than the description of previous theoretical studies. Therefore, a combination of carefully designed surfaces and systematic theoretical models offers a way to evaluate the influence of surface morphology on wettability.

1.4 Wettability of Nanoparticle Decorated Surfaces

Considering that the description of the relationship between the roughness and wettability might be a challenging task, surfaces with simple micro/nanostructure would be ideal candidates for wetting research. With closely apparent spherical morphology, nanoparticles (NPs) provide an ideal option to create nanostructured surfaces for wetting research, *e.g.*, TiO₂ NP painting,⁵¹ or even more directly, *e.g.*, Cu NP deposition by a high-pressure magnetron sputtering system where the production and decoration process can be accomplished in one step.⁵² Moreover, the high-pressure magnetron sputtering can offer homogeneously distributed Cu NPs onto flat substrates without introducing additional chemical ligands,^{52,53} which makes it an ideal candidate to provide nanostructured decoration for wetting research. Through the high-pressure magnetron sputtering method,⁵³ ten Brink et al.⁵² deposited Cu NPs on different substrates with various NP coverages, revealing that the extent of roughness increases with the rise of NP coverage before

the NP coverage goes extremely high, resulting in higher SCA with stronger pinning force between the NPs and the testing liquid. Subsequently, $\text{Ge}_2\text{Sb}_2\text{Te}_5$ (GST) NPs were used for nanostructured decoration, indicating that the crystal structure of the decorating NPs could affect the wettability of the surface by changing the surface energy.

1.5 Effect of Airborne Hydrocarbons on Wettability

Airborne hydrocarbon contaminants, *e.g.*, alkanes, alkenes, aromatics, and alcohols can be easily adsorbed by various types of surfaces including *e.g.*, gold,⁵⁴ graphene,⁵⁵ TiO_2 ,⁵⁶ boron nitride nanotube decorated surfaces⁵⁷ and Ni-Cu-P ternary coating.⁵⁸ By comparison of the results of wetting measurement and Fourier transformed infrared (FTIR) spectroscopy of surfaces before and after ultraviolet-Ozone (UV- O_3) treatments, which is an effective method for removing surface organic contaminants,⁵⁹ Li et al⁵⁵ proved that the wettability variation of graphene was the result of adsorption/removal of airborne hydrocarbons. They attributed the effect of airborne hydrocarbons on the graphene wettability to be the result of reduced surface energy. Although the FTIR results could provide direct evidence of the adsorption-removal of airborne hydrocarbon contaminants, the distribution as well as the morphology of these surface contaminants, which is very important to reveal their effect on surface wettability, is still unclear. Therefore, more detailed characterization is necessary to evaluate the specific effect of airborne hydrocarbons on the enhancement of hydrophobicity of various surfaces, especially for micro/nano-structured surfaces.

1.6 Motivation

It has been widely accepted that the surface morphology plays an important role on surface wettability, and various types of roughness have been created to control the wettability. With the development of nanoscience and micro/nanotechnology, several micro/nanostructured surfaces were created to mimic surface structures in nature, *e.g.*, lotus leaf and rose petal to obtain certain wettability. However, many of the previous works paid more attention to practical applications, and ended up to obtain surfaces with the demanded wettability without studying the theories behind the observed wetting phenomena. Aiming to explore the relationship between nanoscale roughness and wettability, we chose NPs as the nanostructured decoration for the following reasons: i) with spherical morphology, NPs are easy for geometry-related calculations and analyses, which would finally simplify the theory obtained according to the experimental data, ii) the technique (high-pressure magnetron sputtering) for depositing NPs on substrate is available without introducing additional chemical contaminants, which is convenient for the control of surface energy of the decoration. Additionally, we chose GST ($\text{Ge}_2\text{Sb}_2\text{Te}_5$) NPs as one of the material candidates because this phase-change material could change its surface energy by

altering between the amorphous phase and crystalline phase, which could offer more information in further research.

During the research, we found that the adsorbed airborne hydrocarbons play an important role in surface wettability, tending to make the surfaces more hydrophobic. In previous studies, the reason for this effect was attributed to the fact that the airborne hydrocarbons could lower the surface energy. However, the answer appears to be not so simple after our extensive study of the wettability of GST nanoparticle (NP) decorated surfaces. Therefore, we conducted a detailed study of the wettability of surfaces nanostructured with amorphous and crystalline nanoparticles derived from the phase-change material $\text{Ge}_2\text{Sb}_2\text{Te}_5$, where particular attention was devoted to the effect of airborne surface hydrocarbons on surface wetting. Inclined to visualize the airborne hydrocarbons adsorbed by the surface, we used high angle annular dark field (HAADF) scanning transmission electron microscopy (STEM) to observe specially designed GST NP decorated graphene substrates.

With further analysis of our experimental data derived from the GST NP decorated surfaces, we realized that the most widely-used models (Wenzel model and Cassie-Baxter model) could not offer proper explanations of the wettability and the nanostructured roughness we created. Therefore, we combined technologies from both nanoscience and polymer chemistry to design a series of poly(methyl methacrylate) (PMMA) surfaces decorated by Cu NPs with gradually varied morphology by the application of high-pressure CO_2 assisted NP engulfment. The morphology of the nanostructured surfaces was carefully characterized by taking advantage of the superior lateral resolution of transmission electron microscopy (TEM) and the vertical resolution of atomic force microscopy (AFM). The TEM and AFM results not only were cross-checked by each other to gain precision of the NP characterization, but also together allowed to create an accurate 3-dimensional view of the surface morphology. As a result, the apparent height of the decorating NPs was accurately controlled through the different extent of the NP engulfment into PMMA by varying the time spans of the high-pressure treatment, which is important for controlled wetting studies.

Furthermore, a near-linear relationship between the surface wettability and the apparent height of the decorating Cu NPs was measured (for both the static contact angle and the dynamic contact angle hysteresis), and a detailed theoretical model was developed to bridge the gradually varied surface wettability and morphology since the observed tendency contradicts both the Wenzel and the Cassie-Baxter models. In fact, as it is shown the capillary pressure from the nanomeniscus formed between the NPs and the substrate is negative and results in the increase of the contact angle with the apparent height of the Cu NPs decorating the PMMA surface. Furthermore, the van der Waals interaction calculations indicated that the local adhesion force between the NPs and the testing droplet might contribute significantly to the wetting behavior of the NP decorated surfaces.

1.7 Thesis Outline

After this introductory Chapter 1, in Chapter 2, the general methods applied throughout the thesis are presented with focus on: (1) the NPs deposition (GST NPs and Cu NPs) on various substrates, (2) the contact angle measurements involving static and dynamic aspects, (3) the fabrication of amorphous as well as crystalline GST films, (4) TEM characterization of NPs and airborne hydrocarbons adsorbed by GST NPs/graphene samples, (5) the process of preparing the GST NPs/graphene, (6) AFM characterization of NPs on different substrates, (7) NPs engulfment into polymer films assisted by high-pressure CO₂.

Chapter 3 focuses on the effect of airborne surface hydrocarbons on surface wetting. A reversible hydrophilic-hydrophobic wettability switch is revealed by combined ultraviolet-Ozone (UV-O₃) treatments and exposure to hydrocarbon atmospheres. Indeed, the as-prepared surfaces exhibited a hydrophilic state after thermal annealing or UV-O₃ treatment which can partially remove hydrocarbon contaminants, while a hydrophobic state was realized after exposure to hydrocarbon atmosphere. Especially, GST NPs/graphene samples were designed for visualizing airborne hydrocarbons on NP decorated surfaces by using high angle annular dark field (HAADF) scanning transmission electron microscopy (STEM) characterization. As a result, a network of hydrocarbon connecting GST NPs was observed, which could significantly enhance the hydrophobicity of nanostructured surfaces.

Chapter 4 presents a detailed study of a series of poly(methyl methacrylate) (PMMA) surfaces decorated by Cu nanoparticles (NP) with gradually varied morphology, which were prepared by high-pressure CO₂ treatment at various time spans. Combining the characterizations of transmission electron microscopy (TEM) and atomic force microscopy (AFM), an accurate 3-dimensional view of the morphology of the surfaces was presented. Subsequently, the wettability of the surfaces decreases near-linearly with the increase of apparent height of the decorating NPs in both static (static contact angle) and dynamic (contact angle hysteresis) aspects. As a result, the static as well as dynamic wettability of the NPs/PMMA surfaces also gradually varied with the gradual variation of the apparent height (H_N) of the Cu NPs on the PMMA surface. Our experiment demonstrates the important influence of the nanomeniscus on the wettability, which is usually not taken into account. The results in this work provide a comprehensive understanding of how nanostructure affects the wettability of the decorated surfaces and shed light on how to obtain certain wettability through nanostructuring of the surface morphology.

Chapter 5 presents two theoretical studies (a model focused on disjoining pressure and a van der Waals interaction calculation evaluating the adhesion between NPs and the testing droplet) for analyzing the experimental data of the Cu NP decorated PMMA surfaces with NP engulfment obtained in Chapter 4. In detail, a model evaluating the wetting contribution of the nanomeniscus formed between an NP and the substrate were built. The capillary pressure from this meniscus is negative and results in the increase of the contact angle with the apparent height (H_N) of the Cu NPs decorating the PMMA surface. In the meantime, the van der Waals interaction potential

calculations showing a coherent linearity in the relationships of wettability- H_N (SCA- H_N and CAH- H_N) and Φ_{CuN} - H_N indicated that the pinning effect, originating from the vdW interaction between water and the decorating NPs, might lead to the hydrophobic behavior of the surfaces composed by hydrophilic materials. The theoretical analysis provides a comprehensive understanding of how nanostructure affects the wettability of the decorated surfaces, and sheds light on how to obtain certain wettability through nanostructuring of the surface morphology.

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Chapter 2

Experimental Methods

Abstract

This chapter describes mainly the methods applied to prepare the samples and characterize their wettability and morphology. Its structure is as follows:, (1) Deposition of Nanoparticles (NPs) including both GST (amorphous/crystalline) and Cu NPs on separate substrates, (2) Contact angle measurements including static and dynamic aspects, (3) Characterization including both transmission electron microscopy (TEM) as well as atomic force microscopy (AFM), (4) Fabrication of GST (amorphous/crystalline) thin films, (5) Preparation of GST NPs/graphene sample, (6) Drop casting method to make poly(methyl methacrylate) (PMMA) films, and (7) High-pressure CO₂ treatment to induce NP engulfment into PMMA films.

2.1 Nanoparticle Deposition

2.1.1 GST Nanoparticle Deposition

$\text{Ge}_2\text{Sb}_2\text{Te}_5$ (GST) nanoparticles (NPs) were produced by magnetron sputtering with inert gas condensation in a home-modified nanoparticle system NanoGen from Mantis Deposition Ltd. The setup is shown in Figure 2.1. This system consists of two chambers, *i.e.*, the main chamber (indicated by the left dashed square in Figure 2.1a), and the aggregation chamber (marked by the right dashed rectangle in Figure 2.1a). The main chamber is used to collect the produced NPs. The mechanically polished Cu (purity: 99.99%) blocks (area: $1\text{ cm} \times 1\text{ cm}$) having a native surface oxide layer together with a TEM grid (which is used for later characterization for NP coverage) with continuous carbon supporting film was put into the main chamber. Two Leybold turbo molecular pumps with a capacity of 300 lt/s are present to evacuate the two chambers, and they are both backed by one scroll pump (Varian LTH10). The vacuum can reach 1×10^{-8} mbar in the main chamber and 1×10^{-6} mbar in the aggregation chamber. The settings and vacuum are controlled and monitored by the Mantis controller, as shown in Figure 2.1b. The aggregation chamber is the core of the system, which is schematically illustrated in Figure 2.1c. It consists of several parts: (1) a water cooled magnetron head, (2) a double gas inlet system controlled by 2 MKS mass flow meters, (3) pressure readings inside the aggregation chamber and the main chamber and (4) water cooling for both the magnetron head and aggregation chamber wall. A target (2 inches in diameter and with tunable thickness) is placed on top of the magnet head. On top of the target a cylindrical anode is mounted, connected to a TDK-Lambda Genesys Gen 600-1.3 programmable DC power supply with a range up to 600 V and 1.3 A. During deposition the power can be controlled by a build-in voltage and current limiter. Inert gas is used as sputtering gas to minimize the possible interference with the target materials. The gas has three functions throughout the sputtering process: first sputtering, then cooling of the target material vapor, and then finally transporting the formed NPs.

The mechanism of magnetron sputtering can be summarized as follows. When a deposition starts, a noble gas (usually Ar in this thesis) is flown into the aggregation zone. Due to the applied potential between the target and the anode, the inert gas is ionized above the magnetron head to create a plasma. Then the positive ions in the plasma (Ar^+) are accelerated by the DC potential and impacts on the target, thereby breaking off particles which together compose the desired target material vapor. The magnetron under the target can increase the efficiency of the sputtering process by making the ions travel in a helical path through the plasma, leading to the longer effective path therefore higher chance of colliding with the target. The vapor of the target material is then swept to the aggregation volume that is just above the plasma. The relatively high pressure caused by the inert gas and the cooling limit the vapors mean free path, resulting in the supersaturation in which nucleation and growing of the cluster can take place. After their growth the NPs are swept to the main chamber through the small nozzle because of the much higher pressure in the aggregation chamber in comparison to the main chamber. Hydrogen or methane

was used to facilitate the formation of nascent clusters during the deposition process.¹ Note that the amount of hydrogen or methane used, supplied using a needle valve, could only be specified qualitatively, because a gauge measuring the gas flow precisely was lacking. The NPs land on the substrates located in the sample holder in the main chamber. The deposition rate can be monitored by a home-built quartz crystal microbalance (QCM) placed slightly off-center of the conical NPs beam.

There are some parameters that can affect the size and crystallinity of the as-deposited NPs. (1) The length of the aggregation volume can influence the size of the NPs. A longer length provides a longer time and length for the NPs to grow. (2) The addition of He gas (to the Ar) tends to decrease the size of the NPs. Due to the higher thermal conductivity of He compared to Ar, He can cool down the supersaturated vapor faster leading to reduced NPs growth. (3) The discharge current can influence the phase of the as-deposited phase-change NPs. High discharge current (0.3–0.35 A) results in crystalline GST NPs while amorphous GST NPs are produced at low current. (4) A backing plate (usually copper) underneath the target reduces the size of the NPs significantly. The thicker the backing plate is, the smaller the NPs become. Adjusting the above parameters, we have been able to tune the size and crystallinity of the as-deposited phase-change NPs. Additionally, more details about the deposition and properties of GST NPs are seen in our previous work.¹

2.1.2 Cu Nanoparticle Deposition

The system and mechanism applied for Cu NP deposition is almost identical to the case of GST NPs discussed in previous Sec. 2.2.1. After system bake out to achieve $\sim 5 \times 10^{-9}$ mbar base pressure, a small amount of methane or hydrogen gas was introduced, by means of a high precision UHV-leak valve, in the aggregation chamber up to a pressure of $\sim 2 \times 10^{-5}$ mbar or less. Direct measurement of the methane or hydrogen partial pressure during sputtering was not possible because the magnetron is operated at a higher Ar pressure for sputtering (~ 0.5 mbar). The NP production took place within the normal operating window (e.g., 20–40 sccm argon which equals 0.30–0.50 mbar; depending also on the size of the aperture used. More details about Cu NP deposition can be seen in our previous works.^{2,3}

The main difference exists in the discharge current and the substrate used. The current used for the Cu NP deposition is around 0.2 A, and the substrates used were poly(methyl methacrylate) (PMMA)/silica. The latter were prepared as follows: PMMA films were prepared by drop casting a PMMA-chloroform solution (0.1 g/mL) onto silica wafers (1 cm $\times$ 1 cm). Afterward, the substrates were dried in air for 24 h and then annealed at 135 °C for 12 h, and slowly cooled down to room temperature within a furnace. Additionally, the thickness of PMMA films on the silica using the same method was measured by Liu *et al.*⁴ to be around 50 μ m, indicating that the PMMA

films were thick enough for our work because this thickness is much larger than the diameter of the deposited Cu NPs.

Figure 2.1 The high pressure magnetron sputtering system. **a** The cluster source for producing nanoparticles. **b** The corresponding controller. **c** The schematic of the aggregation chamber.

2.2 GST Thin Film Fabrication

Amorphous and crystalline GST films were deposited on flat silicon with native oxide layer using Pulsed Laser Deposition (PLD) under room temperature and 200 °C, separately. A sintered GST225 powder target from KTECH with 99.999% purity was used and the background pressure was below 10^{-7} mBar. The target was ablated using a KrF excimer laser (248 nm), with a fluence of 1.0 Jcm^{-2} and a spot size of 1.3 mm^2 . The deposition was performed at room temperature, in 0.12 mBar argon gas with a 1 sccm flow, and a target-substrate distance of 4 cm. The resulting GST films are flat and homogeneous (see Figure 3.8 in the later Chapter 3). The thicknesses of both films are more than 40 nm, which is larger than the cutoff distance of van der Waals interaction between water and the GST surfaces, as well as thick enough for evaluation of the wettability of GST flat surfaces.

2.3 Contact Angle Measurements

The (contact angle) CA measurements were performed using a Dataphysics OCA25 system. As it is shown in Figure 2.2, a syringe (not shown in the figure) is put into the syringe holder, which is connected to a pump controlled by the software installed in the PC of the Dataphysics system, allowing control of the volume of the droplet onto the sample surface (usually for static CA measurement) and the speed of the injecting/withdrawing process (usually for dynamic CA measurement).

The method used in this work is called static sessile drop method which involves placing a small liquid droplet on a tested surface. The CA can be determined by measuring the angle between the tangent of the droplet surface at the contact line and the surface. In this method, the droplet size should be small enough to eliminate the influence of the droplet's weight. In the static sessile drop measurements in this work, a 2 μL -droplet of pure water (MilliQ) is put on the sample, where a camera recorded the pictures over several seconds. The values of the CA were obtained *via* a fit using the Young-Laplace (YL) equation based on the shape analysis of a complete drop, and also compared to the results obtained from the geometrical CA analysis. For every sample, the CA measurements were repeated for several drops on different sample areas.

Figure 2.2 Dataphysics OCA25 system connected with a computer with relative software installed for controlling the injecting/withdrawing testing liquids and recording the experimental results (images/videos) of contact angle measurements.

For dynamic contact angle measurement, there are mainly two methods to define the advancing contact angle (ACA) and receding contact angle (RCA): one is called dynamic sessile drop method, and the other is called the tilting stage method. The dynamic sessile drop method is very similar to the static sessile method. A small drop of water is carefully added on top of the polymer surface by a syringe with a very thin needle. The needle is kept inside the water droplet after the droplet is settled. A computer program controls the syringe to add a very small quantity of water to the existing droplet to gradually expand the size of the droplet while the contact area between water and polymer is kept the same. Just when this contact area starts to expand, the CA is recorded. The CA obtained during this process is the ACA since water tends to advance to wet the surface (Figure 2.3a). After the ACA is recorded, the reverse process is carried out to slowly decrease the size of droplet by withdrawing water from the droplet. Such process will generate the RCA, which is obtained right when the contact area shrinks (Figure 2.3b). The tilting stage method does not involve addition and subtraction of water. Instead, water droplet is added on a

tilting stage. The stage is tilted by an automated program and water drop will deform into an asymmetric shape (Figure 2.3c). While the stage is tilting, the image of water drop is captured by software right before it rolls down of the tested surface. Both ACA and RCA are measured at this point (Figure 2.3c).

Figure 2.3 Schematic demonstration of the methods for measuring the dynamic contact angles. **a** Measurement for ACA using the dynamic sessile drop method. **b** Measurement for RCA using the dynamic sessile drop method. **c** Tilting stage method for obtaining ACA and RCA.⁵

In this work, the dynamic contact angles were measured using the dynamic sessile drop method. The injecting/withdrawing speeds for advancing/receding contact angle measurements were 0.2 $\mu\text{L/s}$ allowing the movement of the TPL steadily and smoothly. The drop shape was analyzed based on the form of an ideal sessile drop, for which the surface curvature results only from the force equilibrium between the surface tension and the weight of the liquid drop. Similarly to the static sessile drop method, the values of the ACAs and RCAs were obtained *via* a fit using the Young-Laplace (YL) equation that is based on the shape analysis of a complete drop, and compared also to the results obtained from the geometrical CA analysis. In some special cases, *i.e.*, when the RCA is too low to be obtained by the YL equation because the outline of the meniscus is no longer a partial ellipse, then we would define the outline of the meniscus as a triangle and measure it directly. This situation is discussed in detail in Figure 3.3d of Chapter 3. For every sample, the CA measurements were repeated for several drops on different areas of the sample surface.

2.4 Transmission Electron Microscopy

Figure 2.4 Schematics of the signals generated when a high-energy electron beam interacts with a thin specimen and the detectors equipped in a Transmission Electron Microscope (TEM) to collect relevant signals in scanning transmission electron microscopy (STEM) mode. **a** The signals generated when a high-energy electron beam interacts with a thin specimen directions shown for each signal do not always present the physical direction of the signal, but indicate, in a relative manner, where the signal is strongest or where it is detected. **b** The various electron detectors in a STEM. Scintillator-PM detectors are invariably used for SE detection and semiconductor detectors for the BSE. The on-axis and annular forward-scattered and high-angle dark field detectors may be either type, depending on the microscope. The SE detector is rare, the BSE detector is a waste of time: only the forward-scattered electron detectors are standard.⁶

In a TEM, the incident electron beam is transmitted through an ultrathin specimen, and various signals can be generated from the interactions between the highly energetic electron beam with the ultrathin specimen, as shown in Figure 2.4a, among which the elastically scattered electrons are basically responsible for the possibility to perform TEM imaging. The formation of elastically scattered electrons can be attributed to the interaction between the incident electron beam with the nuclei of the atoms in the sample. The scattering results in a relatively large deviation in the path of the electrons. Nevertheless, the velocity (v) and wavelength (λ) exhibit no variation with little or no energy loss. The elastic scattering for non-crystalline materials depends principally on the mass-thickness of the sample, with more electrons scattered for samples with large mass-thickness. For crystalline materials, the scattering mainly results from Bragg diffraction, depending on the crystal structure and the relative orientation with respect to the incident beam.

These elastically scattered electrons are focused by electromagnetic lenses to form images in the electron microscope. Interactions of the beam with orbital electrons generate inelastically scattered electrons, with a slight deviation in the path ($< 10^{-4}$ radians), which are characterized by a loss of energy. The inelastic scattering of the electrons is generally accompanied by specimen damage. However, for TEM samples (usually with a thickness smaller than 100 nm), a most of the highly accelerated electrons transmit through the specimen, accordingly, inelastically scattered ones would be a minor fraction. Image formation in the scanning mode is fundamentally different from static-beam TEM image formation. The scan beam over the specimen is adjusted by the scan coils, these same coils are used to scan the computer display synchronously. The electron detectors shown in Figure 2.4b act as the interfaces between the electrons coming from the specimen and the image viewed on the display screen.⁶

In the traditional TEM mode, the first two condenser lenses (C1, C2) are adjusted to illuminate the specimen with a parallel beam of electrons, typically several micrometers across at reasonable magnifications (20,000 $\times$ -100,000 $\times$). As shown in Figure 2.5a, the C1 lens first forms an image of the gun crossover. In the case of a thermionic source, the size of the original crossover may be several tens of micrometers, and this crossover is de-magnified by an order of magnitude or more. The most direct way to produce a parallel beam is shown in Figure 2.5a in which the C2 lens is weakened to produce an under-focused image of the C1 crossover. In its out-of-focus condition, a lens is over-focused if it is strong and the crossover occurs before the image plane and under-focused if the lens is weak and the crossover occurs after the image plane. While under-focus gives a more parallel beam at the specimen than over-focus.

In STEM mode, the objective-lens optics are a bit more complex than in TEM because the beam must scan parallel to the optic axis at all times so that it mimics the parallel beam in a TEM even though it is scanning. (unlike in an SEM where the scanning beam simply pivots about a point above the specimen). If the incident direction varies, then the electron scattering (particularly the diffraction) processes would change as the beam intercepts the specimen at different angles. Therefore, the image contrast would be rather difficult to be interpreted. As shown in Figure 2.5b, two pairs of scan coils are used to pivot the beam about the front focal plane (FFP) of the upper objective (C3) polepiece to achieve parallel incidence. Subsequently, the C3 lens ensures that all electrons emerging from the pivot point are brought parallel to the optic axis. Subsequently, an image of the C1 lens crossover is formed in the specimen plane. If the objective lens is symmetrical, and the lower objective polepiece is similarly strong, then a stationary diffraction pattern is formed in the back focus plane (this pattern does not move, even though the beam is scanning, since it is conjugate with the FFP). When the beam stops scanning, then a convergent-beam electron diffraction pattern in the back focal plane, which can be projected onto the TEM computer screen.

Figure 2.5 Schematics of the electron beams on a specimen in TEM mode and STEM mode. **a** The electron beam on a specimen in TEM mode, using the C1 and C2 lenses to image the source at the front focal plane of the condenser-objective lens, thus creating a parallel beam at the specimen plane. Therefore, the upper objective is sometimes termed the C3 lens. **b** Scanning the convergent probe for STEM image formation using two pairs of scan coils between the C2 lens (usually switched off) and the upper-objective polepiece. The double-deflection process ensures that the probe remains parallel to the optic axis as it scans across the specimen surface.⁶

In this work, the morphology of the as-deposited NPs was characterized using a JEOL 2010 at 200 kV within 1 hour after sample deposition. The energy dispersive spectroscopy elemental maps and high-resolution STEM images were recorded using a JEOL (Accel) ARM 200F (UHR pole piece) equipped with a single 100 mm² (0.65 srad) EDX detector and FEI Themis Z equipped with SuperX EDX detectors (four 30 mm² detectors providing 0.7 srad). High acceleration voltage (200 kV) was utilized to record overview bright-field TEM images of the GST NPs, while low acceleration voltages (40 and 60 kV) were used to record STEM images when graphene is involved since high voltage (above 80 kV) can easily induce knock-on damage to the monolayer graphene due to the collision of the beam electrons with the nucleus of the graphene target atom.

2.5 GST NPs on Graphene

Figure 2.6 Schematic of the process of the preparation of the GST NPs/graphene samples.

The main process for the preparation of the sample is schematically shown in Figure 2.6. The 25 μm -thick copper foil (Alfa Aesar, 99.8% purity) was cleaned by soaking in acetic acid for 8 hours, rinsed by water and then put into a quartz tube for graphene growth. The quartz tube was filled with 0.1 mbar hydrogen (Messer, purity 5.0) to eliminate the residual copper oxide on the copper surface. Meanwhile, it was heated up to 1035 $^{\circ}\text{C}$. Afterward, 0.2 mbar mixture of argon and methane (5%) was added into the quartz tube at 1035 $^{\circ}\text{C}$ for 2 hours. Thereafter, the copper foil was cooled down to room temperature with all the gasses remaining. Then the graphene was transferred onto Quantifoil R2/1 holey carbon (Electron Microscopy Sciences, Q225-AR1) TEM grids. Firstly, the TEM grids were placed on top of graphene on copper. Two drops of isopropanol (IPA) were deposited on the sample to enhance the bonding between graphene and the carbon membrane of the quantifoil TEM grids after the IPA evaporated. The sample was then annealed at 100 $^{\circ}\text{C}$ for 10 minutes to finally strengthen the contact between graphene and the TEM grids before the copper was etched away in $(\text{NH}_4)_2\text{S}_2\text{O}_8$ 0.1 g/ml for 24 hours. The TEM grids covered

with graphene were eventually rinsed three times in demi-water to eliminate any remaining trace of the etchant. Then the graphene covered TEM grids were placed as substrate and received the GST NPs deposition. The setting for this deposition process is the same as the Cu/GST NPs samples. Therefore, GST NPs were distributed alternatively on graphene and graphene/carbon areas. More details can be seen in our previous work.⁷

2.6 Atomic Force Microscopy

Figure 2.7 Schematics of tapping mode of the MM-SPM. **a** Tapping cantilever in free air. **b** Tapping cantilever on the sample surface.

The MultiMode Atomic Force microscope used in this work (MM-AFM, Bruker Multimode 8) is designed for imaging small (approx. 1.5 cm dia.) samples using a series of interchangeable scanners, and is able to provide images from the atomic scale to 175 μm in size. The MM-AFM is designed around a stationary probe. That is, samples are scanned back and forth beneath the

probe. Typically, the samples are fixed to round 1.5 cm metal (usually made of steel) disks (“pucks”), then they are magnetically attached to the top of the scanner tube. As the scanner moves back and forth, the sample moves with it allowing the probe to extract information from the sample surface much like a phonograph needle plays a vinyl record. The MultiMode can scan up to 200 μm laterally (in X and Y) and 10 μm vertically (Z axis). Therefore, the nanoparticle decorated surfaces in this work are measurable by the MM-AFM.

The tapping mode of the MM-AFM is schematically presented in Figure 2.7, which is the method used for characterizing the topography of the samples in this work. Figure 2.7a shows a cantilever oscillating in free air at its resonant frequency. A piezo stack excites the cantilever substrate vertically, causing the tip to bounce up and down. As the cantilever bounces vertically, the reflected laser beam is deflected in a regular pattern over a photodiode array, generating a sinusoidal electronic signal. The signal is converted to a root mean square (RMS) amplitude value, which is important to describe the extent of surface roughness and displayed in volts on the topmost (TappingMode Output Signal) meter located on the front of the MultiMode base. The situation where the same tapping cantilever is moving on a sample surface is shown in Figure 2.7b. Although the piezo stack continues to excite the cantilever’s substrate with the same energy, the tip is deflected as it encounters the sample surface. The reflected laser beam (return signal) reveals information about the vertical height of the sample surface and some characteristics of the sample material itself. These material characteristics may include elasticity (hardness), magnetic and/or electric forces present.

The present process creates a tip which has symmetry from side to side with a 17° half cone angle (refer to top of Figure 2.8). Front-to-back, along the length of the lever, the tip is asymmetric (refer to Figure 2.8). Another factor affecting the interaction of the tip shape with the surface is the substrate mounting angle. Along the front edge of the tip, the half angle is nominally 25° , and at the back edge of the tip the half angle is approximately 10° (see Figure 2.8), with both of these numbers not accounting for the tilt of the substrate. With the mounting angle of the substrate taken into account, the front is 35° and the back is zero degrees. From the tip side, the cross-section of the tip near the lever is approximated by an inverted “kite” shape. All of these subtleties arise from the etching process used to make the tip, which employs caustic solutions to perform wet anisotropic etching of the silicon. The best orientation of the sample to measure sidewall angles, uses the back edge of the tip (that which faces back towards the cantilever substrate) to measure step angles (refer to bottom of Figure 2.8). Using the back edge, step angles approaching 80 degrees can be measured routinely, depending on the step height. This method does not work well in small openings of less than 5 μm where, depending on the depth of the step, other edges of the tip could contact the other faces of the small opening. Wall angle measurements are best measured in open areas for these reasons. Measurements of line pitch are often best measured using the side-to-side faces of the tip, which exhibits symmetry. Because of the approximate 17° half angle of the tip, the line or space measurement is best done at the top of the line for simplification of the measurement artifacts (see the left of Figure 2.8). Because of the morphology

of the tip and the scanning mode trace of the tip on the surface, there would be some “blind” areas (marked with blue dashed circles in Figure 2.8) of the tested surfaces that the tip could not reach, and the relative details of the samples would be missed. However, the vertical measurement of this mode is ideal because the tiny top end of the tip could reach the deepest part of the sample easily. Therefore, the vertical resolution of the tapping mode measurement is much better than the lateral one, and this tip-morphology caused difference between the lateral resolution and vertical resolution of the AFM measurement is termed as the tip effect.

Figure 2.8 The profile of the tip used in the MM-AFM and the description of the origin of the tip effect.

The AFM images were obtained by the Bruker Multimode 8 AFM using the tapping mode with a silicon cantilever (HQ: NSC15/No Al) having a resonance frequency of 325 kHz and a spring constant of 40 N/m. Moreover, the apparent heights of individual NPs were analyzed based on the obtained AFM images. The method for deriving the apparent height of an individual isolated NP is shown in Figure 2.9. A typical AFM measurement of an individual NP is shown in Figure 2.9, where a hill-like profile was obtained as it is shown in Figure 2.9b. The distance (red dashed

line in Figure 2.9b) between the foot (blue dashed line in Figure 2.9b) and the peak (green dashed line in Figure 2.9b) of the “hill” was defined as the apparent height of the measured NP. In fact, the measured apparent height of the NP is 15 nm. Additionally, the apparent diameter was defined as the distance (blue dashed line in Figure 2.9b) between the two feet (two blue bars in Figure 2.9b) of the “hill”. As a result, the diameter of the NP was measured to be 45 nm. Comparing with the average diameter measured by TEM (~ 13.2 nm shown in Chapter 4), it becomes clear that the lateral resolution of the AFM image is not as good as the vertical resolution, reconfirming the tip effect as we discussed earlier.

Figure 2.9 Atomic force microscopy (AFM) topography measurements to obtain the apparent height of an individual isolated NP. **a** AFM image of a Cu NPs/PMMA sample without high-pressure CO₂ treatment to induce the NPs to sink into the substrate (the same image is shown in Figure 4.4a.) **b** The height profile extracted from a line scan (shown in the dashed circular area in Figure 2.9a) through the center of an isolated NP.

2.7 High-Pressure CO₂ Assisted NP Engulfment

PMMA films were prepared by drop casting a PMMA-chloroform solution (0.1 g/mL) onto silica wafers (1 cm $\times$ 1 cm). The PMMA we used is a commercial product labeled with “Diakon LG156”, and we suppose this PMMA is replaceable by the PMMA with other brands or molecular weights. Afterwards, the substrates were dried in air for 24 h and then annealed at 135 °C for 12 h, and slowly cooled down to room temperature within the furnace. Additionally, the thickness of PMMA films on the silica using the same method was measured by Liu *et al.*⁸ to be around 50 μ m, indicating that the PMMA films were thick enough for this work because this thickness is much larger than the diameter of the deposited Cu NPs. Then the Cu NPs/PMMA samples (shown in Figure 2.10c) were placed inside a high-pressure vessel (see Figure 2.10a). The setup

temperature was 40 °C, and the pressure of CO₂ was 58 bar, which it was generated by the high-pressure CO₂ supplying system shown in Figure 2.10b. Moreover, the time span for the CO₂ treatment was controlled to generate samples with various morphologies. After each CO₂ treatment, the valve connecting the high-pressure vessel and the open air would be slowly opened releasing the CO₂ into the open air.

Figure 2.10 The system used for high-pressure CO₂ treatment. **a** The high-pressure vessel including the pressure controller and the heater for treating the samples while high-pressure CO₂ treatment. **b** The system to supply high-pressure CO₂. **c** Schematic of the Cu NPs/PMMA sample.

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Chapter 3

Effect of Airborne Hydrocarbons on the Wettability of Phase Change Nanoparticle Decorated Surfaces

Abstract

We present here a detailed study of the wettability of surfaces nanostructured with amorphous and crystalline nanoparticles (NPs) derived from the phase-change material $\text{Ge}_2\text{Sb}_2\text{Te}_5$ (GST). Particular attention was devoted to the effect of airborne surface hydrocarbons on surface wetting. Our analysis illustrates that a reversible hydrophilic-hydrophobic wettability switch is revealed by combined ultraviolet-Ozone (UV- O_3) treatments and exposure to hydrocarbon atmospheres. Indeed, the as-prepared surfaces exhibited a hydrophilic state after thermal annealing or UV- O_3 treatment which can partially remove hydrocarbon contaminants, while a hydrophobic state was realized after exposure to hydrocarbon atmosphere. Using high angle annular dark field (HAADF) scanning transmission electron microscopy (STEM) for the specially designed GST NP decorated graphene substrates, a network of hydrocarbon connecting GST NPs was observed. Our findings indicate that airborne hydrocarbons can significantly enhance the hydrophobicity of nanostructured surfaces. Finally, the experiments reveal that previously defined hydrophilic materials can be used for the design of hydrophobic surfaces even if the meniscus is highly adhered to a solid surface, which is in agreement with our qualitative model involving the contribution of the nanomeniscus formed between the substrate and a decorating NP.

3.1 Introduction

Nowadays relentless efforts have been devoted to creating different types of roughness in order to control the wettability of surfaces, including mimicking of natural structures to generate the well-known “lotus”^{1–3} and “rose petal”⁴ effects. The drive is to meet various demands for technology applications or realize certain functions such as self-cleaning,⁵ anti-icing,⁶ heat exchangers,⁷ and fog harvesters.⁸ Processes to form hydrophobic surfaces involve combinations of surface roughening with the alteration of surface chemistry using low surface energy materials to mimic for example the structure of the lotus leaf or butterfly wings that show strong hydrophobicity.

In general, the surface wettability is characterized by the static contact angle (SCA), as well as by the dynamic contact angles termed as advancing and receding contact angles (ACA / RCA) between a testing water droplet and a surface. The SCA of a testing droplet on a flat surface can be described by the Young’s equation⁹ $\gamma_{sv} = \gamma_{sl} + \gamma_{lv} \cos \theta_Y$, where γ_{sv} , γ_{sl} and γ_{lv} are the surface energies of solid-air, solid-liquid, and liquid-air, respectively, and θ_Y represents the SCA of the liquid on the flat solid surface. When $\gamma_{sv} - \gamma_{sl} < 0$, one obtains $\theta_Y > 90^\circ$ and the surface is termed as hydrophobic, while when $\gamma_{sv} - \gamma_{sl} > 0$, one obtains $\theta_Y < 90^\circ$ and the surface is termed as hydrophilic. However, for rough surfaces, Wenzel¹⁰ and Cassie-Baxter¹¹ models have been widely used to describe the effect of roughness on surface wettability. In Wenzel theory the testing droplet wets the surface cavities leading to increased interaction area with the liquid droplet. In terms of Wenzel model the apparent SCA θ_W is given by the expression¹⁰ $\cos \theta_W = r \cos \theta_Y$, where r is the roughness factor. The latter is given by $r = A_r / A_p$ where A_r is the actual rough surface area, and A_p is the projected surface area on the average surface plane. Since $r > 1$ the absolute value of $\cos \theta_W$ is increased, indicating consistency in wettability so that the hydrophilic/hydrophobic surfaces would become more hydrophilic/hydrophobic with increasing surface roughness. However, in several cases, *e.g.*, the lotus effect,^{1–3} the droplet will not wet fully the surface, leaving air pockets within surface cavities. This case is described as Cassie-Baxter model, where the apparent SCA θ_{CB} is given by the expression¹¹ $\cos \theta_{CB} = f \cos \theta_Y + (f - 1)$, where f is the fraction of the solid surface area wetted by the liquid. This model does not preserve consistency of wettability as in Wenzel state, since a hydrophobic surface can be obtained also from a hydrophilic one.

Nevertheless, several other studies^{12–14} have demonstrated complex cases of surface wettability, where Wenzel and Cassie-Baxter models could not explain the experimental data. Using the concept “work of adhesion” that was introduced by Dupré,¹⁵ and taking the air-liquid interface on a solid as a one-dimensional system, Pease¹² emphasized that the SCA is the result of an equilibrium position that the three-phase contact line (TPL) could reach. Then the dynamic contact angles RCA and ACA were also expressed in terms of the work of adhesion.^{14,16} Through experiments on nanofibrous membranes, Wang¹⁷ argued that the 90° could not be used as mathematical wetting threshold between the hydrophobicity and hydrophilicity in designing

nanofibrous surfaces. Derjaguin^{18,19} discovered the solid surface is pre-wetted by a wetting film when in contact with a liquid droplet, and described the film with the concept of the disjoining pressure.

Furthermore, airborne hydrocarbon contaminants, *e.g.*, alkanes, alkenes, aromatics, and alcohols can be easily adsorbed by various types of surfaces including gold,²⁰ graphene,²¹ TiO₂,²² boron nitride nanotube decorated surfaces²³ and Ni-Cu-P ternary coating.²⁴ By comparison of the results of wetting measurement and Fourier transformed infrared (FTIR) spectroscopy of surfaces before and after ultraviolet-Ozone (UV-O₃) treatments, which is an effective method for removing surface organic contaminants,²⁵ Li *et al*²¹ proved that the wettability variation of graphene was the result of adsorption/removal of airborne hydrocarbons. They attributed the effect of airborne hydrocarbons on the graphene wettability to be the result of reduced surface energy. Although the FTIR results could provide direct evidence of the adsorption-removal of airborne hydrocarbon contaminants, the distribution as well as the morphology of these surface contaminants, which is very important to reveal their effect on surface wettability, is still unclear. Therefore, more detailed characterization is necessary to evaluate the specific effect of airborne hydrocarbons on the enhancement of hydrophobicity of various surfaces, especially for micro/nano-structured surfaces.

In this framework, nanoparticles (NPs) provide an ideal decoration method able to create nanostructured surfaces and achieve certain wettability, *e.g.*, TiO₂ NP painting,²⁶ or even more directly, *e.g.*, Cu NP deposition by a high-pressure magnetron sputtering system where the production and decoration process can be accomplished in one step.²⁷ In addition, NPs derived from the phase-change material (PCM) Ge₂Sb₂Te₅ (GST), which has been used as an active medium in rewritable optical disks, *i.e.*, CD, DVD, and Blu-Ray Disks,^{28,29} offer more extensive possibilities to study wetting on nanostructured surfaces than other material systems. This is because the surface energy of PCMs can be altered by the amorphous to crystalline phase transformation without significant alteration of its composition and morphology, providing another degree of freedom to tailor the surface wettability.

Therefore, we used here GST NPs both in their amorphous and crystalline phases as a means of nanostructuring in order to study in depth the intrinsic relationship of the wettability of nanostructured surfaces and airborne hydrocarbons. Moreover, graphene, which has found promising applications in sequencing,³⁰ energy storage,³¹ filtration³² and surface coating,³³ offers superior mechanical properties³⁴ that allowed the designing of GST NPs/Graphene samples to observe the distribution, as well as the morphology of airborne hydrocarbons on nanostructured surfaces by high angle annular dark field scanning transmission electron microscopy (HAADF-STEM). Hence, the effect of hydrocarbon adsorption on the wettability of GST NP decorated surfaces was extensively investigated *via* a wettability switch between hydrophilic-hydrophobic states due to the removal/adsorption of hydrocarbons by UV-O₃ treatments/ hydrocarbon exposure. Subsequently, the experimental results were theoretically explained by introducing the

contribution of the nanoscale meniscus between the substrate and a NP to the wettability of NP decorated surfaces.

3.2 Results and Discussion

3.2.1 Wettability of Flat Substrate Surfaces Prior to NP Deposition

Figure 3.1 Wettability measurements on relatively flat surfaces of the substrate materials used for decoration with GST NPs. **a** Evolution of SCA of the bare Cu substrate surface. **b** Evolution of SCA on amorphous and crystalline deposited GST thin films.

The evolution of the wettability of the bare Cu substrate surface with time is shown in Figure 3.1a. The bare Cu substrates (for bare Cu surface wetting measurement as well as GST NPs deposition which will be discussed later) were made from mechanically polished polycrystalline Cu blocks with purity of 99.99%. Then the Cu substrates were ultrasonically cleaned with acetone, ethanol, and water, respectively, where each step of ultrasonic cleaning lasted at least 30 minutes. After UV-O₃ treatment the SCA of the Cu surface is $34 \pm 1^{\circ}$, while after further exposure to air the SCA rose to $64 \pm 1^{\circ}$ within 1 day, and finally after 3 days was saturated at $79.5 \pm 1.5^{\circ}$ without any significant change for the next 3 weeks ($79 \pm 1^{\circ}$). Similarly, the wettability of amorphous and crystalline GST films is shown in Figure 3.1b. Indeed, both the amorphous and crystalline GST thin films show superhydrophilicity (SCA $\sim 0^{\circ}$) after 20 min UV-O₃ treatment. Then the SCA of

the two surfaces increased to 48° and $27.5 \pm 0.5^\circ$, respectively, and stabilized to the values of $48.5 \pm 0.5^\circ$ and $31 \pm 1^\circ$ within a week (Figure 3.1).

For convenience, the SCAs of the surfaces in Figure 3.1 are redefined as follows: i) the SCAs of the freshly UV-O₃ treated surface is defined as θ^U ($\theta_{Cu}^U, \theta_{Amo}^U$ and θ_{Cry}^U for bare Cu, amorphous GST, and crystalline GST film, respectively), and ii) the SCAs after long-time exposure in air, where the surfaces can adsorb hydrocarbons, are defined as θ^H ($\theta_{Cu}^H, \theta_{Amo}^H$ and θ_{Cry}^H for bare Cu, amorphous GST, and crystalline GST films, respectively). The wettability of the involved surfaces from Figure 3.1 are summarized in Table 3.1.

Table 3.1 θ^U and θ^H of the flat surfaces made of Cu, amorphous GST and crystalline GST

Materials	$\theta^U (^\circ)$	$\theta^H (^\circ)$
Substrate Cu	34	79
Amorphous GST	0	48.5
Crystalline GST	0	31

θ^U : Contact angle of the flat surface with the relevant material measured immediately after UV-O₃ treatment. θ^H : Contact angle of the flat surface with the relevant material measured after long-time exposure in air.

3.2.2 Wettability Variation in Air After Thermal Annealing and UV-O₃ Treatments

A GST NP decorated Cu surface was fabricated using high-pressure magnetron sputtering,³⁵ having high coverage of NPs (ratio of area covered NPs with respect to the overall area determined by TEM images) of $\sim 95\%$ as it is shown in Figure 3.2a. The selected area electron diffraction (SAED) pattern, (inset of Figure 3.2a) shows that the GST NPs are in the amorphous state. CA measurements were conducted afterward and the results are shown in Figure 3.2b. The SCA of the as-prepared sample was $88.5 \pm 0.5^\circ$, and then rose to $135 \pm 2^\circ$ after storing the sample in air for 7 days. Subsequently, the sample was annealed at 180°C for 5 minutes in a quartz tube with base pressure in the ultrahigh vacuum range ($\sim 10^{-9}$ mbar), and then was cooled down to room temperature. The CA measurements were conducted immediately after the thermal annealing process, and the low SCA value ($42 \pm 2^\circ$) indicates an annealing-induced hydrophobic-hydrophilic transition. Then the SCA of the sample increased to $99 \pm 1^\circ$ after keeping it in air for 4 days, indicating a hydrophilic-hydrophobic transition. After 20 days the SCA slightly increased to $\sim 101.5 \pm 1.5^\circ$. The annealing temperature 180°C is higher than the crystallization temperature

(T_c) of GST NPs (the T_c of the as-prepared GST NPs was deduced to be 148 °C to 150 °C in our previous work³⁵), and the annealing time (5 min) is sufficiently long to ensure full crystallization of the GST NPs.³⁵ Thermal annealing has been reported to lower the SCA of surfaces because adsorbed hydrocarbons can be partly removed by this process²¹ yielding hydrophobic-hydrophilic transitions. Nevertheless, the SCA of the sample could not recover back to the initial hydrophobic ($135\pm 2^\circ$) state after nearly one-month storage in air. We attributed this change in SCA to the changes of the surface topography, as well as the surface energy of the GST NPs after crystallization by thermal annealing³⁶ as it will be discussed later on.

Figure 3.2 Experimental data of GST NPs on Cu substrates. **a** TEM image of amorphous GST NPs deposited on a TEM grid simultaneously with the NPs deposited on the Cu substrate. **b** Evolution of the SCA of the as-deposited amorphous GST NPs on a Cu substrate with subsequent thermal annealing at 180 °C. **c** TEM image of as-deposited crystalline GST NPs on a TEM grid. **d** Evolution of the SCA for the as-deposited crystalline NPs on a Cu substrate after several UV- O_3 treatments and subsequent exposures to air.

Furthermore, we evaluated the wettability of Cu surfaces decorated with the as-deposited crystalline GST NPs. Indeed, the SAED pattern (inset of Figure 3.2c) shows an identical structure as in our previous studies,³⁵ confirming the crystalline nature of the GST NPs. The coverage of the GST NPs was $\sim 96\%$, which is similar to that of the amorphous GST NPs sample used for thermal annealing in Figure 3.2a. The evolution of SCA shows similar behavior as the amorphous one, as shown in Figure 3.2d. The SCA of the as-prepared sample with crystalline GST NPs was $66\pm 2^\circ$ and increased to $105\pm 0.5^\circ$ after the sample was kept in air for 7 days. The SCA

immediately dropped down to 30° after 20 min of UV- O_3 treatment. After 1 day of storage in air, the SCA of the sample rose to $81.5 \pm 1.5^\circ$, remained at the same value for another day, and then increased to $100.5 \pm 0.5^\circ$ within an additional day. Finally, the SCA was measured to be $101.5 \pm 1.5^\circ$ after 2 weeks showing agreement with the results of the annealed sample (Figure 3.2b). For consistency, the as-prepared crystalline GST NPs sample underwent another 20-min UV- O_3 treatment, and the SCA decreased again to around 30° . Given the fact that the adsorbed hydrocarbons can be partially removed by thermal annealing or UV- O_3 treatment, it is evident that airborne hydrocarbons play an important role in the wettability of NP decorated surfaces. Hence, in order to investigate further the effect of airborne hydrocarbons on the wettability of NP decorated surfaces, an atmosphere with a higher concentration and better control of hydrocarbons was created to compare to the effects triggered by exposure to ambient air.

3.2.3 Wettability Switch in Designed Hydrocarbon Atmosphere and UV- O_3 Treatment

Two specimen based on Cu surfaces decorated with amorphous GST NPs, labeled as sample 1 (S1) and sample 2 (S2), were made using the high-pressure magnetron sputtering system.³⁵ The CA measurements in Figure 3.3a were conducted for both samples immediately after the GST NPs deposition. Then the measurements were taken every 24 hours (or immediately after each UV- O_3 treatment) to check the temporal evolution of the wettability of the samples. The SCAs of S1 and S2 were $\sim 63 \pm 4^\circ$ and $\sim 59 \pm 3^\circ$, respectively (marked as “Measurement 1” in Figure 3.3a). After being kept in ambient air for 7 days, the SCAs of both samples increased to around $\sim 120^\circ$ (marked as “Measurement 2” in Figure 3.3a). After 20 minutes of UV- O_3 treatment using a UV- O_3 sterilizer (labeled with NZX Sahne portable), the CA of both samples dramatically drop to around 25° (marked as “Measurement 3” in Figure 3.3a), showing an obvious hydrophobic-hydrophilic transition. Aiming to extensively evaluate the effect of hydrocarbons adsorbed by the NP decorated surfaces, more CA measurements were conducted subsequently on S1 and S2. Indeed, S1 was kept in ambient air, while S2 was kept in the hydrocarbon atmosphere (H-A) that was created in a petri dish by using octane (see Figure 3.6 in Appendix). After one day, the SCA of S1 increased to $91.5 \pm 1.5^\circ$, while the SCA of S2 increased to $119 \pm 1^\circ$ (marked as “Measurement 4” in Figure 3.3a). Both samples experienced a hydrophilic-hydrophobic transition, and the SCA rose faster when the samples were exposed to a hydrocarbon atmosphere.

Figure 3.3 Characterization of amorphous GST NP decorated samples. **a** Variation of SCA of two amorphous GST NP decorated Cu samples after UV-O₃ treatments. **b** SCA of the amorphous GST NP decorated Cu sample after UV-O₃ treatment. **c** SCA of the amorphous GST NP decorated Cu sample after being kept in ambient air. **d** Receding contact angle of an amorphous GST NP decorated Cu sample after being kept in ambient air. **e** TEM image of NPs deposited on a TEM grid simultaneously with the NPs that decorated the Cu samples. The coverage of the amorphous was 72% and the diameter of the NPs 9.8 ± 0.5 nm.

In order to crosscheck the previous result and exclude the difference in SCA concerning the individual difference between S1 and S2, the storage conditions of the two samples were exchanged after second UV-O₃ treatment. The SCA of the two samples decreased back to around $\sim 25^\circ$ after the second UV-O₃ treatment (see “Measurement 5” in Figure 3.3a), which is identical with the “Measurement 3” in Figure 3.3a. Then the sample S1 and S2 were kept in hydrocarbon

atmosphere and ambient air separately. After one day, the hydrophilic-hydrophobic transition appeared again for both samples, where the SCA of S1 and S2 rose to $117\pm1^\circ$ and $98\pm2^\circ$ respectively (see “Measurement 6” in Figure 3.3a). The latter shows consistency with the results of “Measurement 4”, and excluded the individual difference factor between the two samples. Subsequently, the two samples were kept in their original conditions for 3 days (*i.e.*, S1 in H-A and S2 in air) where the SCA of S1 saturated to values $120\pm3^\circ$, while the SCA of S2 steadily climbed to $117\pm4^\circ$. Comparing the storage conditions of ambient air and H-A, the main difference lies in the concentration of hydrocarbons, and the results in Figure 3.3a indicate that higher airborne hydrocarbon concentration could boost the process of transforming the hydrophilic to the hydrophobic state for the as-prepared samples after UV-O₃-induced removal of adsorbed hydrocarbons. Therefore, it is reasonable to expect that the hydrocarbons adsorbed by the surfaces play an important role in the hydrophilic-hydrophobic transition of GST NP decorated Cu.

Additionally, the wetting state of the two samples immediately after UV-O₃ treatment is termed as a “hydrophilic state” with a typical image as in Figure 3.3b, while the wettability of the samples after one-day storage in H-A or four-day storage in ambient air, which show strong hydrophobicity (SCA $>100^\circ$) is termed as a “hydrophobic state” with a typical image as in Figure 3.3c. Moreover, the ACA was measured to be 123° , while the RCA was measured to be 15° (see Figure 3.3d). The RCA was indicated directly on the image instead of using the fitting model based on the ellipse outline. This is because the sectional view of the outline of the testing droplet tends to show a triangular shape due to the strong adhesion force between the surface and the testing droplet. Subsequently, the hysteresis (θ_H) of the as-prepared sample, which is defined as the difference between ACA (θ_A) and RCA (θ_R) with $\theta_H = \theta_A - \theta_R$,³⁷ was calculated to be 108° .

3.2.4 Characterization of Hydrocarbons on GST NP Decorated Surfaces

In order to understand the effect of hydrocarbons adsorbed on NP decorated surfaces, we performed HAADF-STEM imaging measurements to gain insight on the distribution and morphology of adsorbed hydrocarbons. Because the contrast in HAADF-STEM is related to the thickness and the square of average atomic number of the corresponding atomic column, the thin thickness and low average atomic number of adsorbed hydrocarbons will yield weak contrast for the adsorbed hydrocarbons that will be obscured by the substrate material. Therefore, not only the average atomic number but also the thickness of the substrate should be low enough to minimize the contrast interference during HAADF-STEM measurements. Monolayer graphene, having a low atomic number (6 C) and being extremely thin (1 atomic layer thick), is a perfect candidate satisfying the stringent criteria of this particular sample design to observe the adsorption of surface hydrocarbons. Moreover, the superior mechanical properties (elastic modulus and intrinsic breaking strength) of graphene³⁴ renders this system as a promising candidate to support decoration with GST NPs by the magnetron sputtering deposition. Hence, a monolayer (partly bi-layer or tri-layer) graphene was synthesized by chemical vapor deposition

(CVD), and subsequently, the graphene layer was transferred onto a Quantifoil R2/1 holey carbon (Electron Microscopy Sciences, Q225-AR1) TEM grid, which served as the substrate for NPs deposition in the magnetron sputtering system. Finally, the sample was kept in ambient air for three weeks to adsorb sufficient coverage of hydrocarbons for later TEM observations.

Figure 3.4 TEM measurements of a GST NPs/graphene sample. **a** Bright field (BF) TEM image of the GST NPs/graphene sample **b** HAADF-STEM image of the graphene sample with the Fast Fourier Transform (FFT) image at the top right corner. **c** HAADF-STEM image of the sample. **d** BF STEM image of the sample taken from the same area of **c**. **e** HAADF-STEM image of another area of the same sample. **f-h** Energy-dispersive X-ray spectroscopy (EDX) mapping of the GST elements Ge, Sb, Te, respectively.

The morphology of GST NPs/graphene sample is shown in Figure 3.4a. The dark circles are GST NPs, and there is an obvious difference in the contrast with the background. The left bottom part of Figure 3.4a, divided by the red dashed line, refers to graphene/carbon support, while the top right part, where the contrast is relatively brighter is mostly the suspended monolayer graphene shown in Figure 3.4b. The bright areas with spherical like features in Figure 3.4c (with high contrast) are the GST NPs, while the dark areas (with low contrast) are supposed to be the graphene. However, there are also some “conjunctions” among the NPs showing a “cloudy” contrast (obviously distinct in between the bright and dark parts), which are presumably the adsorbed airborne hydrocarbons. Figure 3.4d is the bright field (BF) STEM image, which in line with Figure 3.4c also shows the outline of the GST NPs. However, the “cloudy” areas are not visible in Figure 3.4d, proving that the “cloudy” areas among the NPs in Figure 3.4c do not present some “heavy” atoms from the materials during sample preparation. Therefore, together with Figure 3.4c, the BF STEM image also implies that the “cloudy” areas belong to airborne hydrocarbons. The “cloudy” areas are also shown in Figure 3.4e, where the EDX mapping data in Figures 3.4f-h show the material contrasts of the GST NPs. This material outlines overlap with that of the bright areas in Figure 3.4e, showing that the Ge/Sb/Te elements mainly locate at this bright area, reconfirming that the “cloudy area” is the hydrocarbon contamination. The results of Figure 3.4 prove that there are airborne hydrocarbons on the surface of the as-prepared samples after exposure to ambient conditions. The width of the adsorbed hydrocarbons assemblies was measured to be ~7-20 nm in Figure 3.4c, in equivalent scale with the size of the deposited GST NPs. Moreover, the adsorbed hydrocarbons not only cover the GST NPs, but also the intervals of individual NPs on the corresponding substrates.

3.2.5 Effect on Wettability Due to Airborne Hydrocarbons

Here we will attempt to analyze the wettability of the hydrophobic-state of samples decorated by GST NPs where the influence of surface hydrocarbons is the most pronounced. Considering the large hysteresis, which implies high adhesion force, Wenzel model¹⁰ comes naturally into consideration. At a first glimpse, this model appears unsuitable for the GST NP decorated surfaces, because it has been applied to mono-component systems instead of a surface decorated with different materials. Considering the substrate and the decorating NPs are materials that can be completely wetted by the testing droplet, Wenzel model can be modified for describing the binary component system in the form

$$\begin{aligned} \cos\theta'_W &= f_S \cos\theta_S + f_N \cos\theta_N, \\ f_S + f_N &= r, \end{aligned} \quad (3.1)$$

where θ'_W is the apparent SCA of a binary composite surface in Wenzel state, and θ_S and θ_N are the SCAs for the substrate exposed surfaces and NPs, respectively. Here r (≥ 1) is the roughness factor with the same definition as indicated before, while f_S and f_N are the ratios of the

actual surface area of the exposed substrate and NP surfaces to the projected surface area on a plane that is parallel with the substrate, respectively. Therefore, if the surfaces of the substrate and NPs are both hydrophilic, the binary composite surface would preserve its hydrophilicity, and vice versa if both materials are hydrophobic the NP decorated surfaces will be hydrophobic.

The wettability of as-prepared amorphous GST NP decorated Cu surfaces with sufficient coverage C_G ($\sim 72\%$) was analyzed by the modified model of Eq. (3.1). Indeed, from Figure 3.3a the SCA of the freshly UV- O_3 treated sample was measured to be $\theta_{Amo/Cu}^U = 25^\circ$, while the SCAs of the involved materials (in planar form, see Table 1) were measured immediately after UV- O_3 treatment to be $\theta_{Cu}^U = 34^\circ$ and $\theta_{Amo}^U = 0^\circ$. Assuming that the contacts between GST NPs and the Cu substrate are point-like contacts, we can set for the contact area of the testing water on the Cu substrate $f_S \approx 1$. Because most of amorphous GST NPs are spherical, the factor f_N can be roughly calculated by $f_N \approx 4\pi r_N^2 C_G / \pi r_N^2 \approx 4C_G$, where r_N is the radius of the NPs. Substituting these parameters in Eq. (3.1) we obtain for the theoretical SCA for the freshly UV- O_3 treated sample $\cos\theta_{Amo/Cu}^{UT} > 1$, indicating a superhydrophilic state or $\theta_{Amo/Cu}^{UT} = 0^\circ$. The difference between the calculated and experimental SCAs may stem from the two following reasons: i) The liquid-solid contact area used in the calculation may differ from the real one (which will be discussed latter and schematically shown in Figure 3.5), which lead to over estimation of f_S and f_N , giving a lower theoretical SCA. ii) It is more difficult for adsorbed hydrocarbons to be removed by UV- O_3 treatment on GST NPs than on flat GST surfaces, because the NPs form a porous network with higher content of residual hydrocarbons than the flat GST surface. The latter leads subsequently to stronger surface hydrophobicity. Nevertheless, the experimental value $\theta_{Amo/Cu}^U$ is still lower than θ_{Cu}^U , indicating that the surface roughness due to the deposited NPs can make the original substrate more hydrophilic. Therefore, Eq. (3.1) can explain qualitatively the experimental results for the fresh UV- O_3 treated surfaces.

Furthermore, the experimental results from hydrocarbon adsorbed surfaces were also analyzed in terms of Eq. 1. Substituting the experimental values $\theta_{Cu}^H = 79^\circ$ and $\theta_{Amo}^H = 48.5^\circ$ as well as f_S and f_N (with the same values as the previous calculation after a fresh UV- O_3 treatment yielding $f_S \approx 1$, $f_N \approx 4C_G$) into Eq. 1, the calculated value of the theoretical SCA for the amorphous GST NP decorated surface yield again $\cos\theta_{Amo/Cu}^{HT} > 1$, indicating a superhydrophilic state with $\cos\theta_{Amo/Cu}^{HT} = 0^\circ$. However, this value is much lower than that of the SCA for the Cu substrate surface ($\theta_{Cu}^H = 79^\circ$), and it has an obvious difference from the experimental value $\theta_{Amo/Cu}^H = 120^\circ$. Obviously, the modified model fails to offer even a qualitative explanation for the wetting state of the amorphous GST NP decorated surface with hydrocarbons adsorbed. In addition, the as-prepared GST NP decorated surface was not in Cassie-Baxter state, at least in the outer area of the water droplet, because the measured high hysteresis ($\theta_H = 108^\circ$) indicates high adhesion force between the water meniscus and the tested surface. The latter does not occur for Cassie-Baxter wetting state. Therefore, besides lowering the surface energy, the interaction with porous

geometry should be taken carefully into account when evaluating the effect of airborne hydrocarbons on NP decorated surfaces.

Amorphous and crystalline GST NP decorated surfaces are found to have a wettability that can be switched by UV-O₃ treatments and hydrocarbon atmospheres. The microstructure and distribution of hydrocarbons adsorbed by amorphous GST NPs decorating surfaces were measured to aid understanding of the effect of airborne hydrocarbons on the wettability of NP decorated surfaces. The evolution of SCAs of the flat surfaces, before and after airborne hydrocarbon adsorption (Table 1), show that for Cu they change from 34° to 79°, for amorphous GST from ~0° to 48.5°, and for crystalline GST from ~0° to 31°. These results show agreement with previous studies in airborne hydrocarbon tunable wettability of flat surfaces where the SCAs of gold²⁰ and graphene²¹ rose from 0° and 44° to 60° and 80° after adsorption of airborne hydrocarbons, respectively. Compared with the wettability evolution of flat surfaces, the SCAs of GST NPs decorating Cu surfaces display more significant increase in SCAs after airborne hydrocarbon adsorption, where the SCA rose from 25° to 120° (with NP coverage of 72%). However, the significant increase of SCA of the NP decorated surfaces could not be explained by Wenzel model, which is frequently used for describing the wettability of micro-structured surfaces with high wetting hysteresis. Therefore, more efforts should be paid for analyzing our experimental results.

3.2.6 Beyond Wenzel Model

Long ago it was realized^{18,38} that the wetting phenomenon is driven by long-range surface forces. For a wetting film of thickness h , the disjoining pressure $\Pi(h)$ was introduced in 1936 by Derjaguin^{15,16} (as the difference between the pressures in a region of a phase adjacent to a surface confining this phase and the pressure in the bulk of this phase) to describe the effect of surface interactions. The disjoining pressure is related to the contact angle θ by the equation^{18,19}

$$\cos \theta = 1 + \frac{1}{\gamma} \int_{h_0}^{\infty} dh \Pi(h) + \frac{h_0}{\gamma} \Pi(h_0). \quad (3.2)$$

Here $\gamma = \gamma_{lv}$ is the surface tension of liquid, and h_0 is the precursor film thickness ahead of the liquid droplet. In equilibrium the film thickness is determined from the relation $\Pi(h_0) = P_c$, where P_c is the capillary pressure in the bulk liquid. For macroscopic liquid volumes the capillary pressure $|P_c| \sim \gamma/\mathcal{R}$ is small, where $\mathcal{R}$ is a macroscopic curvature radius of the meniscus. In this case the last term in Eq. (3.2) is small $h_0/\mathcal{R} \ll 1$ since h_0 is in the nanometer range. For this reason, Eq. (3.2) is often presented without the last term.³⁹ Furthermore, the wettability of a material is defined by the integral $I_{\Pi} = \gamma^{-1} \int_{h_0}^{\infty} dh \Pi(h)$. For $I_{\Pi} > 0$, the material is superhydrophilic, for $-1 < I_{\Pi} < 0$ the material is hydrophilic, for $-2 < I_{\Pi} < -1$, the material is hydrophobic, and for $I_{\Pi} < -2$, the material is in a non-wetting state. For the case of partial wetting, the typical behavior of the disjoining pressure is shown in Figure 3.7 in Appendix.

Both materials of interest (Cu and GST) stay hydrophilic (see the results in Table 1) even after exposure to hydrocarbons, and according to Eq. (3.1) we cannot obtain the observed hydrophobicity for any parameters of f_S and f_N . Therefore, it is obvious that some important element is missing in the previous analysis. First, let us note that NPs have a small radius of curvature, namely, $R \approx 5$ nm, while Eq. (3.2) was derived for flat surfaces. Generalization for the case of curved surfaces has been analyzed in the work by Boinovich and Emelyanenko.⁴⁰ Using the general thermodynamic approach, it was found that for a spherical surface Eq. (3.2) is modified in the form

$$\cos \theta = 1 + \frac{1}{\gamma} \int_{h_0}^{\infty} dh \Pi(h) \left(1 + \frac{h}{R}\right)^2. \quad (3.3)$$

Here it is assumed that the surface is convex and described by the radius of curvature R ; while for a concave surface one has to change $R \rightarrow -R$. A significant effect of the curvature is possible only for R comparable with the distance range of the surface forces $h \sim 1$ nm. The modification due to surface curvature is, however, not sufficient to explain the observations since the factor $(1 + h/R)^2$ influences rather the repulsive long-distance tail of the disjoining pressure.

Figure 3.5 **a** The configuration used to calculate contact angle with Eq. (3.1). **b** More realistic geometry of the problem: r_1 is the negative radius of curvature, r_2 (not shown) is the positive radius of curvature in the orthogonal direction to the plane, h_1 is the thickness of wetting film on the substrate, h_2 is the thickness of wetting film on the NPs.

Calculations with Eq. (3.1) have been performed for the configuration shown schematically in Figure 3.5a, while the actual geometry has to look like that shown in Figure 3.5b. The most important difference is the presence of a concave meniscus with a nanoscopic radius r_1 . In the orthogonal direction, the meniscus is convex but with a significantly larger radius $r_2 > r_1$.

Eq. (3.3) does not take the nanomeniscus into account, but it can be included following the same line of reasoning as that used in previous work⁴⁰ to deduce Eq. (3.3). The disjoining pressure appears in Eq. (3.3) as the difference between the pressure in the film P_f and the pressure P_b in the bulk. If there is no meniscus this difference is equal to the disjoining pressure: $P_f(h) - P_b = \Pi(h)$. The meniscus will contribute to P_f and in this case one obtains

$$P_f - P_b = -\gamma \left(\frac{1}{r_1} - \frac{1}{r_2} \right) + \Pi(h). \quad (3.4)$$

The radii of curvature are also functions of the film thickness, but the determination of this dependence is out of the scope of this paper. Our purpose here is to give a qualitative description of the effect. Nevertheless, it is important to mention that $r_2 > r_1$, while R is, in general, the largest in length parameter. Both radii become comparable when $r_1 \sim R$. For $h \ll R$ one can expect that $r_1 \sim h$ with r_1 increasing with h . After substitution the contact angle θ_N is given by

$$\cos \theta_N = 1 + \frac{1}{\gamma} \int_{h_0}^{\infty} dh \left(1 + \frac{h}{R} \right)^2 \left[-\gamma \left(\frac{1}{r_1} - \frac{1}{r_2} \right) + \Pi_N(h) \right]. \quad (3.5)$$

For the equilibrium film thickness $h = h_0$ the expression in the square brackets has to be zero (with precision γ/R). The term that includes the capillary pressure of the meniscus is negative and not small in comparison with Π_N . As a result, this term reduces $\cos \theta_N$, and it is exactly what we need to explain the transition to the hydrophobic state. Therefore, we can conclude that the transition to the hydrophobic state can be explained by the formation of the nanomeniscus, when the nanoparticles on the substrate are also wetted.

Comparing the results in Figures 3.2a, b and Figures 3.2c, d, after the adsorbing airborne hydrocarbons, the SCA of the amorphous GST NP decorated Cu is higher than the one of the airborne hydrocarbons adsorbed on the *in situ* crystalized GST NPs. The explanation for this difference may stem from two aspects. On one hand, the surface energy of amorphous GST flat surface with adsorbed airborne hydrocarbons (with SCA of 48.5°) is lower than the surface energy of the crystalline one. Therefore, the SCA when airborne hydrocarbons adsorbed on amorphous GST NP decorated Cu surfaces should show higher SCA than the crystalline GST NPs if they share the same morphology. In addition, the coalescence of NPs is stronger for the *in situ* crystalized GST NPs, so the effective radius of the NPs will be larger, and the SCA would be lower when a larger “ R ” is used in Eq. (3.5).

3.3 Conclusions

In summary, the effect of airborne hydrocarbons on the wettability of GST NP decorated surfaces has been extensively studied in a systematic manner. Besides the effect of lowering the surface energy by airborne hydrocarbons, the geometry of the three phase contact area of GST NP decorated surfaces was discussed in order to shed light on the question: why some nanostructured surfaces do not follow Wenzel model when they show a rose petal type of wettability associated with strong pinning of water droplets. In this respect, our results provide a comprehensive understanding of how strong is the effect of airborne hydrocarbons on the wettability of NP decorated surfaces, indicating that the hydrocarbon adsorption/removal process can effectively manipulate the wettability of nanostructured surfaces. Moreover, our results imply that some previously defined “hydrophilic” materials could be used in a hydrophobic surface design.

Appendix

Hydrocarbon atmosphere

Figure 3.6 Schematic of the hydrocarbon atmosphere created by octane.

As is shown in the Figure 3.6, the sample with the amorphous $\text{Ge}_2\text{Sb}_2\text{Te}_5$ (GST) NPs (with NP coverage $\sim 72\%$) deposited on Cu was kept in a glass petri dish (with a diameter of 11 cm). A smaller petri dish (with a diameter of 5 cm) containing 5 ml octane was put into the dish to generate octane vapor and enhance the density of hydrocarbons in the larger petri dish for the sake of higher hydrocarbon adsorption on the sample.

Behavior of the disjoining pressure

Figure 3.7 Qualitative behavior of the disjoining pressure for a partially wetting materials. The specific example shown corresponds to a hydrophilic surface. The distance is given in units of the cutoff distance $h_c = 0.2\sim 0.3$ nm.⁴⁴

Characterization of as-prepared GST films

Figure 3.8 Atomic force microscope (AFM) topography images with scan area of $3 \times 3 \mu\text{m}^2$ and reflection high-energy electron diffraction (RHEED) patterns of as-prepared GST films. (a) AFM image of the as-prepared amorphous GST film with the RHEED pattern at the top right corner. (b) AFM image of the as-prepared crystalline GST film with the RHEED pattern at top right corner.

The RHEED patterns in the top right corner of Figure 3.8a, b show that the as-deposited GST films are amorphous and crystalline, respectively. And the morphology of both films is homogeneous in the AFM images in Figure 3.8. Additionally, the root mean squared roughness (RMS) measured in Figure 3.8 (1.073 nm in Figure 3.8a and 2.693 nm in Figure 3.8b) indicates both films are smooth and can be taken as flat surfaces for evaluation of relevant materials.

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Chapter 4

Tunable Wettability of Polymer Films by Partial Engulfment of Nanoparticles

Abstract

A series of poly(methyl methacrylate) (PMMA) surfaces decorated by Cu nanoparticles (NP) with gradually varied morphology were prepared by high-pressure CO₂ treatment at various time spans. Combining the characterizations of transmission electron microscopy (TEM) and atomic force microscopy (AFM), an accurate 3-dimensional view of the morphology of the surfaces was presented. Subsequently, the wettability of the surfaces decreases near-linearly with the increase of apparent height of the decorating NPs in both static (static contact angle) and dynamic (contact angle hysteresis) aspects. The observed tendency contradicts to the Wenzel or Cassie-Baxter model and is explained by the contribution of nanomeniscus formed between the decorating NP and the flat substrate. As a result, the contact angle increases (almost in a linear method) with the apparent height (H_N) of the Cu NPs decorating the PMMA surface. In addition, the effect of the coverage (C_N) by NPs on the wettability can be explained on the same basis. Our experiment demonstrates the important influence of the nanomeniscus on the wettability, which is usually not taken into account. The results in this work provide a comprehensive understanding of how nanostructure affects the wettability of the decorated surfaces and shed light on how to obtain certain wettability through nanostructuring of the surface morphology.

4.1 Introduction

Nowadays relentless efforts have been devoted to creating different types of roughness to enable control of the wettability of surfaces. With high static contact angle (SCA) and low contact angle hysteresis (CAH), the lotus leaf¹ inspired various applications such as, for example, self-cleaning surfaces² and low-friction surfaces for fluid flow.³ Unlike the lotus leaf, some rose petals⁴, scallions, and garlic exhibit superhydrophobicity with high CAH,⁴⁻⁶ inspiring applications in fields such as droplet transportation⁷ and energy harvesting.⁸ Although the wetting behavior of lotus leaf-like surfaces and rose petal-like surfaces differ a lot with each other, an important path to realizing the certain wettability is building up the microstructure of the surfaces. Therefore, understanding the relationship between wettability and detailed surface morphology is important for designing surfaces with certain wettability for various applications.

Many efforts have been paid for understanding the describing roughness and wettability, and Wenzel⁹ and Cassie-Baxter¹⁰ models are two most widely used ones. In the Wenzel theory, the testing droplet wets the cavities of the surface, enlarging the interaction area with the liquid droplet. And the apparent SCA θ_W in terms of the Wenzel model is given by the expression $\cos\theta_W = r\cos\theta_Y$,⁹ where $r = A_r/A_p$ is the roughness factor with A_r the actual rough surface area and A_p the projected surface area on the average surface plane. However, in several cases, *e.g.*, the lotus effect,¹¹⁻¹³ there are air pockets trapped between the solid surface and the testing droplet. This case is described by the Cassie-Baxter model, where the apparent SCA θ_{CB} is given by the expression $\cos\theta_{CB} = f\cos\theta_Y + (f - 1)$,¹⁰ where f is the fraction of the solid surface area wetted by the liquid.

Although the two well-known models have enabled the explanation of the wettability of surfaces with various types of morphology, several other studies have demonstrated complex cases of surface wettability, where the Wenzel and Cassie-Baxter models could not explain the experimental data. Taking the air-liquid interface on a solid as one-dimensional system, Pease¹⁴ emphasized that the SCA is the result of an equilibrium position that the three-phase contact line (TPL) could reach. This perspective was supported by experiments, where the pinning effect of the contact line was observed on micro-structured¹⁵ and nano-structured surfaces¹⁶, and extensively discussed and summarized by Gao and McCarthy¹⁷. These works illustrated that the reason why the Wenzel model failed to predict the SCA of micro-structured surfaces was that a thermodynamic description could not account for contact line pinning. Therefore, the local equilibrium of the TPL is critical to describe the relationship of the wettability and geometrical features (roughness), inspiring more studies to explore the effects of macro-sized or nano-sized decorations on wettability. Using micro-sized square pillars with various sizes and concentrations, Forsberg *et al.*¹⁸ revealed the microscopic details of the contact line pinning behavior, and bridge the relationship between the wettability and the varied micro-sized decorations. Furthermore, the contact line pinning behavior could be analyzed to a nanometer scale,^{16,19} where the mechanism of pinning at a nanometric scale might be attributed to the nanomeniscus formed between the

substrate and the nanoscale decoration.²⁰ Besides, simulations of the contact line pinning effect on nanoscale textured surfaces²¹ and the pinning effect of a single nanoparticle²² were conducted to give a deep understanding of the relationship between wettability and nanostructure. However, experimental investigations taking into account nanoscale defects are still limited, because such studies are faced with the difficulty of obtaining and characterizing rough surfaces having a controlled morphology of the nanostructure. Therefore, the goal of the present work is to create a series of surfaces with gradually varied nanostructure to understand the influence of nanometric decorations on the wetting properties of a solid surface.

In this framework, nanoparticles (NPs) provide an ideal option to create nanostructured surfaces and achieve certain wettability, *e.g.*, TiO₂ NP painting,²³ or even more directly, *e.g.*, Cu NP deposition by a high-pressure magnetron sputtering system where the production and decoration process can be accomplished in one step.²⁴ Moreover, the high-pressure magnetron sputtering can offer homogeneously distributed Cu NPs onto flat substrates without introducing additional chemical ligand,^{24,25} which made it an ideal candidate to provide nanostructured decoration for wetting research. Besides, Tan *et al.*²⁶ reported the controlled thermally assisted particle embedding of surface deposited silica NPs at the surface of poly(methyl methacrylate) (PMMA) polymer films. Particle embedding was controlled by varying the temperature and time of the thermal treatment, and similar results were obtained for surface-modified silica NPs in PMMA and poly(methyl methacrylate-co-methacrylic acid) films.²⁷ As an alternative to thermal annealing, Yang *et al.*²⁸ reported the embedding of gold NPs in polystyrene (PS) films via CO₂ saturation of the polymer substrate at relatively low temperatures, because CO₂ saturated PS surface exhibits an increased polymer mobility, allowing the particles to sink into the surface. Furthermore, Liu *et al.*²⁹ gave extensive experimental results and theoretical analysis of the high-pressure CO₂ assisted engulfment of NPs on PMMA, proving the high-pressure CO₂ a reliable method to conduct NP engulfment on polymer films. Therefore, we have gathered ideal candidates of nanostructured decoration (magnetron sputtered Cu NPs) and substrate (PMMA) to design nanostructured surfaces for wetting research.

Here we used the high-pressure CO₂ assisted NP engulfment technique, and designed a series of samples with Cu NPs decorated PMMA surfaces with gradually varied apparent height of NPs by controlling the time span of high-pressure CO₂ treatment. Taking advantage of the superior lateral resolution of transmission electron microscopy (TEM) and vertical resolution of atomic force microscopy (AFM), an accurate 3-dimensional view of the morphology of the surfaces was presented. Subsequently, wetting measurements of SCA as well as advancing and receding contact angle (ACA/RCA) were conducted on the surfaces with controlled nanoscale morphology. Finally, a model involving the wettability contribution of the nanomeniscus formed between the decorating NP and the flat substrate was proposed to describe the relationship between the wettability and apparent height (H_N) of the Cu NP decorating PMMA surfaces.

4.2 Results and Discussion

4.2.1 Effect of Airborne Hydrocarbons on Surface Wettability

So far, it has been proved that airborne hydrocarbons contaminants could have a significant effect on both flat surfaces as well as NP decorated surfaces.²⁰ Therefore, after each preparation, all the samples had been kept in air (the condition for keeping the samples is shown in Supporting Information Figure 4.6) for more than one week, which is long enough for the as-prepared surfaces to adsorb enough hydrocarbons²⁰ before the wetting measurements. In this way, the interference of the effect of airborne hydrocarbons on the wettability is excluded, ensuring the comparability of the measured wettability. In addition, all the samples also measured one month kept in air after the first measurements. And the data derived from the repeated measurements did not show any significant difference from the ones obtained from the first measurements. The latter indicates the successful exclusion of any interference effects from the airborne hydrocarbons.

4.2.2 Wettability of PMMA Films

The PMMA films were made using the same method as in the work of Liu *et al.*²⁹ The thickness of the PMMA films was measured to be about 50 μm ,²⁹ which is sufficiently thick to be taken as a bulk in the wetting study in this work. Additionally, the PMMA films on silica wafers were very smooth (see Figure 4.1a), referring them as very suitable substrates for the current wetting research. In addition, the wetting measurements of the different PMMA films showed stable wettability (with SCA $81.5 \pm 0.5^\circ$ in Figure 4.1b). Besides the stable wettability, also the morphology of the PMMA films did not show any significant variation, since there was no evident variation among the height distributions (see Figures 4.1c-f) of the PMMA surfaces after high-pressure CO_2 treatments with various time spans. Besides, the AFM morphology images which offer the height distributions in Figures 4.1c-f are shown in Figure 4.8 in Appendix.

Figure 4.1 Atomic force microscopy (AFM) and wettability studies of the PMMA surfaces with various exposure times to high-pressure CO₂ treatments (58 bar). **a** AFM image of the PMMA without high-pressure CO₂ treatment with scan area of $3 \times 3 \mu\text{m}^2$. **b** SCA of the PMMA without high-pressure CO₂ treatment. **c-f** Height distributions of PMMA samples with 0 min (no treatment), 5 min, 30 min, and 90 min high-pressure CO₂ treatments, respectively, derived from AFM topography measurements with scan area of $3 \times 3 \mu\text{m}^2$.

4.2.3 Effect of Cu NPs on Wettability of PMMA Films

In our previous study,²⁰ a hypothesis has been formulated that the increase of the SCA of a surface could be generated by the nanomeniscus, whose existence has been proved by experiments^{32–34} and theoretical analysis,^{35–37} formed between the substrate and the decorating

NPs. Subsequently, it is reasonable to assume that the effect would become weaker when the NPs are partially submerged into the substrate, and the untreated samples have to demonstrate the highest SCA. Therefore, the first step to check the hypothesis is to allow the Cu NPs to induce a difference in the wettability of the PMMA and then measure the variation of the wettability after high-pressure CO₂ treatments. Knowing that the surfaces with higher NP coverage C_N (the ratio of the area covered with NPs with respect to the overall area as determined by the TEM images, which is the same definition used in our previous works^{20,24}) tend to show large SCA,²⁴ we started from the preparation of high- C_N Cu NPs/PMMA samples. The morphology as well as the SCA of the Cu NPs decorated PMMA samples are shown in Figures 4.2a, b. The C_N was measured to be about 64%, and the SCA of the PMMA film has experienced a significant increase from $81.5 \pm 0.5^\circ$ (see Figure 4.1a) to $122 \pm 1^\circ$ (see Figure 4.2b) after the deposition of Cu NPs. However, the in-plane resolution (see Figure 2.9 in Chapter 2) of the AFM images is not good enough to distinguish two NPs close to each other³⁸ because of the tip shape effect.^{39,40} When the C_N is too high, *i.e.*, 64% in this case, the individual NPs would be too close to each other for the AFM tip to distinguish them. As a result, the AFM image would appear to be totally “covered” by NPs, and apparent heights of the individual NPs are hardly accessible for so high C_N sample, though the AFM vertical resolution is outstanding.⁴¹ Therefore, lower C_N PMMA films are necessary for obtaining the apparent heights of the individual decorating NPs.

4.2.4 Partial NP Engulfment in PMMA

Since the samples with high C_N were not suitable for height measurement of the individual decorating NPs, low- C_N Cu NP/PMMA samples were prepared, offering sufficient flexibility for the size analysis of the Cu NPs. Since an NP could completely sink into PMMA with high-pressure CO₂ treatment when its diameter is below 12 nm,²⁹ the deposition parameters of the sputtering system for Cu NPs were optimized to obtain NPs with a diameter of approximately 12 nm (the method for controlling the diameter of Cu NPs was discussed previously²⁵) so that one can achieve various degrees of engulfment in the PMMA film. The coverage of the samples was measured to be about 12% in Figure 4.2c, which offers NPs with good monodispersity for dimensional measurements. In fact, image analysis with the Image-Pro Plus v6.0 software yielded the distribution of the diameter (D_N) of the NPs as it is shown in Figure 4.2d. The median value of D_N was 11.7 nm by fitting with a Gaussian function, while the standard deviation (SD) was 2.2 nm, indicating a good fit by the Gaussian model as well.

The SCAs of the low (12%)- C_N samples were measured to be approximately 81° , showing no noticeable difference in wettability from bare PMMA films ($81.5 \pm 0.5^\circ$, Figure 4.1). However, the good NP monodispersity makes the low C_N samples suitable candidates for AFM analysis. The apparent heights (H_N) of the individual NPs (see Figure 4.7 in Supporting Information for the method of the measurement of H_N of an isolated NP) on the low (12%)- C_N samples before high-pressure CO₂ treatment were derived from Figure 4.2e and summarized in Figure 4.2f. The

median of H_N (for meaningful statistics the value of H_N for 270 individual isolated NPs were measured) was evaluated as 12.1 nm by fitting with the Gaussian function, while the obtained SD was 2.1 nm indicating that the fit of the data by the Gaussian function is good. Moreover, the median of H_N (12.1 nm) agrees well with the median of D_N (11.7 nm shown in Figure 4.2d) which was measured in the TEM image (Figure 4.2c), indicating the absence of NP engulfment before high-pressure CO_2 treatment. In addition, the agreement between the TEM and AFM studies represent a consistency check of the lateral/vertical resolution of the TEM/AFM images. The latter could allow the reconstruction of an accurate 3-dimensional view of the samples.

Subsequently, high-pressure CO_2 treatments of 30 min and 90 min were conducted to the low- C_N samples, respectively. The corresponding AFM images are shown in Figure 4.2g and Figure 4.2i, respectively. Then the height H_N of 270 isolated individual NPs were measured, and the results were summarized in Figures 4.2h, j. The median of H_N of the 30-min CO_2 treated sample was evaluated to be 5.9 nm by the Gaussian fitting with an SD of 1.5 nm indicating a good fit. However, for the 90-min CO_2 treated sample, the median of H_N was evaluated to be 3.0 nm with a large SD of 2.8 nm. The latter can be understood by the observed asymmetry of the distribution for H_N in Figure 4.2j, which may be caused by the uncertainty of measuring the NPs with H_N lower than 2 nm in the AFM image. Comparing the results in Figures 4.2e-j, it can be concluded that the Cu NPs can gradually sink into PMMA films during the high-pressure CO_2 treatment before reaching the equilibrium position, where the NPs will undergo more engulfment with more extended high-pressure CO_2 treatment.²⁹ Additionally, the number density as well as the distribution of decorating NPs did not vary a lot in the AFM images shown in Figures 4.2e, g, i, indicating that all the individual NPs sank uniformly during the high-pressure CO_2 treatments. Therefore, the high-pressure CO_2 treatment used in this work is an ideal method for controlling the H_N of NPs on PMMA films and creating a series of Cu NPs/PMMA samples with comparable morphologies.

Figure 4.2 Morphology and wetting studies of the high (64%)/low (12%)- C_N samples. **a** AFM image of the high (64%)- C_N sample with scan area of $3 \times 3 \mu\text{m}^2$. **b** TEM image of the Cu NPs deposited on a TEM grid simultaneously with the NPs deposited on the PMMA films including also the SCA (bottom right corner) for the high (64%)- C_N Cu NPs/PMMA sample. **c** TEM image of Cu NPs deposited on a TEM grid simultaneously with the NPs deposited on the PMMA films with the SCA indicated (in the bottom right corner) of the low (12%)- C_N Cu NPs/PMMA sample. **d** Distribution of the diameter of NPs measured in Figure 4.4c. **e, g, i** AFM images (scan area: $3 \times 3 \mu\text{m}^2$) of low (12%)- C_N Cu NPs/PMMA samples with 0 min (no treatment), 30 min, and 90 min high-pressure CO_2 treatments, respectively. **f, h, j** Apparent height distributions of the monodispersed NPs measured in Figures 4.3e, g, i, respectively.

4.2.5 Determination of Optimum NP Coverage

As it emerges from the results in Figure 4.2, a satisfactory Cu NPs/PMMA sample for extensive study should have a proper C_N coverage to offer two main properties: One is having an obvious increase in SCA in comparison with the bare PMMA films (marked as Condition I), which can be achieved for higher C_N samples, the other one is allowing the measurement of the NP height through AFM (marked as Condition II), which requires lower C_N samples. The two mutually contradictory requirements call for a sample with an “intermediate” C_N . Additionally, there is still a supplementary requirement for the C_N that the PMMA films should be covered mainly by a monolayer of NPs (marked as Condition SI), which will offer convenience for the theoretical analysis. Besides the high and low C_N samples shown in Figure 4.2, three more trials were conducted to determine the Cu NPs/PMMA samples with the proper C_N for the subsequent research.

Figures 4.3a, b were derived from the same Cu NPs/PMMA sample with $C_N \approx 46\%$ (termed as “higher” (46%)- C_N sample). The SCA of the sample was $107 \pm 2^\circ$ (see Figure 4.3a), showing a significant increase to address the requirement of Condition I. Nevertheless, the sample did not meet Condition II because the Cu NPs shown in the AFM image (Figure 4.3b) were too dense to be measured as isolated NPs. Additionally, there were areas with double-layer NP as it is shown in the TEM image (Figure 4.3a), which did not meet Condition SI. Figures 4.3c, d were derived from the same Cu NPs/PMMA sample with $C_N \approx 27\%$ (termed as the “lower” (27%)- C_N sample). And most of the Cu NPs in the AFM image (Figure 4.3d) were isolated NPs, which enabled reliable AFM analysis meeting Condition II. Besides, the “lower” (27%)- C_N sample also met Condition SI because the majority of the area shown in Figure 4.3c was covered with a monolayer of NPs. However, the “lower” (27%)- C_N sample did not meet Condition I because the SCA of the sample ($85 \pm 1^\circ$ shown in Figure 4.3c) did not represent any significant increase compared with the bare PMMA films ($\text{SCA} \approx 81.5 \pm 0.5^\circ$). It could be concluded from the results in Figures 4.3a-d that neither the “higher” (46%)- C_N sample and nor the “lower” (27%)- C_N sample met all the

requirements for any subsequent further study. Nevertheless, the results of these two samples indicated that the “proper” C_N coverage of NPs might be somewhere in the range of 27%~46%.

Figure 4.3 Morphology and wetting studies of the Cu NPs/PMMA samples with various C_N coverages. **a** TEM image of Cu NPs deposited on a TEM grid simultaneously with the NPs deposited on the PMMA films together with the SCA (bottom right corner) of the “higher” (46%)- C_N Cu NPs/PMMA sample. **b** AFM image of the “higher” (46%)- C_N Cu NPs/PMMA sample with a scan area of $3 \times 3 \mu\text{m}^2$. **c** TEM image of Cu NPs deposited on a TEM grid simultaneously with the NPs deposited on the PMMA films together with the SCA (bottom right corner) of the “lower” (27%)- C_N Cu NPs/PMMA sample. **d** AFM image of the “lower” (27%)- C_N Cu NPs/PMMA sample with a scan area of $3 \times 3 \mu\text{m}^2$. **e** TEM image of Cu NPs deposited on a TEM grid simultaneously with the NPs deposited on the PMMA films together with the SCA (bottom right corner) of the “intermediate” (37%)- C_N Cu NPs/PMMA sample. **f** Distribution of the diameter of NPs measured in Figure 4.3e.

Subsequently, “intermediate”- C_N Cu NPs/PMMA samples were made and characterized. To begin with, the C_N of the “intermediate”- C_N sample was measured as 37% (termed as “intermediate” (37%)- C_N sample) in Figure 4.3e, and the majority of the area was covered with a monolayer of NPs meeting the Condition SI. Moreover, the SCAs of the “intermediate” (37%)- C_N Cu NPs/PMMA samples were measured around 99° , which is significantly different from the bare PMMA films ($81.5 \pm 0.5^\circ$), meeting Condition I. Finally, most of the Cu NPs in the AFM image (Figure 4.4a) were isolated, which enabled reliable AFM analysis, meeting Condition II. In short, the “intermediate” (37%)- C_N Cu NPs/PMMA samples met all the conditions and offered the “proper” samples for our subsequent extensive study.

4.2.6 Wettability vs. NP Engulfment into PMMA

The Cu NPs/PMMA samples with the “intermediate”- C_N (37%) were studied extensively. The morphology studies of the NP engulfment into PMMA and the wettability studies of the relevant samples are shown in Figures 4.4 and 4.5, respectively. Besides the AFM images in Figures 4.4 a, c, e, g, the height H_N of the isolated NPs were also measured in two additional AFM images (see Figure 4.8 in Appendix) derived from each sample to improve statistics. In fact, the H_N of more than 120 individual isolated particles were analyzed for each H_N distribution and shown in Figures 4.4 b, d, f, h. The distribution of H_N in the “intermediate” (37%)- C_N sample before any high-pressure CO_2 treatment was obtained from Figure 4.4a and shown in Figure 4.4b. The median of H_N was evaluated to be 14.0 nm (by fitting with a Gaussian function with $SD=1.4$ nm). Additionally, the median of D_N was evaluated to be 13.2 nm (by fitting with a Gaussian function with $SD = 1.5$ nm where more than 150 individual isolated particles were analyzed). Similar to the agreement between the results in Figures 4.2f, d, the median of H_N (14.0 nm) agrees well with the median of D_N (13.2 nm) indicating the absence of any NP engulfment before the high-

pressure CO₂ treatment, and the satisfactory accuracy of the lateral/vertical resolution of the TEM/AFM images.

Figure 4.4 Morphology studies of the “intermediate” (37%)-C_N Cu NPs/PMMA samples. **a, c, e, g** AFM images (scan area: $1 \times 1 \mu\text{m}^2$) of the Cu NPs/PMMA samples with 0 min (no treatment), 5 min, 30 min, and 90 min high-pressure CO₂ treatments, respectively. **b, d, f, h** Apparent height distributions of monodispersed NPs measured in Figures 4.1a, c, e, g, respectively.

Then three “intermediate” (37%)- C_N samples were treated separately by high-pressure CO_2 for 5 min, 30 min, and 90 min, respectively. The AFM images and distributions of H_N are shown in Figure 4.4. All the distributions of H_N were fitted by the Gaussian function, and the medians of H_N for the 5-min, 30-min, and 90-min CO_2 treated samples were 10.1 nm ($SD = 1.3$ nm), 5.8 nm ($SD = 2.6$ nm), and 4.7 nm ($SD = 3.6$ nm), respectively. The results in Figure 4.4 are similar to the ones in Figures 4.2e-j, reconfirming that the high-pressure CO_2 treatment used in this work is a reliable way for NP engulfment into PMMA.

Subsequently, the wettability of the “intermediate” (37%)- C_N samples was measured and summarized in Figures 4.5 a, b. The square (blue) spots in Figure 4.5a show the evolution of the SCAs starting from $81.5 \pm 0.5^\circ$ (bare PMMA film) to 99° (NPs/PMMA without high-pressure CO_2 treatment). The SCA appears to increase almost linearly (through the values $87 \pm 1^\circ$, 90° , and $93.5 \pm 0.5^\circ$ for NP/PMMA samples) as a function of medians of H_N (4.7 nm, 5.8 nm, and 10.1 nm, respectively), where $\chi^2 = 0.99$ with linear regression shown in Figure 4.5a (χ^2 is the coefficient of determination defined as $\chi^2 = 1 - SS_{RES}/SS_{TOT}$). Considering the fact that the high-pressure CO_2 treatment changed neither the morphology nor the wettability of the PMMA films (see Figure 4.1), the SCA of the Cu NPs/PMMA samples can only be associated to the variation of H_N of the decorating NPs.

Furthermore, the ACAs and RCAs of the samples were measured to explore the dynamic wettability of the samples, and the results are summarized in Figure 4.5b. In general, the results of ACA show a similar tendency to the results of SCA, where the ACA started from 83° (bare PMMA film, marked as “1”), and went up through $94 \pm 2^\circ$ (90 min, marked as “2”), $98 \pm 1^\circ$ (30 min, marked as “3”), and $101 \pm 1^\circ$ (5 min, marked as “4”) to $105.5 \pm 2.5^\circ$ (0 min, marked as “5”). Specifically, the difference between bare PMMA film and sample “2” for the ACA ($\sim 11^\circ$) was more significant than the one in SCA ($\sim 5.5^\circ$), indicating that the decorating NPs might play a more important role in dynamic wettability as compared with the static one. Furthermore, this phenomenon was more dramatic for the results of RCA, since the RCA started from $70.5 \pm 0.5^\circ$ (sample “1”) and decreased to 67° (sample “2”), 63° (sample “3”), $56.5 \pm 2.5^\circ$ (sample “4”) and $36.5 \pm 1.5^\circ$ (sample “5”). In general, the RCAs of the samples showed an inverse tendency as compared with that of ACAs and SCAs, while the “rate” of variation is higher compared with the ones of the ACA and SCA.

Notably, there was a significant difference ($\sim 20^\circ$) in RCA between the sample “4” and sample “5”, implying that the “southern” hemisphere of the decorating NPs may affect more the RCA than the “northern” one. According to the definition of the CAH $\theta_H = \theta_A - \theta_R$ (with θ_A the ACA and θ_R the RCA),⁴³ the θ_H is marked as the dashed areas in the (green) bars of Figure 4.5b, while it is shown as the circular (red) spots in Figure 4.5a. In detail, the behavior of θ_H for the samples is similar to that of the SCA (almost linear), starting from $12.5 \pm 0.5^\circ$ (bare PMMA) and with subsequent increase through $27 \pm 2^\circ$ (90 min), $35 \pm 1^\circ$ (30 min), $44.5 \pm 3.5^\circ$ (5 min), and $69 \pm 4^\circ$ (0 min). Similar to the dependence of SCA from H_N , the relationship between the CAH and H_N also followed a near-linear way with $\chi^2 = 0.97$ by linear regression. However, the slope of the profile

of CAH- H_N is larger than the one of SCA- H_N , suggesting again that the dynamic wettability is more “sensitive” to decorating NPs than the static one.

In addition, we have also summarized the SCAs derived from the Cu NPs/PMMA samples with various C_N values, as is shown by the square (blue) spots in Figure 4.5c. The profile starts from the PMMA film with an SCA of $81.5 \pm 0.5^\circ$, undergoing no notable change before the SCA of 37%- C_N sample (99°). Subsequently, the SCA increased in an almost linear manner through $107 \pm 2^\circ$ (46%- C_N sample) and $122 \pm 1^\circ$ (64%- C_N sample). Aiming to provide more supporting information by Figure 4.5d, the ACAs and RCAs were also measured from the samples, where the ACA started from 83° (bare PMMA film, marked as “1”), and went up through $89 \pm 1^\circ$ (12%- C_N sample, marked as “2”), $98 \pm 1^\circ$ (27%- C_N sample, marked as “3”), $101 \pm 1^\circ$ (37%- C_N sample, marked as “4”), $105.5 \pm 2.5^\circ$ (46%- C_N sample, marked as “5”), and $124.5 \pm 0.5^\circ$ (64%- C_N sample, marked as “6”). In detail, the difference between bare PMMA film and the 12%- C_N sample in ACA ($\sim 6^\circ$) was more significant than the one in SCA ($\sim 0.5^\circ$), reconfirming the conclusion derived from the results in Figures 4.5a, b that the decorating NPs likely play more important role in the dynamic than the static wettability.

Again, the RCAs of the samples showed an inverse behavior compared with the one of the ACAs or SCAs. Notably, the RCA displayed a sudden drop between the 27%- C_N and the 37%- C_N sample with a difference of 23° . Also, the results of CAH are marked as the dashed areas in Figure 4.5d. In detail, the gap between the 27%- C_N sample and the 37%- C_N sample in CAH ($\sim 36.5^\circ$) is much larger than the one in SCA (14°). On the one hand, the dynamic wettability analysis reconfirmed that the 37%- C_N was located near the critical point of the NP coverage, where the wettability changed strongly enough to indicate that this sample was a good candidate for the subsequent wettability-NP engulfment investigation. On the other hand, the comparison between the results for CAH and SCA supported the suggestion obtained from Figures 4.5a, b that the dynamic wettability is more “sensitive” to the decorating NPs than the static one.

Figure 4.5 Wetting studies of the “intermediate” (37%)- C_N Cu NPs/PMMA samples with various medians of H_N , and the Cu NPs/PMMA samples with various C_N before high-pressure treatments. **a** SCAs and CAH of the “intermediate” (37%)- C_N samples with various medians of H_N , where the square (blue) spots refer to the SCAs, and the circle (red) ones refer to the CAH. **b** ACAs and RCAs of the “intermediate” (37%)- C_N samples with various medians of H_N , where the green bars refer to the ACAs and the purple bars to the RCAs, and the dashed areas in the green bars refer to the CAH of the samples. **c** SCAs and CAH of the samples with various C_N coverages, where the square (blue) spots refer to the SCAs and the circle (red) ones to the CAH. **d** ACAs and RCAs of the samples, where the green bars refer to the ACAs and the purples ones to the RCAs, as well as the dashed areas in the green bars refer to the CAH.

4.2.7 Movability of NPs on PMMA

It has been proved that NPs on flat substrates can move if a lateral force was applied to the NPs.⁴¹ Therefore, scanning electron microscopy (SEM) and AFM measurements were conducted to the residual parts of the CA measured areas of the samples to check the movability of NPs on flat substrates under CA measurement, and discuss the effect of this movability to our results. However, both methods failed to characterize the samples for the following reasons: For SEM

measurement, a gold layer were deposited to the samples through magnetron sputtering because PMMA is not conductive. When a relatively thin layer of gold (5-10 nm) was deposited, the area scanned by the electrons would crack quickly because high magnification was applied to observe the NPs and the current of the electron beam was too concentrated and able to break the structure of the PMMA. Then the thickness of the deposited gold layer was enhanced to 20 nm to protect the sample during SEM measurement, the cracking phenomena was prevented but the morphology features of NPs were “buried” by the thicker gold layer. Subsequently, AFM measurements were used to observe the areas of the wetted areas left by a testing droplet. However, the wetted areas were more “blurred” than the unwetted areas, and we attributed this phenomena to some nanoscale contaminants which were formed during/after contact angle measurement. The nanoscale contaminants were observed by SEM measurement in Figure 4.9, and the contaminants “blurred” the AFM image because the lateral resolution of AFM was limited by the “tip-effect” preventing to distinguish NPs and the “new-born” nanoscale contaminants. Therefore, we could not derive any conclusion if the NPs could move above PMMA by the AFM measurements.

Therefore, the characterization was conducted indirectly, and Cu NPs/silica samples were prepared because silica wafers are smooth (which have similar morphology as the drop casted PMMA films in this work) and conductive, which are visible in SEM. Subsequently, the wetted areas left by static and dynamic CA measurements were observed through SEM and the results are shown in Figure 4.9. In Figure 4.9a-d, each SEM image was “divided” into two parts by a line in the middle, which referred to the boundary of the wetted area left by the CA measurement. The left part referred to the wetted area, while the right part referred to the unwetted area. The NP sliding phenomena were not obvious during the static CA measurement shown by Figure 4.9a, b. Nevertheless, an obvious NP concentration was observed at the edge of the wetted area left by a dynamic CA measurement (see Figure 4.9c, d), indicating that NP sliding took place during dynamic CA measurements. Furthermore, it is known that the movability of NPs on substrate is closely related to the adhesion force between the NPs and substrate.⁴² The substrate hardness is the most significant factor in the NPs adhesion to the substrate based on previous studies. Comparing the hardness of the substrates we used, PMMA, (70-100 MPa) and SiO₂ (5-10 GPa), the hardness of PMMA is much lower than the one of SiO₂, indicating that the Cu NP adhesion force to PMMA substrate is much higher than the NP adhesion force the SiO₂ substrate, which makes the Cu NPs much more difficult to slide on PMMA during the CA measurements. Therefore, it is reasonable to presume that NP movement on PMMA was not obvious during static CA measurement, and the NPs might be “pushed” by the TPL of the droplet during dynamic CA measurements. However, the NP sliding phenomena on PMMA would be less evident than the one on silica (which we actually observed in SEM). Nevertheless, after various time-span high-pressure CO₂ treatments, the NPs were more or less embedded into PMMA, which made the NPs hard to move during wetting measurements. This is also an advantage of high-pressure CO₂ induced NP engulfment, which can stabilize the NPs on PMMA and eliminate the NP-sliding

factor from the experiments. Therefore, even if we exclude the data point belonging to the Cu NPs/PMMA sample prior to CO₂ treatment, we could still obtain similar tendency of the relationship between wettability and the apparent height of NPs. Besides, in Figure 4.5a, we can also extrapolate the data point belonging to the Cu NPs/PMMA sample prior to CO₂ treatment through the other data points. The negligible difference between the experimental result and the extrapolated data indicates that the NP sliding phenomena, if any, does not have significant influence on the conclusions we have derived.

4.3 Conclusions

Using the technique of high-pressure CO₂ assisted NP engulfment, a series of Cu NP decorated PMMA surfaces with gradually varied nanostructured morphology were prepared by varying the time span of the high-pressure CO₂ treatment. Combining the characterization of transmission electron microscopy (TEM) and atomic force microscopy (AFM), an accurate 3-dimensional view of the morphology of the surfaces was presented. Subsequently, both static and dynamic wettability of the latter samples showed a near-linear tendency with the increase of apparent part of the decorating NPs. In addition, the effect of the coverage (C_N) of NPs on wettability was also checked compared with experimental results and theoretical analysis. In summary, our results provide a comprehensive understanding of how nanostructure affects the wettability of the decorated surfaces and shed light on obtaining certain wettability through structuring the surface morphology.

Appendix

The Storage Condition of the Samples

Figure 4.6 The schematic of the containers for keeping the Cu NPs/PMMA samples.

As it is shown in Figure 4.6, the Cu NPs/PMMA samples were kept in a petri dish with lid, and the dish was kept in a box with lid. Then the box was kept in a closet (which is clean and clear inside) in the laboratory. On one hand, this storage condition allow the sample to keep contact with ambient air and adsorb airborne hydrocarbons, on the other hand, this condition protect the samples from other contaminants, *e.g.*, dust and other particles in the open air.

Morphology of PMMA Films

Figure 4.7 AFM topography measurements for obtaining the Height distributions of PMMA samples with 0 min (no treatment), 5min, 30 min, and 90 min high-pressure CO₂ treatments, respectively which is shown in Figures 4.1c-f.

Additional AFM Topography Measurements

Figure 4.8 Additional AFM images obtained from the same samples used in Figure 4.4 for improving the statistics. a, b AFM images of the pristine Cu NPs/PMMA sample. c, d AFM images of the Cu NPs/PMMA sample with 5 min high-pressure CO₂ treatment. e, f AFM images of the Cu NPs/PMMA sample with 30 min high-pressure CO₂ treatment. g, h AFM images of the Cu NPs/PMMA sample with 90 min high-pressure CO₂ treatment.

Scanning Electron Microscopy (SEM) Studies of Wetted Areas

Figure 4.9 SEM studies of the boundaries of the wetted areas left by CA measurements. a Low-magnification SEM image of the boundary of a wetted area left by a static CA measurement. b Locally magnified SEM image of the area referring to the area in the red box in Figure S6a. c Low-magnification SEM image of the boundary of a wetted area left by a dynamic CA measurement. d Locally magnified SEM image of the area referring to the area in the red box in Figure S6c.

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Chapter 5

Modeling and Calculations of the Wettability of Nanoparticle Decorated Surfaces

Abstract

To analyze the experimental data concerning the wettability of the polymer surfaces with nanoparticle (NP) engulfment presented in Chapter 4, a model evaluating the wetting contribution of the nanomeniscus formed between a NP and the substrate, as well as a calculation of the van der Waals potential between the NPs and the testing droplet were conducted. Subsequently, the wettability of the surfaces decreases near-linearly with the increase of apparent height of the decorating NPs in both static (static contact angle) and dynamic (contact angle hysteresis) aspects (Shown in Figure 4.5 in Chapter 4). The observed tendency contradicts the Wenzel or Cassie-Baxter model, and it is explained by the contribution of the nanomeniscus formed between the decorating NP and the flat substrate. The capillary pressure from this meniscus is negative, and results in the increase of the contact angle with the apparent height (H_N) of the Cu NPs decorating the PMMA surface. Besides, the effect of the coverage (C_N) by NPs on the wettability can be explained on the same basis. In addition, the local adhesion effect between water and the decorating NPs were evaluated by calculation of the van der Waals (vdW) interaction potential (Φ_{CuN}). The linearity in the relationships of the wettability- H_N (SCA- H_N and CAH- H_N) and Φ_{CuN} - H_N indicated that the pinning effect originating from the vdW interaction between water and the decorating NPs might lead to hydrophobic behavior of the surfaces composed by hydrophilic materials. Our theoretical analysis provides a comprehensive understanding of how the nanostructure influences the wettability of the decorated surfaces, and sheds light on how to obtain certain wettability through nanostructuring of the surface morphology.

5.1 Introduction

Many efforts have been paid for understanding and describing surface wettability. The SCA (θ_Y) of a liquid droplet on a flat surface can be described using the surface tension of solid-air (γ_{sv}), solid-liquid (γ_{sl}), and liquid-air (γ_{lv}) by the Young's equation¹ $\gamma_{sv} = \gamma_{sl} + \gamma_{lv}\cos\theta_Y$. When $\gamma_{sv} - \gamma_{sl} < 0$, one obtains $\theta_Y > 90^\circ$ and the surface is termed as hydrophobic, while when $\gamma_{sv} - \gamma_{sl} > 0$, one obtains $\theta_Y < 90^\circ$ and the surface is termed as hydrophilic. For rough surfaces, the Wenzel² and Cassie-Baxter³ models have been widely used to describe the effect of roughness on surface wettability.

Although the two well-known models have enabled the explanation of the wettability of surfaces with various types of morphology, several other studies⁴⁻⁸ have demonstrated complex cases of surface wettability, where the Wenzel and Cassie-Baxter models could not explain the experimental data. Therefore, more efforts were paid for understanding the relationship between wettability and surface morphology. Using the concept "work of adhesion" introduced by Dupré,⁹ and taking the air-liquid interface on a solid as a one-dimensional system, Pease⁴ emphasized that the SCA is the result of an equilibrium position that the three-phase contact line (TPL) could reach. Then the dynamic wettability including advancing contact angle (ACA) and receding contact angle (RCA) were also expressed in terms of the work of adhesion.^{6,10} Wang *et al.*¹¹ argued that the 90° could not be used as the mathematical wetting threshold between the hydrophobicity and hydrophilicity in nanostructured surfaces through the results on nanofibrous membranes. Derjaguin^{12,13} discovered the solid surface is pre-wetted by a wetting film when in contact with a liquid droplet and described the film with the concept of the disjoining pressure. Furthermore, Boinovich *et al.*¹⁴ evaluated the wettability of curved surfaces on the basis of the isotherms of the disjoining pressure. In addition, through a series of wetting research of GST decorated surfaces, the nanomeniscus formed between an NP and the substrate was proved to make great contribution to the wetting behavior of NP decorated surfaces in our previous work.⁸ Moreover, the calculation of the van der Waals interaction introduced by Hamaker¹⁵ using the algebraic $1/r^6$ tail of the Lennard-Jones potential that describes the London dispersion energy between nonpolar molecules, was proved to be effective for analyzing wetting behaviors. This is case especially in some extreme situations, *e.g.*, graphene, where traditional wetting measurements were not available to obtain the wettability data.¹⁶ Therefore, a combination of carefully designed surfaces and systematic theoretical models offers a way to evaluate the influence of surface morphology on wettability.

In Chapter 4, A series of poly(methyl methacrylate) (PMMA) surfaces decorated by Cu nanoparticles (NP) with gradually varied morphology were prepared by high-pressure CO₂ treatment at various time spans. An intriguing tendency that the contact angle increases (almost in a linear method) with the apparent height (H_N) of the Cu NPs decorating the PMMA surface was revealed. In addition, the effect of the coverage (C_N) by NPs on the wettability can be explained on the same basis.

Therefore, a model evaluating the wetting contribution of the nanomeniscus formed between an NP and the substrate, as well as a calculation of the van der Waals potential between an NP and the testing droplet were conducted to describe the relationship between the wettability and the apparent height (H_N) of the Cu NP decorating PMMA surfaces. The calculations provide a comprehensive understanding of how nanostructure affects the wettability of decorated surfaces, and shed light on how to obtain certain wettability through nanostructuring of the surface morphology.

5.2 Results and Discussion

5.2.1 Influence of Nanomeniscus on Wettability

It is an experimental fact that neither of the two widely used Wenzel² and Cassie-Baxter³ models are suitable for analyzing the wettability of the Cu NP decorated PMMA surfaces. On the one hand, the materials used in this work are relatively hydrophilic with similar contact angles ($81.5 \pm 0.5^\circ$ for PMMA as the substrate material and 79° for Cu⁸ as the NP material), which makes impossible to generate hydrophobicity within the Wenzel model. On the other hand, the Cu NPs decorated PMMA surfaces were not in the Cassie-Baxter state, because the measured large contact angle hysteresis (see Figures 4.5a, c in Chapter 4) indicates strong adhesion force between the water meniscus and the tested surface. A similar situation for a surface decorated by NP was discussed previously⁸. It was proposed that the paradox can be resolved by taking into account the formation of a nanomeniscus when liquid wets a spherical particle on a flat surface. This concave nanomeniscus shown schematically in Figure 5.1a will give a negative contribution to SCA, increasing the effective contact angle of the decorated surface.

Let θ_S be the SCA of the substrate and θ_N is that for the NP material. In the Wenzel model, the effective SCA can be calculated according to the relation

$$\cos \theta_W = f_S \cos \theta_S + f_N \cos \theta_N, \quad (5.1)$$

where f_S and f_N are the ratios of the true area of the solid surface to the apparent area for the substrate and NP, respectively. For a sphere of radius R submerged to the substrate to a depth H these ratios are

$$f_S = 1 - C_N \frac{H(2R-H)}{R^2}, \quad f_N = C_N \frac{2(2R-H)}{R}, \quad (5.2)$$

where C_N is the surface coverage by the NPs (the derivation of Eq. (5.2) is given in Figure 5.5). The contact angle on the flat substrate is defined by the Derjaguin equation^{12,13}

$$\cos \theta_S = 1 + \frac{1}{\gamma} \int_{h_S}^{\infty} \Pi_S(h) dh. \quad (5.3)$$

Here h_S is the equilibrium thickness of the wetting film and $\Pi_S(h)$ is the disjoining pressure on the substrate. In Eq. (5.3) we neglected a small term $h_S \Pi_S(h_S)/\gamma$. If the wetting film is thin in

comparison with the size of NP $h \ll R$ and the particle is isolated, one could write a similar expression for $\cos \theta_N$ just changing $\Pi_s \rightarrow \Pi_N$ and $h_s \rightarrow h_N$. However, the nanomeniscus that is formed due to contact of the particle and substrate also gives a contribution to the contact angle and $\cos \theta_N$ can be presented as⁸

$$\cos \theta_N = 1 + \frac{1}{\gamma} \int_{h_N}^{\infty} \Pi_N(h) dh - \int_{h_2}^{\infty} \left(\frac{1}{r_1} - \frac{1}{r_2} \right) dh, \quad (5.4)$$

where $r_{1,2}$ are the principal radii of curvature of the meniscus. These radii always have different signs and obey the condition $r_1 \ll r_2$. This condition guarantees that the contribution of the meniscus is always reducing $\cos \theta_N$. Following the procedure described in the work of Boinovich *et al.*,¹⁴ in principle, one can take into account the effects of the order h/R .

Figure 5.1 Schematics for evaluation of nanomeniscus on the wettability of the Cu NP decorated PMMA films. **a** The configuration used to calculate contact angle with Eq. (5.4): R is the radius of the NP, r_1 is the negative radius of curvature, r_2 (not shown) is the positive radius of curvature in the orthogonal direction to the plane, h_1 is the thickness of wetting film on the substrate, h_2 is the thickness of wetting film on the NPs. **b** The schematic of partial NP engulfment into the PMMA film: H is the depth of the Cu NP submerged into PMMA, H_N is the apparent height of

the NP, and α is the angle between the baseline of PMMA and the tangent of the NP from the sectional view.

Let us denote the last term in Eq. (5.4) as

$$\Delta(\cos \theta_N) = - \int_{h_2}^{\infty} \left(\frac{1}{r_1} - \frac{1}{r_2} \right) dh. \quad (5.5)$$

It is responsible for the transition to hydrophobicity, but its direct evaluation is not a simple task. This term cannot be expressed only via the disjoining pressures $\Pi_S(h)$ and $\Pi_N(h)$ in the liquid films on the substrate and on the particle, respectively, because near the apex of the meniscus, a significant contribution comes from the interaction between these films. Moreover, pressure in the liquid gets a nondiagonal tensorial structure that influences the mechanical equilibrium.¹⁷ Equation of mechanical equilibrium in these conditions has been deduced¹⁸, but practically it can be used only for a few simple problems. While we have no a reliable way to estimate $\Delta(\cos \theta_N)$ it is possible to extract some information from the experimental data.

The observed linear dependence of the SCA on the apparent height $2R - H$ suggests that $\Delta(\cos \theta_N)$ is a quadratic function of the parameter $x = H/R$. It is clear from the fact that according to Eqs. (5.1) and (5.2) $\cos \theta_W$ is quadratic in x . To cancel the quadratic term $\Delta(\cos \theta_N)$ also has to include the term proportional to x^2 . The best linear fit of the data for $\cos \theta_W$ gives $\Delta(\cos \theta_N) = -(0.3955 - 0.0728x + 0.0006x^2)$. As obvious from Figure 4.6 the curvature radius r_1 increases when the particle submerges dipper. When the particle sunk completely, this radius has to be infinite and $\Delta(\cos \theta_N) = 0$. The best fit gives $\Delta(\cos \theta_N) = -(0.3955 - 0.0728x + 0.0006x^2)$. Therefore, it is expected that $\Delta(\cos \theta_N)$ has to disappear with the apparent height at $x = 2$. This is not the case, and we have to include explicitly the zero at $x = 2$ in the function $\Delta(\cos \theta_N)$. The behavior of this function at $x \rightarrow 2$ follows from a simple analysis. For $x > 1$ the angle α “(formed by the plane of the substrate and the tangent plane of the NP, which also passes through the intersection point of the substrate and the NP as it is shown in Figure 5b) at the base of the submerged spherical particle is $\alpha = \frac{\pi}{2} - \sin^{-1}(x - 1)$. In the limit $x \rightarrow 2$, it behaves as $\alpha \rightarrow \sqrt{2(2 - x)}$. In this limit, the same behavior is expected for $\Delta(\cos \theta_N)$ that is why at arbitrary x we are looking the function the form

$$\Delta(\cos \theta_N) = -(a_0 + a_1x + a_2x^2)\sqrt{1 - x/2}. \quad (5.6)$$

The best fit of the SCA data in Figure 4.5a (in Chapter 4) gives $a_0 = 0.3955, a_1 = 0.0261, a_2 = 0.0195$. The function (6) is shown in Figure 5.2a. It decreases nearly linear with the apparent height, but at a height below 4 nm, it is going to zero fast. Figure 5.7b shows the experimental data (red circles), the linear fit of the data $\theta_W = 81.70 + 1.228x$ (red dashed line), and the function that corresponds to Eq. (5.1) with $\Delta(\cos \theta_N)$ given by (5.6) (blue solid curve). One can see that the solid curve describes the data as good as the linear fit.

As a function of surface coverage, the SCA shows the threshold behavior. Although the Wenzel model (1) does not predict the threshold, it is clear that it has to exist since one particle on a large area cannot influence the contact angle. Above the threshold $\cos \theta_W$ behaves linearly with the

coverage. Modeling the threshold with a smooth transition, we look for the C_N dependence in the form

$$\cos \theta_W = \cos \theta_S + \frac{a(x)}{2} \left(1 + \tanh \frac{C_N - C_N^0}{\Delta C_N} \right) C_N, \quad (5.7)$$

where C_N^0 is the position of the threshold and ΔC_N is its width. The amplitude $a(x)$ depending on the parameter x is equal

$$a(x) = (2 - x)[-x \cos \theta_S + 2 \cos \theta_N + 2\Delta(\cos \theta_N)]. \quad (5.8)$$

Figure 5.2 Relationships between the wettability and morphology of Cu NP decorated PMMA surfaces. **a** The relationship between $\Delta(\cos \theta_N)$ and H_N fitted by Eq. (5.6). **b** The relationship between SCA and H_N , showing the experimental data (red circles), the linear fit (red dashed line), and the function that corresponds to Eq. (5.1) with $\Delta(\cos \theta_N)$ given by Eq. (5.6) (blue solid line). **c** The relationship between SCA and C_N , showing the experimental data (red circles), the best fit according to Eq. (5.8) (red dashed line), and the best fit by introducing a factor κ (which is positively correlated with the average number of the NP layer on the substrate) into Eq. (5.8) (blue solid line).

To compare this dependence with the data in Figure 4.5c (in Chapter 4) we take $x = 0$ that gives $a(0) = 4(\cos \theta_N - 0.3955)$. For this case the best fit of the data is shown in Figure 5.2c by the red dashed line. It can be seen that such a dependence fails to describe the data at high coverage. One would expect that above the threshold, the coverage is not reduced exactly to a monolayer of NPs. If we allow the amplitude $a(0)$ to be augmented by a factor κ , then the data are well described by the dependence (7) as shown by the blue solid line. The parameters corresponding to the best fit are $\kappa = 1.278$, $C_N^0 = 0.3202$, $\Delta C_N = 0.0868$. They correspond to the average distance between particles at the threshold equal $3.1R$. It means that any additional particle will form the second layer that justifies the value of κ larger than 1. In addition, the CAH data of the Cu NP decorated PMMA surfaces in Figures 4.5a, c (in Chapter 4) showed similar tendency as the SCAs of the relevant samples, which agreed with the theoretical model in the aspect of dynamic wettability.

5.2.2 Pinning Effects of Water Drops

Since the as-prepared Cu NPs decorated PMMA surfaces were not in the Cassie-Baxter state, because the measured high hysteresis ($69 \pm 4^\circ$) indicates high adhesion force between the water meniscus and the tested surface. Therefore, more efforts should be devoted to analyzing the observed rose petal-like wettability. It is known that the pinning effect of the three-phase contact line (TPL) of a rose petal-like surface yields strong resistance against the movement of the meniscus. Therefore, an evaluation of the pinning effect can be helpful for gaining understanding of the rose-petal-like wettability of the as-prepared samples.

Since the wetting behavior of the as-prepared samples could be closely related to the pinning effect between water and the decorating NPs, more efforts were devoted to calculate the van der Waals (vdW) interaction potential between the water and the decorating NPs. The latter was performed under the assumptions that: (i) the vdW interaction dominates the interactions between the Cu surface and liquid, and (ii) the vdW interactions are additive. Hence, we used the summation of vdW forces between atom-molecule pairs, as proposed by Hamaker¹⁵, which is a reasonable approximation to calculate qualitatively the vdW interaction potential W_{NL} between

one NP in the water droplet and one liquid molecule. The latter gave for the interaction potential W_{NL}

$$W_{NL} = \rho_N \int P_{NL} dV_N = - \int_{R-R_0}^{R+R_0} \frac{A_{NL}}{r^6} \pi \frac{r}{R} [R_0^2 - (R-r)^2] dr = -\pi A_{NL} \rho_N \frac{4R_0^3}{3(R+R_0)^3(R-R_0)^3}, \quad (5.9)$$

where ρ_N is the volume density of atoms in the NPs, P_{NL} is the vdW interaction potential between one atom in the NP and one liquid molecule, dV_N is the differential volume of the NP, A_{NL} is the vdW interaction parameter between one atom in the NP and one liquid molecule, R_0 is the radius of the NP, and R is the distance between the liquid molecule and the center of the NP. (The detailed calculation of the integral in this equation inspired by the work of Hamaker¹⁵ is seen in Appendix.) Using Eq. (5.9), one obtains the vdW interaction potential (Φ_{SN}) between a partly engulfed NP with apparent height H and the surrounding water molecules, which is given by the relation

$$\Phi_{SN} = \rho_L \int W_{NL} dV_L = -\pi A_{NL} \rho_N \rho_L \int_0^{2\pi} d\varphi \int_{\theta_0}^{\pi} d\theta \int_{R_0+\delta_N}^{\infty} \frac{4R_0^3}{3(R+R_0)^3(R-R_0)^3} R^2 \sin\theta dR, \quad (5.10)$$

with $\cos\theta_0 = (H - R_0)/R$ (see Figure 5.3a), ρ_L the volume density of the liquid, dV_L the differential volume of the surrounding liquid molecules, H_N the apparent height of the decorating NPs, and δ_N the equilibrium contact separation limiting the continuum calculations. Subsequent integration yields

$$\begin{aligned} \Phi_{SN} &= -2\pi^2 A_{NL} \rho_N \rho_L \int_{R_0+\delta_N}^{\infty} [(H_N - R_0)R + R^2] \frac{4R_0^3}{3(R+R_0)^3(R-R_0)^3} dR = \\ &= -\frac{1}{6} \pi^2 A_{NL} \rho_N \rho_L \left\{ \frac{2R_0 [2(H_N - R_0)R_0^2 + (R_0 + \delta_N)R_0^2 + (R_0 + \delta_N)^3]}{[(R_0 + \delta_N)^2 - R_0^2]^2} + \ln(\delta_N) - \ln(2R_0 + \delta_N) \right\}. \end{aligned} \quad (5.11)$$

Similarly, the vdW interaction potential Φ_B between one liquid molecule and a bulk substrate with an infinitely large flat surface and thickness is given by¹⁶

$$\Phi_B = \rho_B \int V_{BL} dV_B = -\frac{\pi \rho_B A_{BL}}{6z^3}, \quad (5.12)$$

where ρ_B is the atom volume density of the bulk. V_{BL} is the vdW interaction potential between one atom of the solid bulk and one liquid molecule, A_{BL} is the vdW interaction parameter between one atom of the bulk solid and a liquid molecule, and z is the separation distance between the substrate and the liquid molecule. Therefore, the vdW interaction potential per unit area between the bulk substrate and the liquid Φ_{BL} is given by

$$\Phi_{BL} = \rho_L \int_{\delta_B}^{\infty} \Phi_B dz = -\frac{\pi A_{BL} \rho_B \rho_L}{12\delta_B^2}, \quad (5.13)$$

where δ_B is the equilibrium contact separation limiting the continuum calculations. For convenience, we defined from Eq. (5.13) the parameter $\eta = A_{BL} \rho_B \rho_L = -12\Phi_{BL} \delta_B^2 / \pi$. Subsequently, Eq. (5.11) can be rewritten as

$$\Phi_{SN} = 2\pi \Phi_{BL} \delta_B^2 \left\{ \frac{2R_0 [2(H_N - R_0)R_0^2 + (R_0 + \delta_N)R_0^2 + (R_0 + \delta_N)^3]}{[(R_0 + \delta_N)^2 - R_0^2]^2} + \ln(\delta_N) - \ln(2R_0 + \delta_N) \right\}. \quad (5.14)$$

To proceed further with Eq. (5.14) one must calculate the potential Φ_{BL} for the case of a Cu surface. In fact, the surface wettability and the vdW interaction potential of a flat surface were connected by the modified Young-Dupré equation^{19,20}

$$\gamma_L(1 + \cos\theta) = -\Phi_{BL}, \quad (5.15)$$

where γ_L is the surface tension of the testing liquid, θ is the SCA, and Φ is the vdW interaction potential per unit area between liquid and the solid surface. If we consider a water droplet on a flat bare Cu surface, where the contact angle θ_{Cu} was measured to be 79° in our previous work,⁸ and take into account for the surface tension of water the value $\gamma_W = 72.8 \text{ mJ/m}^2$,²¹ Eq. (5.15) yields for the vdW interaction potential (per unit area) between water and a bare Cu surface the value $\Phi_{BL} = -86.7 \text{ mJ/m}^2$. In addition, R_0 in Eq. (5.14) was set to the half of the median of the apparent height of the NPs (14 nm) of the as-prepared Cu NPs/PMMA/silica sample without high-pressure CO_2 treatment. Since there are no experimental and theoretical data about the equilibrium contact separation δ_B between Cu surfaces and water molecules, we considered the value $\delta_B \approx 3 \text{ \AA}$, which is usually in the range 2-6 $\text{\AA}$ for other material systems.^{16,22-24} Finally, since all the parameters but H_N in Eq. (5.14) are constants, the relationship between Φ_{CuN} and H_N is linear as it is demonstrated in Figure 5.3b.

Figure 5.3 Calculation of vdW interaction potential between water and a decorating NP. **a** Schematic for the calculation of the integral for the vdW interaction potential between one NP

and the surrounding water molecules, where the volume element is indicated by the hatched area. **b** The vdW interaction potential between one decorating NP and surrounding water Φ_{SN} as a function of the apparent height H_N of the NPs.

As it is shown in Figure 5.3b, the vdW interaction potential between water and a decorating NP Φ_{SN} increases (the negative sign in Figure 5.3b means the force between the NP and water is attractive) linearly with the apparent height H_N of the NP. Since the NP distributions of the five samples measured in Figure 4.5a (in Chapter 4) were the same, the tendency of the vdW interaction potential between water and all the decorating NPs wetted by the meniscus should be identical as the one between water and one decorating NP (Φ_{SN}). With the assumption that the vdW interaction between the Cu NPs and the liquid is the dominant factor, the local adhesion between water and the NPs is expected to follow the same linear tendency. Moreover, the SCAs, as well as the CAHs of the “intermediate”- C_N samples in Figure 4.5a (in Chapter 4) show a near-linear tendency with the increase of H_N ($R^2 = 0.99$ in the linear regression shown in Figure 4.5a (in Chapter 4)). Therefore, the similarity in the dependence with H_N indicates a strong relationship between the local adhesion of water and NPs and wettability for both the static and dynamic aspects. Furthermore, the coherence in the tendencies of SCA- H_N and Φ_{CuN} - H_N of the as-prepared samples indicates the strong relationship between the rose petal effect and local adhesion between the meniscus and nanostructured decorations.

5.3 Conclusions

The experimental data concerning the wettability of the polymer surfaces with nanoparticle (NP) engulfment presented in Chapter 4 is analyzed based on two methods: one is a model evaluating the wetting contribution of the nanomeniscus formed between an NP and the substrate, and the other is a the evaluation of the adhesion effect between the NPs and the testing droplet, which is calculated by the van der Waals interaction potential between the NP and testing droplet.

Subsequently, the wettability of the surfaces decreases near-linearly with the increase of apparent height of the decorating NPs in both static (static contact angle) and dynamic (contact angle hysteresis) aspects (Shown in Figure 4.5 in Chapter 4). The observed tendency contradicts both the Wenzel and Cassie-Baxter models, and it is explained by the contribution of nanomeniscus formed between the decorating NP and the flat substrate. The capillary pressure from this meniscus is negative and results in the increase of the contact angle with the apparent height (H_N) of the Cu NPs decorating the PMMA surface. Besides, the effect of the coverage (C_N) by NPs on the wettability can be explained on the same basis.

Finally, the local adhesion between water and the decorating NPs was evaluated by calculation of the van der Waals (vdW) interaction potential (Φ_{CuN}) though other electrostatic type

contributions can play strong role since water is polar. The coherent linearity in the relationships of wettability- H_N (SCA- H_N and CAH- H_N) and Φ_{CuN} - H_N indicated that the pinning effect originated from the vdW interaction between water and the decorating NPs might lead to hydrophobic behavior of the surfaces composed by hydrophilic materials. In any case, our theoretical analysis provides a comprehensive understanding of how nanostructure affects the wettability of the decorated surfaces, and shed light on how to obtain certain wettability through nanostructuring of the surface morphology.

Appendix

Calculation of vdW Interaction Potential Between an Atom and a Particle

Figure 5.4 Schematic for the calculation of the integral for the vdW interaction potential between an atom and an NP.¹⁵

As it is shown in Figure 5.4, the sphere with radius of R_0 is “cut” by a sphere with radius r where the position of the atom (point P) is at the center. The integral is calculated with the interaction part (dashed area in Figure 5.4) as the integral element. The distance between the atom and the center of the sphere (OP) is R . Then the surface area ABC is calculated to be

$$Surface(ABC) = \int_0^{2\pi} d\varphi \int_0^{\theta_0} d\theta r^2 \sin \theta, \quad (5.16)$$

where θ_0 is given by

$$R_0^2 = R^2 + r^2 - 2Rr \cos \theta_0, \quad (5.17)$$

Therefore, the integration yields:

$$Surface(ABC) = \pi \frac{r}{R} [R_0^2 - (R - r)^2], \quad (5.18)$$

With the volume element indicated by the hatched area shown in Figure 5.4, the vdW interaction potential is given by

$$W_{NL} = - \int_{R-R_0}^{R+R_0} \frac{A_{NL}}{r^6} \pi \frac{r}{R} [R_0^2 - (R - r)^2] dr = -\pi A_{NL} \rho_N \frac{4R_0^3}{3(R+R_0)^3(R-R_0)^3}. \quad (5.19)$$

Derivation of the Ratios of the True Area of the Solid Surface to the Apparent Area

Figure 5.5 Schematics of the calculations of the ratios of the true area of the solid surface to the apparent area of Cu NPs/PMMA samples with NP engulfment. a Sectional view. b Top view.

Imagining that the whole PMMA substrate was homogeneously divided into n (n is the number of the decorating NPs) circular parts with radii R_P , and each part has an NP standing on it. Then we take each part as a “unit” (the shape of the “unit” does not affect the result, but the circular shape would simplify the process of the calculations). Since every “unit” share the same property, the ratios of the true area of the solid surface to the apparent area of Cu NPs/PMMA samples, f_S for the substrate and f_N for the NPs, are identical to the ones of the “unit”. Here we assume the shape of the PMMA surface of the “unit” as a circle, then the calculation was simplified, as it is shown in Figure 5.5. A spherical NP of radius R was submerged into the substrate to a depth H , and the circular interface (interfacial area) of the NP and the substrate with radius R_i is more clearly shown in Figure 5.5b, and it is marked with green color. Subsequently, the ratio of the apparent area of the substrate, f_S , is given by

$$f_S = \frac{A_P - A_i}{A_P} = 1 - \frac{A_i}{A_P} = 1 - \frac{\pi R_i^2}{\pi R_P^2}, \quad (5.20)$$

where A_P is the area of the PMMA surface prior to NP deposition, and A_i is the area of the interface of the NP and the PMMA. As it is shown in Figure 5.5a, $R_i^2 = R^2 - (R - H)^2$. Then Eq. (5.20) can be rewritten as

$$f_S = 1 - \frac{R^2 - (R - H)^2}{R_P^2}. \quad (5.21)$$

Since the NP coverage (C_N) is defined as $C_N = \pi R^2 / \pi R_P^2$, Eq. (5.21) is rewritten as

$$f_S = 1 - \frac{R^2 - (R - H)^2}{R^2 / C_N} = 1 - C_N \frac{H(2R - H)}{R^2}. \quad (5.22)$$

As it is shown in Figure 5.5a, the ratio of the apparent area of the NP, f_N , is given by

$$f_N = \frac{A_N}{A_P}, \quad (5.23)$$

where A_N is the surface area of the apparent part of the NP that can be calculated by

$$A_N = \int_0^{2\pi} d\varphi \int_{\theta_0}^{\pi} R^2 \sin \theta d\theta, \quad (5.24)$$

with $\cos \theta_0 = (R - H)/R$. Integration of Eq. (S5) yields:

$$A_N = 2\pi R(2R - H), \quad (5.25)$$

And Eq. (5.23) can be rewritten as

$$f_N = \frac{2\pi R(2R-H)}{\pi R^2/C_N} = C_N \frac{2(2R-H)}{R}. \quad (5.26)$$

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Summary

The studies in this thesis deal with wetting research. Wetting is a topic studied over more than 200 years. Dating as early as 1804, the Young's equation is the beginning of the efforts to explain the wetting phenomena. The Wenzel and the Cassie Baxter models are currently used to understand wetting research. Moreover, it is now widely accepted that the surface morphology plays as an important role on the wettability of real surfaces. Current developments in nanoscience and micro/nanotechnology allow the creation of several micro/nanostructured surfaces mimicking structures seen in nature, as for example the self-cleaning lotus leaf and the rose petals. Although many efforts have been performed to research the relationship of the surface condition (morphology as well as chemical composition) and wettability, it is still difficult to predict the wettability of a surface based on theories. The interactions among the solid surface, testing droplet, and the surrounding atmosphere are very complex. To investigate the relationship between nanoscale roughness and wettability, we use a monodisperse cluster beam of nanoparticles (NPs) to decorate well defined flat substrates, for the following reasons:

- i) with spherical morphology, the NPs are convenient for geometry-related calculations and analysis. The NPs can simplify the theory obtained from and applied to experimental data,
- ii) the High-Pressure Inert Gas Condensation with magnetron sputtering technique allows the depositing of NPs on a substrate without introducing additional chemical contaminants, crucial to control the contribution of the surface energy of the substrate and the NPs.

In Chapter 3, we present a systematic study of the wettability of nanostructured surfaces. These surfaces were fabricated with amorphous and crystalline NPs made from the phase-change material, in specific $\text{Ge}_2\text{Sb}_2\text{Te}_5$ (GST). Great care and attention was given in the effect of airborne surface contaminants (hydrocarbons) that greatly affect the surface wetting. A reversible hydrophilic-hydrophobic wettability "trigger" switch was seen by UV-Ozone treatments and subsequent exposure to hydrocarbons. Indeed, the as-prepared surfaces exhibited a hydrophilic state after thermal annealing or UV-O₃ treatment which can partially remove hydrocarbon contaminants, while a hydrophobic state was realized after exposure to hydrocarbon atmosphere. Using high angle annular dark field (HAADF) scanning transmission electron microscopy (STEM) for the specially designed GST NP decorated graphene substrates, a network of hydrocarbon connecting GST NPs was observed. Our findings indicate that airborne

hydrocarbons can significantly enhance the hydrophobicity of nanostructured surfaces. Also, the experiments reveal that previously defined hydrophilic materials can be used for the design of hydrophobic surfaces even if the meniscus is highly adhered to a solid surface, which is in agreement with our qualitative model involving the contribution of the nanomeniscus formed between the substrate and a decorating NP.

In chapter 4, we continued to study the intriguing phenomenon from where hydrophilic NPs that render a surface more hydrophobic. A series of poly(methyl methacrylate) (PMMA) surfaces decorated by Cu NPs with varying morphology were prepared by high-pressure CO₂ treatment (at various time intervals). We combine the TEM characterization and AFM data to produce, an accurate 3-dimensional view of the morphology. The wettability of these fabricated surfaces decreases near-linearly with the increase of apparent height of the decorating NPs in both static contact angle and in dynamic contact angle mode. The observed phenomena contradict the Cassie-Baxter and or Wenzel model and this is explained by the contribution of nanomeniscus formed between the decorating NPs and the flat substrate. As a result, the contact angle increases (almost in a linear method) with the apparent height (H_N) of the Cu NPs decorating the PMMA surface. Furthermore the effect of the coverage (C_N) by NPs on the wettability can be explained in the same reasoning. This experiment shows the important influence of the nanomeniscus on the wettability, normally not taken into account.

In chapter 5 a model is presented to describe and evaluate the experimental data for the wettability of the polymer surfaces with nanoparticle (NP) engulfment. The model evaluating the wetting contribution of the nanomeniscus formed between a NP and the substrate as well as calculation of the van der Waals potential between NP and testing droplet. The wettability of the surfaces decreases near-linearly with the increase of apparent height of the decorating NPs in both static and dynamic aspects. Again the observed phenomena contradicts both Cassie Baxter and Wenzel model. The model explains the contribution of nanomeniscus formed between the decorating NP and the flat substrate. The capillary pressure from this meniscus is negative and results in the increase of the contact angle with the apparent height (H_N) of the Cu NPs decorating the PMMA surface. Besides, the effect of the coverage (C_N) of the NPs on the wettability can be explained on the same basis. In addition, the local adhesion effect between water and the decorating NPs was evaluated by calculation of the van der Waals (vdW) interaction potential (Φ_{CuN}). The coherent linearity in the relationships of wettability- H_N (SCA- H_N and CAH- H_N) and Φ_{CuN} - H_N indicated that the pinning effect originated from the vdW interaction between water and the decorating NPs might lead to hydrophobic behavior of the surfaces composed by hydrophilic materials. By studying the wettability of simple NP/plain substrate morphology, we present a series of experimental results and relevant new theoretical analysis. As a result we provide a comprehensive understanding how the nanostructure affects the wettability of NPs decorated surfaces, and provide insight how to obtain a certain wettability through nanostructuring the surface morphology.

Finally, focusing our studies on the wettability of a simple NP/plain substrate morphology, we presented a series of experimental results and relevant theoretical analysis that provide a comprehensive understanding of how nanostructure affects the wettability of the decorated surfaces. These studies also shed light on how to obtain certain wettability through nanostructuring of the surface morphology. For future research, we would like to design surfaces with more complex nanostructure and reveal the relationship between wettability and surface morphology, which would introduce our study closer to practical use. In addition, the experimental results in this work are open to explanation by other models or calculations in the future.

Samenvatting

De studies in deze thesis gaan over wetting in het Nederlands bevochtiging genaamd. Het is een onderwerp dat al meer dan 200 jaar wordt bestudeerd. Al in 1804 heeft Thomas Young de grondbeginselen van bevochtiging beschreven. Het Cassie-Baxter en Wenzel model zijn de gangbare theorieën die het bevochtigings fenomeen beschrijven en zijn van toepassing op “echte” oppervlakken. Young is een meer theoretisch model. In de huidige zienswijze is het algemeen aanvaard dat de morfologie van het oppervlak een zeer belangrijke rol speelt bij de bevochtigbaarheid van het oppervlak. Dankzij een huidige ontwikkeling van Nano wetenschap en micro/nanotechnologie zijn verschillende micro/nano gestructureerde oppervlakken gecreëerd om oppervlaktestructuren zoals er in de natuur zijn na te bootsen, bijv. een lotusblad en rozenblaadjes. Het doel van deze kunstmatige oppervlakken is om een zekere bevochtigbaarheid te verkrijgen. Hoewel er veel inspanningen zijn geleverd om de relatie tussen de oppervlaktetoestand (zowel morfologie als chemische samenstelling) en bevochtigbaarheid te onderzoeken, is het nog steeds moeilijk om de relatie tussen bevochtigbaarheid en oppervlakte morfologie te voorspellen op basis van huidige theorieën, mede omdat de interacties tussen het vaste oppervlak, de test vloeistof, en de omringende atmosfeer (lucht) erg complex is. Om de relatie tussen ruwheid op nanoschaal en bevochtigbaarheid te onderzoeken, hebben we nanodeeltjes (NDs) gekozen als de nanogestructureerde decoratie om de volgende redenen:

- i) met sferische morfologie zijn de NDs beter geschikt voor geometrie-gerelateerde berekeningen en analyse, zodat de theorie te vereenvoudigen is, verkregen uit experimentele data,
- ii) de gebruikte techniek (hogedruk magnetron sputteren) voor produceren van NDs op substraat is mogelijk zonder gebruik te maken van chemische contaminanten (liganden etc), noodzakelijk om de oppervlakte energie van het substraat en de ND's bijdrage te kunnen onderzoeken.

In Hoofdstuk 3 presenteren we een systematische studie van de bevochtigbaarheid van nanogestructureerde oppervlakken met amorphe en kristallijne NDs. Deze zijn afgeleid van het fase-verandering materiaal $\text{Ge}_2\text{Sb}_2\text{Te}_5$ (GST). In het bijzonder is aandacht besteed aan het effect van koolwaterstoffen in de lucht die een “groot” effect hebben op de oppervlaktebevochtiging. Een reversibel/omkeerbaar hydrofiel-hydrofobe gedrag is aangetoond door een gecombineerde Ultra-Violet Ozone (UV- O_3) behandelingen en blootstelling aan koolwaterstof atmosfeer. De

Inderdaad vertoonden de zoals geprepareerde oppervlakken een hydrofiele toestand na thermisch uitgloeien of UV-O₃ behandeling die koolwaterstofverontreinigingen gedeeltelijk kan verwijderen, terwijl een hydrofobe toestand werd gerealiseerd na blootstelling aan een koolwaterstofatmosfeer.

Met behulp van HAADF STEM beelden (hoge hoek ringvormig donker veld scanning transmissie elektronen microscopie) van de hiervoor speciaal ontworpen GST NDs TEM grids met grafeen substraat, zijn een een netwerk van koolwaterstof verbindende GST NDs waargenomen. Onze bevindingen geven aan dat koolwaterstoffen in de lucht de hydrofobiciteit van nanogestructureerde oppervlakken aanzienlijk kunnen veranderen. De experimenten laten eveneens zien dat intrinsiek hydrofiele materialen kunnen worden gebruikt voor het ontwerp van hydrofobe oppervlakken, waarbij de meniscus sterk hecht aan oppervlak, alles in overeenstemming is met ons kwalitatieve model waarbij de bijdrage van de nanomeniscus wordt gevormd tussen het substraat en een decorerende ND.

In hoofdstuk 4 gaan we verder in het onderzoeken van het intrigerende fenomeen dat hydrofiele NDs het oppervlak meer hydrofoob zouden kunnen maken, hebben we een reeks poly (methylmethacrylaat) (PMMA) oppervlakken geprepareerd met Koper NDs (CuNDs) met een geleidelijk variërende morfologie. Deze zijn gesynthetiseerd door een hogedruk CO₂ behandeling op verschillende tijdspannes. Met behulp van TEM en AFM karakterisatie is een nauwkeurig 3-dimensionaal beeld van de oppervlakte morfologie gecreeerd. De gemeten contact hoek laat een relatie zien van een bijna lineair af met de toename van contact hoek en de schijnbare hoogte van de decorerende NDs. Dit in zowel de statische (statische contacthoek) alsook in de dynamische contacthoek. Deze waargenomen relatie is in tegenspraak met gangbare modellen te weten het Wenzel of Cassie-Baxter model. Het verschil kan worden verklaard in de bijdrage van nanomeniscus gevormd tussen de decorerende ND en het vlakke substraat. Als gevolg hiervan neemt de contacthoek toe (practisch lineair) met de schijnbare hoogte (H_N) van de Cu NDs die het PMMA-oppervlak decoreren. Bovendien kan het effect van de dekking (C_N) door NDs op de bevochtigbaarheid op dezelfde basis worden verklaard. Het experiment toont de belangrijke invloed van de nanomeniscus op de bevochtigbaarheid aan, doorgaans wordt hier geen rekening mee gehouden.

Om de experimentele gegevens betreffende de bevochtigbaarheid van de polymeeroppervlakken met nanodeeltjes (ND) verzwelging gepresenteerd in Hoofdstuk 4 te analyseren, een model dat de bevochtigingsbijdrage van de nanomeniscus gevormd tussen een ND en het substraat evalueert, evenals een berekening van de van der Waals potentieel tussen ND en testdruppel werden uitgevoerd. Vervolgens neemt de bevochtigbaarheid van de oppervlakken bijna lineair af met de toename van de schijnbare hoogte van de decorerende NDs in zowel statische als dynamische aspecten. De waargenomen neiging is in tegenspraak met het Wenzel of Cassie-Baxter-model en wordt verklaard door de bijdrage van nanomeniscus gevormd tussen de decorerende ND en het vlakke substraat. De capillaire druk van deze meniscus is negatief en

resulteert in een toename van de contacthoek met de schijnbare hoogte (H_N) van de Cu NDs die het PMMA-oppervlak decoreren. Bovendien kan het effect van de dekking (C_N) door NDs op de bevochtigbaarheid op dezelfde basis worden verklaard. Bovendien werd het lokale adhesie-effect tussen water en de decorerende NDs geëvalueerd door berekening van het van der Waals (vdW) interactiepotentiaal (Φ_{CuN}). De coherente lineariteit in de relaties van bevochtigbaarheid- H_N (SCA- H_N en CAH- H_N) en Φ_{CuN} - H_N gaf aan dat het vastzetten effect afkomstig was van de vdW interactie tussen water en de decorerende NDs, zou kunnen leiden tot hydrofoob gedrag van de oppervlakken die zijn samengesteld door hydrofiele materialen.

Gericht op het bestuderen van de bevochtigbaarheid van eenvoudige ND/gewone substraatmorfologie, presenteerden we een reeks experimentele resultaten en relevante theoretische analyses, die een uitgebreid begrip gaven van hoe nanostructuur de bevochtigbaarheid van de versierde oppervlakken beïnvloedt en licht werpen op hoe een bepaalde bevochtigbaarheid kan worden verkregen door middel van nanostructurering van de oppervlaktmorfologie. Voor toekomstig onderzoek willen we oppervlakken ontwerpen met een meer complexe nanostructuur en de relatie tussen bevochtigbaarheid en oppervlaktmorfologie blootleggen, wat onze studie dichterbij praktisch gebruik zou introduceren. Bovendien staan de experimentele resultaten in dit werk in de toekomst open voor verklaring door andere modellen of berekeningen.

Acknowledgements

Four years ago, I arrived in Groningen together with other 17 new Ph.D. candidates by the same flight. How time flies, and now it is time to say goodbye and thanks.

Firstly, I would like to thank my supervisor, Prof. George Palasantzas, who offered me the chance to be a member of this group and meet my dear colleagues. You are always ready to help, I am impressed by the feedbacks and supports in the e-mails from you on your holidays and midnights which were practically your off-work time. I am grateful for your inspiration and long-time support. Also, I have learned the philosophy from you that one should give freedom to his student as a supervisor.

Many thanks goes to my second promoter, Prof. Bart J. Kooi. Thanks a lot for the discussions and suggestions from you, I am impressed by your knowledge which covered every colleague's project, the fluency of your speeches used to made me feel that you were a talk-show artist. Many thanks also goes to Prof. Vitaly B Svetovoy, your knowledge of theories in liquid-solid interactions really helped me a lot, I appreciate the support and encouragement from you. Also, I would like to thank Prof. Harold Zandvliet, Prof. Patrick Onck and Prof. Marleen Kamperman for being part of the assessment committee. Moreover, I would like to acknowledge the financial support of China Scholarship Council. Thanks also goes to Xingxu and Weifeng, who has helped me a lot with the application of CSC

I would like to thank all the members in my group nanostructured materials and interfaces (NMI). Gert, many thanks go to you for your help to solve my technique problems, and thank you for the translation of the summary. Also, you have offered a lot of fun to the group, I cherish the talks we have made and wish you good luck for your Ph.D. ceremony. Anna, thank you for your support to solve the problems in my daily life. Bin, you are the "Dashixiong" in our group, and you are also my "daily-supervisor" in my first stage of scientific work in our group, thank you for the guidance and suggestions. Thank you also for your training of badminton, I miss the time when you get our group members together to play badminton, and I wish you have a bright research career and a happy life. Thanks also go to Lijuan, our "Dashijie", you were a professional consultant when I was a new Ph.D. candidate, which benefited me a lot when I faced problems in the Netherlands. Also, you can cook really delicious Chinese food, I miss them a lot. I hope you enjoy your life with Peiliang. Jamo, a handsome guy who is like John Snow in "Game of the Throne", thank you for your help for figuring out my problems in daily life, e.g., making the

phone calls in Dutch, and I am pleased to be your colleague for 4 years. Paul, a sunshine big boy, thank you for your funny stories about the Netherlands, I enjoyed a lot to discuss Dutch culture with you and Jamo. Xukai, “dashixiong II”, a warm-hearted guy, I feel very lucky to be your colleague and in the same office for my whole Ph.D. career. We are from the same province in China, and we experienced a lot of similar issues in Groningen and helped each other during our hard time. I hope you enjoy your life in Dusseldorf and good luck with your application for the Humboldt foundation. Xiaotian, the most handsome Chinese guy in the physics chemistry building, thank you for the discussions and supports when I faced problems, I believe your broad view in science will help you become a brilliant researcher. Heng Zhang, it is really a coincidence that we both are from the school of Materials Science and Engineering of CSU. Thank you for the discussions and your abundant ideas, wish you good luck for your future scientific life. Zahra, the most beautiful Iranian girl I have ever met, I am glad to be your colleague for four years and wish you happy life in Europe. Sytze, thank you for the introduction of the culture and the education system of the Netherlands, I am looking forward to more high-IF papers written by you. Daniel, an energetic scientist, I cherish the discussion we have made, and I am happy to hear that you have moved in a satisfying apartment. Prof. Xiaolan Hu, thank you for the suggestions from your life experience. Prof. Jian Sun, thank you for the discussions. Lingyu, I hope you and Dong lead a happy life with your baby. Jing, an efficient and intelligent girl, thank you for the discussions when I was in a hard time. Atul, an optimistic and talkative guy, thank you for the joy and happiness you have brought to us. Julian, I am happy to see you getting your Bachelor and Master degrees in our group, and I am glad to hear that you will continue your scientific career under the supervision of George, I hope you will have a fruitful Ph.D. life here. Lam, I was moved when you offered me the samples the day after my first Christmas in Groningen, thank you for your contribution to our work, and I am lucky to cooperate with you.

I would like to thank my paranymphs, Xiaotian and Heng Zhang, for the preparations for my Ph.D. ceremony.

I would like to thank my friends I met in Groningen. Hong Lian, we are from the same city, and you are the first friend I made in Groningen, I appreciate the friendship and the delicious dishes you have made. I would like to thank the friends in Stationsplein 9, Jian Gao, Shun Fang, Yafeng, Shuai Feng, Jiajia, Qian Chen, Fangyuan, Beibei, Mengfan, Yukun, Yi Yu, Lulu, Xiu Jia, Liping, Jianjun. You swept my anxiety of being new in Groningen and made me feel like I was in a big family. I would not forget the barbecues and the dinners (which were often organized by Yi Yu, who was called “Director Yu” for his technique in photography, also thank you for the organizations), especially for the dinner of the Spring Festival in 2017, although I was the only one cried after my playing the violin. Jiajia, thank you for your suggestion when I was confused about my future, wish you lead a happy life in Wuxi. Qian Chen, thank you for the interesting stories and the discussions, good luck with your research. Fangyuan, I still miss the days we went to Dutch classes and then shopping in the Albert Heijn near the fish market. Xiu Jia, it is great to

go spring outing with you because you almost know the names of all the plants we meet, and you have a lot of stories to share with us. Special thanks goes to Mengfan, I enjoyed a lot to share the same house with you, you taught me a lot about cooking, house-cleaning and many other living skills. I also enjoyed the talks according to medicine, career and life. Especially, I appreciate your suggestions when my mother met healthy problems, which helped me to get through that hard time. I hope you can become a famous doctor and save a lot of lives in the future. Many thanks also goes to Rongjing, you and Jian Gao make me feel I have a family in Groningen, I can't forget each time I visited you, the "eating and taking" of the baozi and jiaozi always make me feel like I was visiting my parents. Wish you lead a happy life with Jian and have a bright future. Thanks also goes to Pu Yang for the fun you shared with me, wish you happy life in Taiyuan. Ling Liu, your achievements in your academic career (you have published many high IF papers) as well as in your life (owns a house with a fish pond, which is my dream) have inspired me a lot, wish you stay healthy and happy with Zhiwei in the Netherlands. Huatang, you are always ready to help others, and you are the most popular guy I met in Groningen, thank you for the talks and suggestions. Changsen and Yingying, I feel lucky to meet you in Groningen and wish you happy life in the Guangzhou. Xiaohong, it is interesting to meet you by selling you a hair dryer, I admire the contribution you have made to fighting the COVID-19 as a doctor in Wuhan. Wenze and Yingying, I am glad to meet you in Groningen, wish you have a great future. Chongnan, thank you for the interesting stories you shared with me, you are the most talkative person I have ever met, and I will definitely buy a ticket if you have a talk show, wish you stay happy with Yuhan. Hongping, I had great times to discuss with you during SEM operation times, I was impressed with your humor and wisdom, good luck with your application for your next state of scientific career. Minpeng, I am happy to be your neighbor during my last year in Groningen. Lisheng, I had great time to share the room with you when we went skiing in Winterberg, Germany, and I was also surprised that you had spent 4 years in my hometown, Handan, to get your bachelor's degree. Zhiwen, the most kind-hearted Chinese in Groningen, thank you for sharing the watermelon and stories with me. Fei Wu, thank you for cleaning my pot after borrowing it from me, which really saved its life, wish you can take Heavy back to China successfully and continue your stories. Jane Wu, I am lucky to meet a beautiful elder sister in Groningen, your insistence and optimism have inspired me a lot, I wish you will find a nice city to work and live in. Liqiang and Yuanyuan, you are the winners here for not only both of you have got Ph.D. but also giving birth to an adorable baby here in Groningen. Many thanks also goes to Ang Sha and Xiaoling. Ang, thank you for practicing taekwondo with me, I have learned a lot about martial arts from you. Xiaoling, you are my shijie from CSU, and you also acted as an elder sister, offering me a lot of suggestions. I wish you stay happy with each other. Shuai Fang, a real genius who has been excellent since his childhood, thank you for the pizza and discussions, hope you keep your dream and realize it one day. Thanks also goes to Prof. Feng Chen and Prof. Hao Bian for helping me apply for a funding at the end of my Ph.D. period. Bei Tian and Miao Guo, how fascinating the life is to meet you in Groningen. I had not imagined what would happen among us when I firstly met Miao when we visited the same apartment and tried to rent it. Thank you for bringing a lot

of fun and social connections during my difficult time under the shadow of COVID-19, which is also my last period in Groningen. Combined with the beauty and humor of Bei and wisdom and reliability of Miao, I believe you will create more interesting stories and stay happy. Thanks also goes to Puhua, Hongyu, Junjie, Lin Chen, Jin Li, Qikai, Yang Heng, Chunli, Xiaoyan, Yuan He, Shanshan, Yana, Yizhou, Xiaocui, Jing Liu, Jing Li, Wen Zhou, Feng Yan, Wei Zhang, Tinghua, Jie Zong and Zhenlei, Huaizhou and Fan Xu, Yu Li and Jing Zhao, Cheng Wang and Yuequ, I am happy to meet you in this city, and wish you good luck in the future.

Thank you Groningen, I love this city, quiet and peaceful, comfortable to live in, and suitable for studying and thinking. See you again, Groningen! See you again, RUG! See you again, my friends!

此外，我还要感谢我的亲友们，感谢你们一直以来对我以及我父母的照顾，让我在海外免去很多后顾之忧，特别感谢我的两户老邻居们，感谢多年以来对我的关怀与照顾，希望每年过年都能见到大家，祝李玢琛老弟一切顺利，也祝亚萌哥和家奇嫂子白头偕老，朵朵健康成长。

最后，我要感谢我的父母，感谢你们的养育之恩，也感谢你们对我在海外漂泊多年的理解与支持，我在荷兰学习工作的背后是你们的担忧与付出，希望你们能够健康平安。

Weiteng Guo

Groningen

September, 2020

List of Publications

- (1) Effect of Airborne Hydrocarbons on the Wettability of Phase Change Nanoparticles Decorated Surfaces. Weiteng Guo, Bin Chen, Van Lam Do, Gert H. ten Brink, Bart J. Kooi, Vitaly B. Svetovoy, and George Palasantzas. *ACS Nano* 13, 13430-13438
- (2) Tunable Wettability of Polymer Films by Partial Engulfment of Nanoparticles. Weiteng Guo¹, Chongnan Ye, Gert H. ten Brink, Katja Loos, Vitaly B. Svetovoy, and George Palasantzas. *Submitted*

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