View metadata, citation and similar papers at core.ac.uk
brought to you by CORE
provided by Christ University Bengaluru: Open Journal Systems

Mapana Journal of Sciences
2020, Vol. 19, No. 2, 73-93
ISSN 0975-3303 | https://doi.org/10.12723/mjs.53.5

Wettability Gradients on Soft Surfaces

Soorya S Raj*, Saya Ann Suresh*, and T P Vinod*†

Abstract

Properties, behaviors, and applications of soft materials depend decisively on the characteristics of their surfaces. Physical features and chemical functionality of the soft surfaces control their interactions with the surroundings thereby deciding their responses to various surface phenomena. A gradient of such surface features i.e., a gradual directional change in a chemical or physical characteristic across a surface will result in a gradual change in the response of the surface to its surroundings in the same direction. The resolution and stability of large-scale surface gradients with controlled directionality enable their applications in the fields of microfluidics, sensing, optics, and biology. Wettability gradients are prominent classes of gradients which are constituted by gradual increase or decrease of hydrophobicity/ hydrophilicity across a surface. This short review will summarize the advancements in the preparation, properties, and applications of wettability gradients on soft surfaces. Qualitative description of the fabrication processes, properties, and practical applications of the gradients are included along with our views about the future prospects of these systems.

Keywords: Soft surfaces, wettability, surface gradients, droplet movement, hydrophobicity, hydrophilicity.

* Department of Chemistry, CHRIST (Deemed to be University), Bengaluru, India
*†vinod.tp@christuniversity.in (Corresponding author)

1. Introduction

During the past few decades, various new methods were developed for furnishing the surfaces of materials with appropriate chemical and physical properties [1]. Properties and applications of soft surfaces depend significantly on the characteristics of their surfaces. Physical and chemical properties of a uniform surface show spatial uniformity whereas gradient surfaces possess properties which gradually change over a given distance. Gradients are observed ubiquitously in natural systems such as carnivorous plants like the Venus flytrap. Artificial methods to create gradients on surfaces can generally be divided into two groups: direct deposition and post-deposition treatment methods. In the direct deposition methods, gradients are built up on a substrate by gradually depositing the materials by natural or artificial methods. In the post-deposition methods, desorption or controlled removal of coated materials from a substrate is used to create the gradients [2]. Gradient surfaces can be classified on the basis of dimensionality, time dependency, length scale, composition, functionality, and directionality. Gradients of various types exhibit different physicochemical nature and functionality [3]. Based on the fundamental characteristics, gradients are classified as physical and chemical gradients (**Figure 1**). Chemical gradients (wettability gradients, in most cases) on soft surfaces can be prepared by increasing or decreasing the concentration of a surface bound species gradually across the surface. Morphological gradients (physical gradients) are obtained by altering specific morphological features across the soft surfaces in incremental or decremental fashion [4].

The ability of a liquid to maintain close contact with a solid surface is usually referred to as the wettability and it is determined by adhesive and cohesive forces in operation. For hydrophilic surfaces, the degree of wettability (of water) is high and for hydrophobic surfaces it is low.

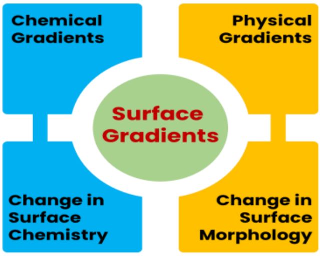

Figure 1: Schematic representation of the classification and characteristics of surface gradients

Among various types of gradients, wettability gradients have been attracting attention from various disciplines of materials research. Surface wettability can be changed by the surface physical and chemical properties. Gradients are created by the gradual variation of hydrophobicity/hydrophilicity across a surface. Generally, surface chemical gradients are fabricated by gradual removal or addition of a material on a substrate [8]. Chemical gradients facilitate the directed motion of liquid droplets on substrate surface and this phenomenon is responsible for directing several physical and biological processes. Wettability gradients can also be created by changing the physical features of the surface such as roughness, flatness etc. Surface chemical and physical gradients with controlled wettability and directionality provide new pathways for the development of materials and methods related to surface microfluidic devices, cell adhesion, protein adsorption, and engineered surfaces for fluid handling potentially applicable to bio-analytical procedures [10].

Gradients are obtained using natural as well as artificial phenomena and processes. Among the various methods for the creation of gradients, bio-inspired preparation of special wettable surfaces caught the attention of researches from various fields and is a fast-growing field [10].Self-cleaning property of lotus leaves, the superior water-walking ability of water striders, the directional adhesion of butterfly wings, the antifogging functionality of mosquito eyes, the antireflection of superhydrophobic cicada wings, the water collection of the Namib Desert beetle and spider silk, and the submarine self-cleaning ability of fish scale are some of the peculiar biological systems that exhibit special wettable surfaces. These surfaces find applications in the field of patterned wettability, superhydrophobic surfaces and integrated devices [5-7,9]. Several research groups had investigated the possibilities of preparing gradients on soft surfaces. An important initial work was published by Chaudhury and Whitesides, using vapor diffusion and distance-dependent exposure of a polished Si wafer to vapours of decyltrichlorosilane [11].This strategy of creating chemical gradients was used on different types of surfaces in the following years.A variety of physical, chemical and physicochemical strategies were demonstrated for the fabrication of wettability gradients on soft surfaces, which are based on plasma, UVO, diffusion, photolithography, photo-degradation, and several other methods. The existing methods for the preparation of wettability gradients are based on complex and expensive procedures. Hence, there is a demand for simple and inexpensive methods for the fabrication of surface wettability gradients and active research is happening in this area. This short review will briefly summarize the recent developments and future prospects of chemical as well as physical wettability gradients of soft surfaces.

2. Observation and characterization of wettability gradients

Wettability gradients can be qualitatively and quantitatively observed and analysed using various techniques such as contact angle measurements, X-ray photo electron spectroscopy, Atomic force microscopy, micro droplet density, polarization modulation etc. Measurement of wettability is usually done using the direct visualization of the shape of a droplet (mostly aqueous droplet) on the gradient surface. Spectroscopic techniques and other sophisticated techniques are used for the detailed analysis of the composition and morphology of the gradients **(Table 1)**.

Table 1: Analytical techniques used for the characterization of surface gradients

Technique	Property measured	Inference
Contact Angle	Contact Angle	Wettability
XPS	Number of electrons emitted per unit time	Surface chemical composition
AFM	Measures local properties such as height, friction, magnetism with a probe	Topographical data
Microdroplet Density	Density	Wettability
Polarization Modulation	Frequency	Interaction between polarized IR light and the molecular dipoles

2.1 Contact angle measurements

Contact angle is the angle between the tangential to the liquid surface and the solid surface at a point where a liquid vapor interface meets a solid surface. Contact angle determines the solids wettability with a particular liquid (**Figure 2**). Measuring contact angle helps in determining the wettability and surface energy of solid surfaces. It is also used to determine the work of adhesion for different liquids [12, 13]. Contact angle quantifies the wettability of a solid surface by the liquid according to the Young's equation.

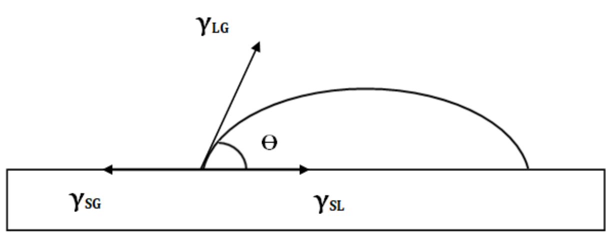

Figure 2: Water droplet on a surface. The resulting surface interfacial tensions γ_{LG}, γ_{SG} and γ_{SL} are related to contact angle θ through Young's equation.

$$\gamma_{LG} \text{ Cos } \theta = \gamma_{SG} - \gamma_{SL} \quad (1)$$

Equation (1) represents Young's equation for a water droplet on a surface where γ_{LG} is the surface tension of the liquid that acts tangential to the drop surface, γ_{SG} is the surface tension of the liquid that acts along the solid surface, γ_{SL} is the solid-liquid interfacial energy and θ is the contact angle. If the wettability of the surface is not uniform across the surface or if there is a gradient of wettability present on the surface, the contact angles measured at two ends of the same droplets will not be the same. The droplet edge present on more hydrophilic region will show a lower value for contact angle and the droplet edge present on the less hydrophilic region will show a higher contact angle. This difference in contact angle can be used as a tool for the detection of wettability gradients.

2.2 X- Ray photoelectron spectroscopy (XPS)

This technique is used for the compositional analysis of surfaces. It makes use of photo electric effect to determine the surface chemical composition of the sample surface. X-rays emitted from the anode material which is usually Mg or Al will initiate the photoelectric effect [14]. If the energy of the incoming photons is large enough to overcome the work function of the material, electrons will be emitted from the atomic shells which then travel to the analyzer. The analyzer detects the number of electrons emitted per minute with a particular kinetic energy (E_{kin}) which gives an energy spectrum. This E_{kin} is then converted into binding energy E_B using the equation,

$$E_B = h\gamma - E_{kin} - \phi \quad (2)$$

Based on the binding energy of electrons measured, each peak can be assigned to electrons from a particular orbital of a specific atom. Relative intensity of the peaks can be correlated to the abundance of that particular atom or element on the surface. If the gradient on the surface is created by varying concentration of a surface-bound species, site specific XPS measurements or XPS mapping would give a direct evidence for the existence of the gradient.

2.3 Atomic force microscopy

Atomic force microscopy helps in the topographical surface study of materials in atomic level resolution. This set up consists of a cantilever which is fitted with a sharp tip at the end. This sharp tip scans over the surface of the sample. The movement of the cantilever is from the lateral and normal forces that acti upon it. The reflection of a laser beam from the back of the cantilever determines the deflection which is detected by a position sensitive photo diode. The deflection depends on the distance between the tip and the surface. A scan of the tip over the entire surface will give the 3D morphology of the surface. There are two modes of AFM operations: tapping mode and contact mode. Strong repulsive force close to the surface is used in contact mode. Van der Waals forces at a distance of 10 to 100 nm from the surface are utilized in tapping mode measurement. AFM can be used for friction force measurement and for the study of biological specimens. AFM is used for the analysis of morphological gradients constituted of varying physical features on surfaces [15-18].

2.4 Micro droplet density- semi quantitative technique

The soft surfaces when allowed to cool down in humid environment condense water vapour to water droplets. This condensation figures can be determined by measuring the density of the water microdroplet at a specific time after the first droplet nucleates on the surface. The condensation figures differ based on wettability, roughness and contamination. Water condenses more on surfaces that are hydrophilic, rough and contaminated than surfaces that are hydrophobic, smooth and clean. Even surfaces with higher hydrophilicity differ in the microdroplet density because of non-uniformity in the submicron range [20]. Surfaces with a wettability gradient will show a gradual variation in the number and size of water droplets across their lengths.

2.5 Polarization modulation- infrared reflection adsorption spectroscopy

This technique is used to study chemical bonds and its orientation on surfaces. It makes use of the interaction between polarized IR light and the molecular dipoles. Depending upon the atoms involved and the nature of vibrations involved, the chemical bonds at the surface of the adsorbate absorb the IR light at a certain frequency. It is a non-destructive and highly sensitive technique. But the characterization is limited to the IRrange [19].Site-specific measurements using this technique provides a direct indication of chemical wettability gradients on surfaces.

3. Wettability gradients from chemical gradients

Nature of functional groups present on the soft surfaces determines their wettability. Presence of hydrophilic functional groups such as polyelectrolytes and polar moieties increases the wettability while nonpolar functional groups present on the surfaces decreases the wettability. A gradual increase or decrease of the concentration of polar or nonpolar functional groups on the surface facilitates the formation of wettability gradients. Surface modification of the soft surfaces towards the formation of wettability gradients can be realized through appropriate chemical treatments. Functional groups inherently present on the surfaces can interact with other functional groups during chemical treatment and can alter the surface chemical properties of the soft material.

3.1 Preparation of surface chemical gradients

Wettability gradients can be created on soft surfaces by changing the chemical composition of a surface in a particular direction (**Table 2**). These gradients can be created mainly through two ways: (i) by modifying the outermost layer of the material using electrochemical treatment (ii) by chemically transforming the outer surface using high energy radiations, and (iii) by applying a suitable surface coating [10].

3.1.1 Electrochemically generated wettability gradients.

Surface gradients in which physicochemical properties are fixed during the time of creation are termed as static surface gradients whereas those which can alter the properties are regarded as dynamic gradients. Electrochemical gradient fabrication techniques can be used for creating both static and dynamic surface gradients, which are useful for cell-adhesion studies. These techniques are versatile and highly compatible with various kinds of solvent systems.

Table 2: Experimental methods for the creation of surface chemical gradients

Method	*Experimental Strategy*
Diffusion	Through controlled vapor deposition on the surface
Electrochemical method	Through polyatomic ion deposition by applying potential between the electrodes
Plasma treatment	Surface etching through treatment highly ionized gas
Immersion Technique	Controlled immersion and withdrawal of a substrate to a solution with variable velocity
Differential thermal treatment	Applying variable amount of thermal energy during thermal curing

Abbott and co-workers fabricated electrochemical gradients by making use of surface pressure and they used these surfaces for the controlled motion of liquids on millimeter scales [21]. Hanley and Fuoco successfully manufactured chemical gradient surfaces on poly(methyl methacrylate) surface using poly atomic ion deposition method. These surfaces exhibit a gradient of wettability between 10° to 120° [22]. Reversible and controlled movement of droplets on a wettability surface by applying electrochemical potential was studied by Tada and Yamada [23]. This method is useful for the transportation of small droplets on a surface within small spaces. Berggren and colleagues studied controlled water movement on poly aniline surface with a static wettability gradient created by in-plane potential gradient [24]. Droplet manipulation on wettable gradient surface was also studied by Zheng and his co-workers. They used electro-deposition method for the fabrication of variously shaped wettable gradients on conductive substrates like copper and aluminium [25]. Feng and his colleagues developed radial wettability gradients on the surface of a graphite plate by simple one-step anodic oxidation process and these gradients find application in the field of microfluidic devices and biotechnology [26].

3.1.2 Surface chemical gradients through diffusion methods.

Diffusion methods for creating surface wettability gradients are of different types; in the form of vapor diffusion, solvent diffusion and matrix diffusion. The pioneering work in the field of surface wettability gradients was done by Chaudhury and Whitesides. They used vapor diffusion methods for the creation of gradients on the surface of silicon wafer using decyltricholrosilane [11]. This method is used by Zhao and Beysen for conducting the droplet growth studies on a heterogenous silicon wafer surface. Solvent diffusion method for the creation of surface density gradients using octadecyldimethylsilyl chains (C18) on silica was also reported in literature. These surfaces exhibited a contact angle varying between 12° to 105°. The vapour diffusion method was extensively used by various groups to create wettability gradient surfaces usable for the fabrication of grafted brushes on to polymer surfaces, force measurements of water droplet on these surfaces, studies regarding the effect of grafting densities of polymer chains and, for droplet manipulation studies. Genzer's group presented several variations of vapor diffusion-based methods for the formation of gradients on surfaces and they used these surfaces as templates for the controlled assembly of materials and for controlled movement of droplets. Yang and co-workers used these methods for the formation of wettability gradients to study the spontaneous transport and coalescence of droplets. Diffusion by means of a matrix method was used for the generation of molecular gradients, fibronectin gradients [27-37].

3.1.3 Surface chemical gradients through plasma treatment

Plasma treatment is a surface modification technique which uses highly ionized gas to etch the surface. Plasma treatment can modify surfaces for improved bonding, wetting characteristics, in order to establish hydrophobic and hydrophilic properties etc. Radio frequency plasma discharge method was used for the fabrication of continuous wettability gradients on different polymer surfaces, to study the interaction of different types of cells and its reproduction rate on these surfaces. Vasilev's group used oxygen plasma method to produce pH tunable wettability gradients whereas the role of surface wettability on osteoblast response was studied by Schwartz group. Gradients of poly(butylene terephthalate) on fibrous material with controllable pore size was fabricated by researchers at Donghua University and this method overcomes the inherent disadvantage of the method of centrifugation. Shielded gas plasma was also used for the preparation of gradient surfaces on polyethylene surface and it has application in protein adsorption [38-44].

3.1.4 Surface chemical gradients through immersion technique

Nicholas Spencer's group developed simple methods for the formation of surface chemical and morphological gradients using controlled slow immersion of substrates into solutions [1,45]. Superwettability is an exceptional phenomenon of wetting surfaces in which contact angle reaches high values; such kind of surfaces can be fabricated using an immersion technique. A superwettability gradient surface obtained contact angle varying from 30° to 150° by slowly immersing a gold substrate into a solution containing lipoic acid derivatives. Another method was reported by Chen and Zhu in which these surfaces were developed by the electroless displacement of zinc coated carbon steel by nickel ions using chemical immersion technique[46,47].Various other methods like corona discharge [48-50], irradiation and replacement [51], differential thermal treatment [52,53], printing [54,55], degrafting[56], laser fabrication [57], physically controlled polymerisation [58,59] etc are also used for the fabrication of surface chemical gradients.

3.2 Properties and applications of surface chemical gradients

Based on the characteristic features, chemical gradients have various types of applications such as protein adsorption, cell adhesion, microfluidics, DNA barcoding etc. (**Figure** 3).

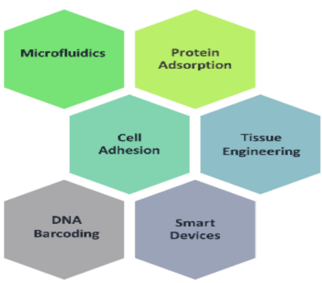

Figure 3: Applications of surface chemical gradients

3.2.1 Protein adsorption

Non-specific protein adsorption on surfaces with different wettability and polymer chain density plays an important role in biomedical field for the creation of biocompatible implant surfaces to resist foreign body response. In the case of biosensors, specific protein adsorption is required. Depending on the type of protein and adsorption condition, its behaviour of adsorption vary for the same kind of wettability gradient. The adsorption of fibrinogen and immunoglobulin was reduced when albumin was present in the solution due to the difference in adsorption kinetics between the proteins [44,56,52].

3.2.2 Cell adhesion

Cell adhesion finds a significant role in many of the biomedical applications. Adhesion and proliferation of cells on surfaces depend upon surface properties like wettability, roughness etc. Different type of wettability gradients are used for cell adhesion studies [46].

3.2.3 Microfluidics

Microfluidics is basically the manipulation of liquids at the microscale. The directional transportation of droplets is of great importance in microfluidic devices, for that it requires external energy. Wettability gradients present on the the devices provides this external energy input that drive the liquids on a microscale [60-62].

3.2.4. DNA barcoding

Surface wettability gradients were used for the alignment and elongation of double stranded DNA for a wide variety of genomic investigations. Unlike common methods where the sample is withdrawn from the surface slowly, here it is spontaneously moved from hydrophobic to hydrophilic end [63].

Other applications of surface chemical gradients include drug discovery [64], tissue engineering, oil- water separation [66], Smart devices [65], liquid transportation [56] etc.

4. Wettability gradients from morphological gradients

Over last few decades, various approaches have been used for the fabrication of different kinds of morphological gradients by modifying the surface roughness, shape, size and length. Morphological gradients are created by changing the physical dimensions of certain surface features gradually across the surface.

4.1 Preparation of morphological gradients

Several physical and chemical processes are used for the creation of morphological gradients on soft surfaces **(Table 3)**

Table 3: Experimental methods for the creation of physical gradients on surfaces

Method	*Experimental Strategy*
Laser etching method	simple one step process for the creation of rough surfaces
Dip coating	Adsorption of negatively charged silica particles on to positively charged surfaces
Electrochemical etching	The pore size of the substrate can be changed by adjusting the concentration of the electrolyte and current density
Chemical polishing	Polishing the surface using suitable chemical reagents
Lithography	Process of printing from a plane surface

4.1.1 Laser etching method

Laser etching is a simple one step process for the creation of rough surfaces. Hierarchical micro and nano structures on a silica surface were fabricated by various researches using this method and those surfaces exhibited a change of contact angle from hydrophilic to superhydrophobic[57,65].

4.1.2 Dip coating procedure

This method is based on the adsorption of negatively charged silica particles onto positively charged surfaces. The adsorption of silica particles is a type of kinetically controlled process and thus a nanoparticle density gradient can be created by a simple dip coating process [68].

4.1.3 Electrochemical etching

In this process, silicon is used as anode because of its pore size. The pore size can be changed by adjusting the concentration of the electrolyte and current density. By selecting appropriate electrodes, current density gradient along the substrate can be achieved leading to porosity gradient in the silicon. Another approach to obtain porosity gradient in silicon is by placing unpolished sides of two silicon wafers facing each other. When voltage is applied between the wafers the current density decreases from the edges to the centre, thus making the pores of different diameters ranging from 20nm to 3nm from the edge to the centre [10].

4.1.4 Chemical polishing

Herein the morphological gradients are fabricated by gradually polishing the surface. There are two steps in this process. The first step is the particle erosion followed by the chemical polishing. Aluminium is the most suitable material for this process. But it cannot be used as a general procedure. Therefore replicas of this material can be formed. Negative impressions are created using poly vinyl siloxane replica material. An epoxy positive is casted from the negative creating a replica roughness gradient. These replicas can be made functional by coating them with metal oxides. The morphological gradients created by these techniques have a wide range of applications especially in the biomedical fields and for studying wetting phenomenon [10].

4.1.5 Lithography

Lithography is an extensively used method for the fabrication of morphological gradients. Depending upon the amount of photon energy needed in different locations during exposure we can use variety of lithographic techniques such as photolithography, capillary force lithography etc [67] to create protrusions and dips on surfaces.

4.2 Properties and applications of morphological gradients

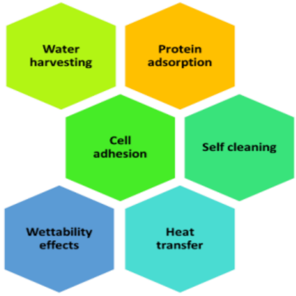

Figure 4: Applications of physical or morphological gradients

4.2.1 Protein adsorption

During the past few years protein adsorption on gradient surfaces has become an interesting field of research. Major studies are conducted based on the adsorption of albumin and fibrinogen proteins. Research studies have found that the adsorption of albumin and fibrinogen proteins increased to half amount with the increase in the roughness of titanium roughness gradient [69]. Morphological gradients on titanium surfaces have more affinity towards high molecular weight fibronectin proteins than fibrinogen. Rechendorff's group reported that the amount of fibrinogen increased due to the increasing of RMS roughness [70]. Protein adsorption test were conducted to determine the amount that get adsorbed on the surface. In case of multiple protein system, high mobility proteins get adsorped on the surface first. Then it was replaced by proteins with large surface affinity [71]. Specific and non-specific protein adsorption on surfaces with different wettability and roughness play an important role in biomedical applications but it is not studied extensively because the porosity gradients are difficult to characterize due to the change in the thickness of the porous layer and the pore size [72, 73].

4.2.2 Cell adhesion

Different types of wettable gradient surfaces are used for the study of cellular adhesion. Cell growth and attachment is highly influenced by the surface roughness of the biological specimen.

Cell adhesion on a particular surface depends upon the presence of certain kind of proteins, hence protein density gradients are also prepared and tested. A variety of cells including fibroblast, osteoblast and endothelial cells are used for adhesion studies on various surface having nanoscale morphological gradients. Dalby's group reported that there is an increase in the cellular adhesion and osteoblastic differentiation with increase in nanoscale disorder [74]. Other applications include heat transfer, self-cleaning and water harvesting etc [10].

5. Conclusions and outlook

Gradients of properties on soft surfaces offer greater functionality and applications of soft materials. Periodic variation of surface properties can provide directionally tuned responses of the surfaces, which are pertinent to applications in various areas such as materials science, analytical science, sensing, coating, construction, biomedical devices, microfluidics and many more. Versatile methods and strategies providing rational control of directionality and functionality have been reported in the literature for the creation of chemical as well as physical gradients on soft surfaces. Recent advances in the analysis and characterization of soft surfaces has enhanced the understanding of the formation and the physicochemical responses of wettability gradients on soft surfaces. Processes leading to the formation of wettability gradients on soft surfaces are being further investigated for better resolution, stability, and scalability. Future development in this area is expected to enable the diversification and effectuation of the applications in these materials.

6. Acknowledgements

Soorya S Raj is thankful to Council of Scientific & Industrial Research (CSIR) for research fellowship and T. P. Vinod is thankful to Centre for Research, CHRIST (Deemed to be University) for its research support. Authors are thankful to Mr. Sreekumar Nair for support regarding library and resources.

References

[1] J. Genzer and R. R. Bhat, “Surface-bound soft matter gradients,” *Langmuir*, vol. 24, no. 6, pp. 2294–2317, 2008, doi; 10.1021/la7033164

[2] J. Genzer, “Soft Matter Gradient Surfaces,” *A John Wiley & Sons, Inc., Publication,* doi;10.1002/9781118166086

[3] J. Genzer, “Surface-Bound Gradients for Studies of Soft Materials Behavior,” *Annu. Rev. Mater. Res.*, vol. 42, no. 1, pp. 435–468, 2012, doi; 10.1146/annurev-matsci-070511-155050

[4] S. H. Oh, T. H. Kim, G. Il Im, and J. H. Lee, “Investigation of pore size effect on chondrogenic differentiation of adipose stem cells using a pore size gradient scaffold,” *Biomacromolecules*, vol. 11, no. 8, pp. 1948–1955, 2010, doi; 10.1021/bm100199m.

[5] S. Zhang, J. Huang, Z. Chen, and Y. Lai, “Bioinspired Special Wettability Surfaces: From Fundamental Research to Water Harvesting Applications,” *Small*, vol. 13, no. 3, pp. 1–28, 2017, doi; 10.1002/smll.201602992

[6] M. N. Kavalenka *et al.*, “Adaptable bioinspired special wetting surface for multifunctional oil/water separation,” *Sci. Rep.*, vol. 7, pp. 1–10, 2017, doi; 10.1038/srep39970

[7] K. Liu, X. Yao, and L. Jiang, “Recent developments in bio-inspired special wettability,” *Chem. Soc. Rev.*, vol. 39, no. 8, pp. 3240–3255, 2010, doi; 10.1039/B917112F

[8] J. Miles, S. Schlenker, Y. Ko, R. Patil, B. M. Rao, and J. Genzer, “Design and Fabrication of Wettability Gradients with Tunable Pro fi les through Degrafting Organosilane Layers from Silica Surfaces by Tetrabutylammonium Fluoride,” 2017, doi; 10.1021/acs.langmuir.7b02961

[9] X. Yao, Y. Song, and L. Jiang, “Applications of Bio-Inspired Special Wettable Surfaces,” pp. 719–734, 2011, doi; 10.1002/adma.201002689

[10] S. Morgenthaler, C. Zink, and N. D. Spencer, “Surface-chemical and -morphological gradients,” *Soft Matter*, vol. 4, no. 3, pp. 419–434, 2008, doi; 10.1039/B715466F

[11] C. Mk and W. GM, “How to make water run uphill,” *Science (80-.).*, vol. 256, no. June, pp. 1539–1541, 1992, doi; 10.1126/ science .256. 5063.1539

[12] H. J. Butt, I. V. Roisman, M. Brinkmann, P. Papadopoulos, D. Vollmer, and C. Semprebon, “Characterization of super liquid-repellent surfaces,” *Curr. Opin. Colloid Interface Sci.*, vol. 19, no. 4, pp. 343–354, 2014, doi; 10.1016/j.cocis.2014.04.009

[13] X. Wang and L. Wang, “Dynamic Contact Angle on a Surface with Gradient in Wettability,” 2016, http:// docs.lib.purdue.edu/ iracc/ 1806

[14] Z. Huang *et al.*, "Preparation and characterization of gradient wettability surface depending on controlling Cu(OH) 2 nanoribbon arrays growth on copper substrate," *Appl. Surf. Sci.*, vol. 259, pp. 142–146, 2012, doi; 10.1016/j.apsusc.2012.07.006

[15] Cohen, S. and Lightbody, M. Atomic Force Microscopy/Scanning Tunneling Microscopy. Kluwer Academic Press, New York, 1999.

[16] Wiesendanger, R. Scanning Probe Microscopy and Spectroscopy - Methods and Applications. Cambridge University Press, Cambridge, 1994.

[17] Binnig, G., Quate, C. and Gerber, C. Atomic Force Microscope. Physical Review Letters,56, 930–933, 1986,doi; 10.1103/PhysRevLett.56.930

[18] Parkinson, B. Procedures in Scanning Probe Microscopies. John Wiley and Sons Ltd., Chich-ester U.K., 1997.

[19] S. Morgenthaler, "Surface Chemical Gradients," no. 17278, pp. 1–177, 2007.

[20] R. J. Van Tatenhove-pel, J. A. Hernandez-valdes, O. P. Kuipers, and M. Fischlechner, "Microdroplet screening and selection for improved microbial production of extracellular compounds," *Curr. Opin. Biotechnol.*, vol. 61, pp. 72–81, 2020, doi; 10.1016/j.copbio.2019.10.007

[21] N. L. Abbott, "References and Notes 1.," vol. 283, no. January, pp. 57–60, 1999.

[22] M. B. J. Wijesundara, E. Fuoco, and L. Hanley, "Preparation of chemical gradient surfaces by hyperthermal polyatomic ion deposition: A new method for combinatorial materials science," *Langmuir*, vol. 17, no. 19, pp. 5721–5726, 2001, doi; 10.1021/la010592e

[23] R. Yamada and H. Tada, "Manipulation of droplets by dynamically controlled Wetting Gradients," *Langmuir*, vol. 21, no. 10, pp. 4254–4256, 2005, doi; 10.1021/la046982t

[24] J. Isaksson, N. D. Robinson, and M. Berggren, "Electronic modulation of an electrochemically induced wettability gradient to control water movement on a polyaniline surface," *Thin Solid Films*, vol. 515, no. 4, pp. 2003–2008, 2006.doi; 10.1016/j.tsf.2006.04.001

[25] Y. P. Hou, S. L. Feng, L. M. Dai, and Y. M. Zheng, "Droplet Manipulation on Wettable Gradient Surfaces with Micro-/Nano-Hierarchical Structure," *Chem. Mater.*, vol. 28, no. 11, pp. 3625–3629, 2016, doi; 10.1021/acs.chemmater.6b01544

[26] S. Feng *et al.*, "Radial wettable gradient of hot surface to control droplets movement in directions," *Sci. Rep.*, vol. 5, pp. 1–7, 2015, doi; 10.1038/srep10067

[27] H. Zhao and D. Beysens, "From Droplet Growth to Film Growth on a Heterogeneous Surface: Condensation Associated with a Wettability

Gradient," *Langmuir*, vol. 11, no. 2, pp. 627–634, 1995, doi; 10.1021/la00002a045

[28] S. L. City and S. L. City, "Human serum albumin adsorption onto gradient surface," vol. 2, 1994, doi: 10.1016/0927-7765(94)80056-1

[29] H. Zhao and D. Beysens, "From Droplet Growth to Film Growth on a Heterogeneous Surface: Condensation Associated with a Wettability Gradient," *Langmuir*, vol. 11, no. 2, pp. 627–634, 1995, doi; 10.1021/la00002a045

[30] C. Engineering *et al.*, "Combinatorial Study of the Mushroom-to-Brush Crossover in Surface Anchored Polyacrylamide," pp. 9394–9395, 2002,doi; 10.1021/ja027412n

[31] H. Suda and S. Yamada, "Force Measurements for the Movement of a Water Drop on a Surface with a Surface Tension Gradient," pp. 529–531, 2003,doi; 10.1021/la0264163

[32] B. Zhao, "A Combinatorial Approach to Study Solvent-Induced Self-Assembly of Mixed Poly (methyl methacrylate)/ Polystyrene Brushes on Planar Silica Substrates : Effect of Relative Grafting Density," no. 23, pp. 11748–11755, 2004, doi; 10.1021/ja027412n

[33] J. Genzer, K. Efimenko, and D. A. Fischer, "Formation mechanisms and properties of semifluorinated molecular gradients on silica surfaces," *Langmuir*, vol. 22, no. 20, pp. 8532–8541, 2006, doi; 10.1021/la061016r

[34] S. Y. W. Fang, "Droplets coalescence and mixing with identical and distinct surface tension on a wettability gradient surface," pp. 785–795, 2013, doi; 10.1007/s10404-012-1096-2

[35] B. Liedberg and P. Tengvall, "Molecular Gradients of ω-Substituted Alkanethiols on Gold: Preparation and Characterization," *Langmuir*, vol. 11, no. 10, pp. 3821–3827, 1995, doi; 10.1021/la962053t

[36] J. T. Smith, J. K. Tomfohr, M. C. Wells, T. P. Beebe, T. B. Kepler, and W. M. Reichert, "Measurement of Cell Migration on Surface-Bound Fibronectin Gradients," vol. 41, no. 17, pp. 8279–8286, 2004, doi; 10.1021/la0489763

[37] K. Mougin, A. S. Ham, M. B. Lawrence, E. J. Fernandez, and A. C. Hillier, "Construction of a Tethered Poly (ethylene glycol) Surface Gradient For Studies of Cell Adhesion Kinetics," no. 18, pp. 4809–4812, 2005, doi; 10.1021/la050613v

[38] Willi A. M. G. Pitt, "Fabrication of a Continuous Wettability Gradient by Radio Frequency Plasma Discharge," vol. 133, no. 1, pp. 223–227, 1989., doi; 10.1016/0021-9797(89)90295-6

[39] J. H. Lee, G. Khang, J. W. Lee, and H. B. Lee, "Interaction of Different Types of Cells on Polymer Surfaces with Wettability Gradient," vol. 330, pp. 323–330, 1998, doi; 10.1006/jcis.1998.5688

[40] J. Choee, S. J. Lee, Y. M. Lee, J. M. Rhee, H. B. Lee, and G. Khang, "Proliferation Rate of Fibroblast Cells on Polyethylene Surfaces with Wettability Gradient," 2003, doi; 10.1002/app.20048

[41] J. Hwa *et al.*, "The responses to surface wettability gradients induced by chitosan nano fi lms on microtextured titanium mediated by speci fi c integrin receptors," *Biomaterials*, vol. 33, no. 30, pp. 7386–7393, 2012, doi; 10.1016/j.biomaterials.2012.06.066

[42] D. A. Links, "pH-tunable gradients of wettability and surface potential †," pp. 8399–8404, 2012, doi; 10.1039/C2SM25221J

[43] P. Jiang, Y. Gao, X. Chen, Q. Ke, X. Jin, and C. Huang, "Poly(butylene terephthalate) Fiber Assembly with Controllable Pore Size and Gradient Wettability: Potential in Simplifying Cell Culture Procedure," pp. 1192–1197, 2018,doi; 10.1021/acsmacrolett.8b00545

[44] H. T. Spijker, R. Bos, W. Van Oeveren, J. De Vries, and H. J. Busscher, "Protein adsorption on gradient surfaces on polyethylene prepared in a shielded gas plasma," vol. 15, pp. 89–97, 1999, doi; 10.1016/S0927-7765(99)00056-9

[45] S. Neuhaus, C. Padeste, and N. D. Spencer, "Versatile Wettability Gradients Prepared by Chemical Modification of Polymer Brushes on Polymer Foils," pp. 6855–6861, 2011,doi; 10.1021/la2005908

[46] A. Popelka *et al.*, "Modulation of wettability , gradient and adhesion on self-assembled monolayer by counterion exchange and pH," *Journal of Colloid and Interface Science* vol. 512, pp. 511–521, 2018, doi; 10.1016/j.jcis.2017.10.086

[47] C. Xu, H. Liu, W. Liang, L. Zhu, W. Li, and H. Chen, "Creating gradient wetting surfaces via electroless displacement of zinc-coated carbon steel by nickel ions," *Appl. Surf. Sci.*, vol. 434, pp. 940–949, 2018, doi; 10.1016/j.apsusc.2017.11.022

[48] J. I. N. H. O. Lee and H. A. I. B. A. N. G. Lee, "Characterization of Wettability Gradient Surfaces Prepared by Corona Discharge Treatment," vol. 15, no. 2, pp. 563–570, 1992, doi; 10.1016/0021-9797(92)90504-F

[49] J. H. Lee and H. B. Lee, "A wettability gradient as a tool to study protein adsorption and cell adhesion on polymer surfaces," *Journal of Biomaterials Science* no. January 2015, pp. 37–41, doi; 10.1163/156856293X00131

[50] J. H. Lee and H. B. Lee, "Platelet adhesion onto wettability gradient surfaces in the absence and presence of plasma proteins," *J. Biomed. Mater. Res.*, vol. 41, no. 2, pp. 304–311, 1998, doi; 10.1002/(sici)1097-4636(199808)41:2<304::aid-jbm16>3.0.co;2-k

[51] R. Article and J. A. Szymczyk, "Experimental investigation of the motion and deformation of droplets on surfaces with a linear

wettability gradient," vol. 158, pp. 155–158, 2009, doi; 10.1140/ epjst/ e2009-00898-6

[52] X. Lu, J. Zhang, C. Zhang, and Y. Han, "Low-Density Polyethylene (LDPE) Surface With a Wettability Gradient by Tuning its Microstructures," pp. 637–642, 2005, doi; 10.1002/marc.200400626

[53] X. Fan *et al.*, "Surface & Coatings Technology Template synthesis of raspberry-like polystyrene / SiO 2 composite microspheres and their application in wettability gradient surfaces," *Surf. Coat. Technol.*, vol. 213, pp. 90–97, 2012, doi; 10.1016/j.surfcoat.2012.10.025

[54] Z. He *et al.*, "Fabrication of polydimethylsiloxane films with special surface wettability by 3D printing," *Compos. Part B*, 2017, doi; 10.1016/j.compositesb.2017.07.025

[55] D. Julthongpiput, M. J. Fasolka, W. Zhang, T. Nguyen, and E. J. Amis, "Gradient chemical micropatterns: A reference substrate for surface nanometrology," *Nano Lett.*, vol. 5, no. 8, pp. 1535–1540, 2005, doi; 10.1021/nl050612n

[56] J. Miles, S. Schlenker, Y. Ko, R. Patil, B. M. Rao, and J. Genzer, "Design and Fabrication of Wettability Gradients with Tunable Profiles through Degrafting Organosilane Layers from Silica Surfaces by Tetrabutylammonium Fluoride," 2017, doi; 10.1021/acs.langmuir.7b02961

[57] X. Xie, Q. Weng, Z. Luo, J. Long, and X. Wei, "Thermal performance of the flat micro-heat pipe with the wettability gradient surface by laser fabrication," *Int. J. Heat Mass Transf.*, vol. 125, pp. 658–669, 2018, doi; 10.1016/j.ijheatmasstransfer.2018.04.110

[58] X. Wang and P. W. Bohn, "Anisotropic In-Plane Gradients of Poly (acrylic acid) Formed by Electropolymerization with Spatiotemporal Control of the Electrochemical Potential," no. 21, pp. 6825–6832, 2004, doi; 10.1021/ja0400436

[59] J. D. Whittle *et al.*, "A method for the deposition of controllable chemical gradients †," pp. 1766–1767, 2003,doi; 10.1039/B305445B

[60] C. Liu, J. Sun, J. Li, C. Xiang, L. Che, and Z. Wang, "Long-range spontaneous droplet self-propulsion on wettability gradient surfaces," *Sci. Rep.*, no. July, pp. 1–8, 2017, doi; 10.1038/s41598-017-07867-5

[61] S. Feng *et al.*, "Radial wettable gradient of hot surface to control droplets movement in directions," *Sci. Rep.*, vol. 5, pp. 1–7, 2015, doi; 10.1038/srep10067

[62] X. Fan *et al.*, "Template synthesis of raspberry-like polystyrene / SiO 2 composite microspheres and their application in wettability gradient surfaces," *Surf. Coat. Technol.*, vol. 213, pp. 90–97, 2012, doi; 10.1016/j.surfcoat.2012.10.025

[63] D. Giri, Z. Li, K. M. Ashraf, M. M. Collinson, and D. A. Higgins, "Molecular Combing of λ - DNA using Self-Propelled Water Droplets on Wettability Gradient Surfaces," 2016, doi; 10.1021/acsami.6b08607

[64] Y. Nakashima, Y. Nakanishi, and T. Yasuda, "Automatic droplet transportation on a plastic microfluidic device having wettability gradient surface Automatic droplet transportation on a plastic microfluidic device having wettability gradient surface," vol. 015001, 2015, doi; doi.org/10.1063/1.4905530

[65] Y. P. Hou, S. L. Feng, L. M. Dai, and Y. M. Zheng, "Droplet Manipulation on Wettable Gradient Surfaces with Micro-/Nano-Hierarchical Structure," *Chem. Mater.*, vol. 28, no. 11, pp. 3625–3629, 2016, doi; 10.1021/acs.chemmater.6b01544

[66] C. Chen *et al.*, "Microhole-Arrayed PDMS with Controllable Wettability Gradient by One-Step Femtosecond Laser Drilling for Ultrafast Underwater Bubble Unidirectional Self-Transport," vol. 1900297, pp. 1–9, 2019, doi; 10.1002/admi.201900297

[67] C. Hsu and L. Kuo, "Classification of surface wettability and fabrication methods in surface modification: A review," no. February 2012, 2016, doi;

[68] D. Thesis, "Research Collection," 2006.

[69] G. P. Rockwell, L. B. Lohstreter, and J. R. Dahn, "Fibrinogen and albumin adsorption on titanium nanoroughness gradients," *Colloids Surfaces B Biointerfaces*, vol. 91, no. 1, pp. 90–96, 2012,doi; 10.1016/j.colsurfb.2011.10.045

[70] K. Rechendorff, M. B. Hovgaard, M. Foss, V. P. Zhdanov, and F. Besenbacher, "Enhancement of protein adsorption induced by surface roughness," *Langmuir*, vol. 22, no. 26, pp. 10885–10888, 2006,doi; 10.1021/la0621923

[71] R. J. Green, M. C. Davies, C. J. Roberts, and S. J. B. Tendler, "Competitive protein adsorption as observed by surface plasmon resonance," *Biomaterials*, vol. 20, no. 4, pp. 385–391, 1999,doi; 10.1016/S0142-9612(98)00201-4

[72] M. Zhao and M. Keswani, "Fabrication of Radially Symmetric Graded Porous Silicon using a Novel Cell Design," *Nat. Publ. Gr.*, no. April, pp. 1–6, 2016, doi; 10.1038/srep24864

[73] J. J. Gooding, K. A. Kilian, T. Bo, K. A. Kilian, and T. Bo, "The importance of surface chemistry in mesoporous materials : lesson s from porous silicon biosensors materials with live biological," 2009,doi; 10.1039/B815449J

[74] M. A. Verschuuren, M. Megens, Y. Ni, H. Van Sprang, and A. Polman, "Large area nanoimprint by substrate conformal imprint lithography (SCIL)," *Adv. Opt. Technol.*, vol. 6, no. 3–4, pp. 243–264, 2017,doi; 10.1515/aot-2017-0022