Mikroskopie mit Doughnut-Moden
A. J. Meixner et al.

Hydratisiertes Elektron
B. Abel und K. R. Siefermann

Highlights: Massenspektrometrie · Ferndetektions-NMR · Einzelmolekülspektroskopie
Eine lithographiefreie nanolückenbasierte Chemosensormethode nutzt die Bildung von Brüchen in einem dünnen Pd- oder PdNi-Film, die durch Strecken des Films auf einem Elastomersubstrat erzeugt wurden. Diese preiswerte, skalierbare Methode, die auf einem hoch mobilen dünnen Film auf einem Elastomer (MOTIFE) beruht, liefert zuverlässige und hoch empfindliche H₂-Sensoren, wie W. Lee et al. in der Zuschrift auf S. 5413 ff. zeigen.

Mikroskopie mit Doughnut-Moden

Phthalocyanine
R. Berndt et al. beschreiben in der Zuschrift auf S. 5406 ff. die kontrollierte Metallierung einzelner Phthalocyaninmoleküle auf einer Silberoberfläche mithilfe eines Rastertunnelmikroskops.

Benetzungsarten
Der Wechsel von Wassertropfen vom Spreiten zum Abprellen auf hydrophilen, hydrophoben, superhydrophilen und superhydrophoben heißen Oberflächen wird von J. Wang, L. Jiang et al. in der Zuschrift auf S. 5423 ff. untersucht.
**Author Profile**

Gernot Boche (1938–2011)

**Obituaries**

R. W. Hoffmann, M. Famulok

**Books**

From Non-Covalent Assemblies to Molecular Machines

Jean-Pierre Sauvage, Pierre Gaspard

reviewed by J. Nitschke

High Energy Density Lithium Batteries

Katerina E. Aifantis, Stephen A. Hackney, R. Vasant Kumar

reviewed by B. Scrosati
**Highlights**

**Polymer Processing**

F. A. Feist, T. Basch® 5256 – 5257

The Folding of Individual Conjugated Polymer Chains during Annealing  

**Chain reaction**: Single-molecule spectroscopy can be used for the real-time observation of the translational and conformational dynamics of individual conjugated polymer chains during the annealing of solid films. Thus, a detailed molecular understanding of annealing mechanisms is at hand.

---

**Remote Detection**

E. Paciok, B. Blümich® 5258 – 5260

Ultrafast Microscopy of Microfluidics: Compressed Sensing and Remote Detection  

**Zooming in on microfluidics**: The potential of conventional NMR microscopy is limited by poor sensitivity and long measurement times. Recent advances in remote-detection NMR spectroscopy overcome these limitations and give unique insight into microfluidic processes with unprecedented spatial and temporal resolution (picture: high-resolution three-dimensional velocity maps of fast flow in a microcapillary).

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**Mass Spectrometry**

F. Coelho,® M. N. Eberlin® 5261 – 5263

The Bridge Connecting Gas-Phase and Solution Chemistries  

**Charged wings for flying fish**: Mass spectrometry allows the investigation of chemical reactions at the molecular level with ease, speed, selectivity, sensitivity, and great flexibility. Modern mass spectrometry provides a bridge that allows chemical reactions that occur in the gas phase to be studied in solution, and vice-versa (see picture).

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**Minireviews**

**Electrons in Water**

K. R. Siefermann, B. Abel® 5264 – 5272

The Hydrated Electron: A Seemingly Familiar Chemical and Biological Transient  

**Two recent milestones** in the research of the hydrated electron were the determination of its vertical binding energy and the discovery of a long-lived hydrated electron near the surface of liquid water. The results bear relevance for many fields, e.g., electron attachment to DNA bases (see picture).
**Microscopy Techniques**

T. Züchner, A. V. Failla, A. J. Meixner* 5274 – 5293

**Light Microscopy with Doughnut Modes: A Concept to Detect, Characterize, and Manipulate Individual Nanoobjects**

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**Controlled Metalation of a Single Adsorbed Phthalocyanine**

**Communications**

**Vesicles**

P. Bauduin, S. Prevost, P. Farràs, F. Teixidor, O. Diat, T. Zemb 5298 – 5299

**A Theta-Shaped Amphiphilic Cobaltabisdicarbollide Anion: Transition From Monolayer Vesicles to Micelles**

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**Doughnuts for nanotechnology**: Higher-order laser modes with a doughnut-shape and a tunable polarization (see picture) have an extraordinary potential for new applications in nanotechnology. They already serve as versatile tools in microscopy and are finding use in many fields of science from pure optics to different branches of applied science including bio- and materials science.

**Silvered molecules**: The controlled metalation of individual phthalocyanine (H₂Pc) molecules to form AgPc was observed by low-temperature scanning tunneling microscopy (STM). Stepwise dehydrogenation was followed by Ag⁺ implantation; tautomerization and hydrogen atom hopping within the H₂Pc inner ring were also induced by electron injection from the STM tip.

**Sandwiched**: The cobaltabisdicarbollide (mono-)anion ([3,3'-Co(1,2-C₂B₉H₁₁)]^-, COSAN⁻) forms monolayer vesicles at low concentrations in water (see picture). An increase in concentration leads to a Coulomb explosion of the closely packed vesicles into small micelles, which results in the coexistence of both aggregation states at higher concentrations.
**Chemical Sensors**


Highly Mobile Palladium Thin Films on an Elastomeric Substrate: Nanogap-Based Hydrogen Gas Sensors

**MOTIFE chemical sensors**: A novel, low-cost, scalable, and lithography-free but nanogap-based chemical sensing method is presented. This method, termed highly-mobile thin film on elastomer (MOTIFE), utilizes crack formation in a Pd and PdNi thin film generated by stretching the film on an elastomeric substrate to reliably and reproducibly provide highly sensitive H₂ sensors.

**CO Oxidation**


Supported Rhodium Oxide Nanoparticles as Highly Active CO Oxidation Catalysts

**Bigger is not always better**: Rhodium metal particles smaller than 2.5 nm are oxidized and stabilized by reducible supports such as ceria under CO oxidation conditions, whereas metal particles larger than 4 nm remain metallic. The very small Rh oxide particles are more active by two orders of magnitude in CO oxidation than Rh metal particles (see picture; TOF = turnover frequency).

**Surface Chemistry**

T. Zhang, J. Wang*, L. Chen, J. Zhai, Y. Song, L. Jiang* 5311 – 5314

High-Temperature Wetting Transition on Micro- and Nanostructured Surfaces

**Wet, wet, wet**: Typical wetting transition (from spreading to bouncing) of water droplets on micro- and nanostructured surfaces at high temperatures has been investigated. The spreading and bouncing behavior varies on substrates with different wettabilities (see picture; substrate brown, water droplet blue, water vapor white), and the bouncing temperature changes when the microstructure of the surface changes.

**Alkane Activation**

N. Kawakami, O. Shoji, Y. Watanabe* 5315 – 5318

Use of Perfluorocarboxylic Acids To Trick Cytochrome P450BM3 into Initiating the Hydroxylation of Gaseous Alkanes

**It has long been believed** that the fatty acid hydroxylase wild-type P450BM3 is unable to oxidize gaseous alkanes. However, the simple addition of a perfluorocarboxylic acid as a dummy substrate to initiate the P450BM3 catalytic cycle enabled the efficient hydroxylation of butane and propane (see picture).
**Luminescent Materials**

S. H. Huang, S. L. Wang* 5319 – 5322

Variant Luminescence from an Organic–Inorganic Hybrid Structure with an Isolated 4-Ring Zinc Phosphate Tecton

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**Organic Materials**


[\(n\)]Cyclo-2,7-naphthylenes: Synthesis and Isolation of Macroyclic Aromatic Hydrocarbons having Bipolar Carrier Transport Ability

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**Phase-Transfer Catalysis**

L. Wang, S. Shirakawa, K. Maruoka* 5327 – 5330

Asymmetric Neutral Amination of Nitroolefins Catalyzed by Chiral Bifunctional Ammonium Salts in Water-Rich Biphasic Solvent

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**Oxidation**

M. Uyanik, D. Suzuki, T. Yasui, K. Ishihara* 5331 – 5334

In Situ Generated (Hypo)Iodite Catalysts for the Direct \(\alpha\)-Oxyacylation of Carbonyl Compounds with Carboxylic Acids

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The same but different: Four samples of an organic zinc phosphate hybrid material prepared at four different temperatures have the same structure but show distinct luminescence (see pictures of two of the samples).

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**Mothball macrocycles:** Naphthalene has been coupled to form macrocyclic oligomers composed of five, six, and seven naphthalene units (see picture). Thermally stable macrocycles bearing 50, 60, or 70 \(\pi\) electrons within the hydrocarbon structure form columnar assemblies in crystals and serve as bipolar carrier transport materials in organic light-emitting diode devices.

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It’s just a phase: Environmentally benign title reaction was achieved under neutral phase-transfer conditions in the presence of 0.05 mol% of a chiral bifunctional ammonium bromide. The importance of bifunctional design of the chiral phase-transfer catalysts (PTC) was clearly shown in the transition-state model of the reaction based on the single-crystal X-ray structure. \(\text{Bn} = \text{benzyl, Boc} = \text{tert-butoxy-carbonyl.}

---

It’s the iodine: The intra- and intermolecular title reaction is catalyzed by an in situ generated ammonium (hypo)iodite species. Either \(\text{H}_2\text{O}_2\) or tert-butyl hydroperoxide (TBHP) can be used as an environmentally benign oxidant and a wide range of substrates react to give the corresponding \(\alpha\)-acyloxy carbonyl compounds in good to excellent yields.
Syngas Chemistry

Y. H. Zhao, K. J. Sun, X. F. Ma, J. X. Liu, D. P. Sun, H. Y. Su, W. X. Li* 5335 – 5338

Carbon Chain Growth by Formyl Insertion on Rhodium and Cobalt Catalysts in Syngas Conversion

HCO insertion into CH\textsubscript{x} exhibits superior or similar activity to CO insertion and carbene coupling according to DFT calculations, which thus reveal a new reaction channel for chain growth in syngas conversion. The picture shows schematically the lower reaction barrier for HCO versus CO insertion and the optimized transition state for insertion of HCO into CH\textsubscript{2}.

Metal-Free Electrocatalysts

S. Yang, X. Feng, X. Wang, K. Müllen* 5339 – 5343

Graphene-Based Carbon Nitride Nanosheets as Efficient Metal-Free Electrocatalysts for Oxygen Reduction Reactions

Sandwich-like, graphene-based carbon nitride nanosheets (G–CN), among many other advantages, show an enhanced electrical conductivity. Oxygen atoms can thus access the catalyst surface easily and the rapid diffusion of electrons in the electrode during the oxygen reduction process is facilitated. G–CN nanosheets can hence serve as metal-free electrocatalysts for oxygen reduction reactions (ORR) with excellent performance.

Analytical Methods


In Vivo Solid-Phase Microextraction: Capturing the Elusive Portion of Metabolome

Metabolites with fast turnover rates and/or unstable metabolites can be captured directly from circulating blood using a new solid-phase microextraction (SPME) device based on a hypodermic needle. Such metabolites are not observed using solvent precipitation and ultrafiltration methods, indicating traditional approaches based on blood withdrawal are not adequately capturing complete metabolome at the time of sampling.

Glycoproteins


Glycan Structure of a High-Mannose Glycoprotein from Raman Optical Activity

A revealing signature: The glycan structure of intact yeast external invertase, a high-mannose glycoprotein used as bio-catalyst, was investigated by using Raman optical activity (ROA) spectroscopy. The conformational preferences present in mannose-containing di- and trisaccharides were found to be preserved in the glycan chains, with secondary polypeptide backbone structure suppressed.
A selective route: Hypermetallyl germanium(II) and tin(II) compounds (see scheme) were prepared using dimetallyl magnesium reagents and were fully characterized. These derivatives, which contain good leaving substituents, might be suitable candidates for the preparation of nanomaterial alloys.

Mix and go: The quinidine amide 1 catalyzed [2+2] cycloaddition between N-sulfonylimines 2 and alkyl 2,3-butadienoates 3 afforded the R-configured azetidines 4 in excellent yields and enantioselectivities (M.S. = molecular sieve). The S enantiomer was obtained when a quinine amide catalyst, the pseudoenantiomer of 1, was used.

Biologically significant polysubstituted dihydropyrans have been prepared in high to excellent yields and enantioselectivities (see scheme). The interaction between functional groups in the zwitterionic intermediate, which is generated by addition of the amine catalyst to the allenoate substrate, is thought to play a crucial role in the stereochemical outcome. Bn = benzyl, DMAP = 4-dimethylamino-pyridine.

Doubling up: The highly regioselective C3 heteroarylation of either an indole or a pyrrole with an array of electron-rich and electron-poor N-heteroarenes has been carried out using a palladium/copper co-catalytic system. The double C–H activation selectively delivers the unsymmetrical bi-heteroaryl product instead of the homocoupled products.
Experimental Evidence of Phosphine
Oxide Generation in Solution and
Trapping by Ruthenium Complexes

Phosphine oxide (H₃PO), the first defined
compound of phosphorus in the oxidation
state −1, was obtained in solution by
electrochemical methods starting from
white phosphorus (see picture). H₃PO
was characterized by NMR solution specc-
troscopy as a free molecule and isolated
as a ligand in ruthenium(II) complexes
following tautomerization to phosphinous
acid, H₂P(OH).

A specialty of silicon: A stable dimeric
silaisonitrile (ArNSi₂), (see picture;
Ar = 2,6-bis(2,4,6-trisopropylphenyl)-
phenyl) was prepared by the reduction of
dichlorosilaimine IPr·Cl₂Si=NAr with KC₈.
The dimer is the first base-free disilylene
with two-coordinate silicon atoms; reac-
tion with trimethylsilyl azide affords the
first bis(silaimine) (ArNSi=NSiMe₃)₂ with
three-coordinate silicon atoms.

Cascade Formation of Isoxazoles: Facile
Base-Mediated Rearrangement of
Substituted Oxetanes

Give me five! Nitro compounds and
oxetan-3-one react through an intriguing
cascade sequence to give isoxazole-4-
carbaldehydes using inexpensive reagents
in a one-pot procedure (see scheme;
Ms = methanesulfonyl). A variety of
3-substituted isoxazole-4-carbaldehydes
were obtained in high overall yields.

Cold-Ion Spectroscopy Reveals the
Intrinsic Structure of a Decapeptide

Trapped, cooled, solved: Cold-ion spec-
troscopy was used to solve the three-
dimensional gas-phase structure of the
natural decapeptide gramicidin S. Experi-
ments provide a detailed set of spectro-
scopic and structural constraints that
unambiguously identify the most stable
calculated structure of the isolated pep-
tide. These results provide new informa-
tion for modeling the biological activity of
this antibiotic.
**Rally from C to N:** The goal of the race concerns connecting carbon and nitrogen. While the $S_n2$-type mechanism constitutes a one-way road to produce $\text{CH}_3\text{NH}_3^+$ from $\text{Zn(CH}_3)_2^+$ and $\text{NH}_3$, activation of the $\text{C}$$-$H bond of methane in the $\text{Zn(NH}_2)_2^+/\text{CH}_4$ system is a blind alley (see scheme).

**A one light strand:** $2'$-Deoxyguanosine was made fluorescent by attaching a vinyl group at the $\text{C}8$ position (see structure). The resulting fluorophore is highly sensitive towards DNA double-strand formation and alterations in the secondary structure of its parent oligonucleotide, such as formation of different quadruplex structures. These differences can be readily detected in the emission spectrum (see picture).

**Pucker up!** The $2'\text{OH}$ group in RNA is responsible for the change in the predominant sugar conformation, which is key to the catalytic activity and involved in critical H-bonding interactions. In a combined NMR spectroscopic and quantum chemical investigation, the conformational dependence of $J(C1',\text{H1'})$ and $J(C2',\text{H2'})$ coupling constants is derived. The precise conformation of the sugar, nucleobase, and the $2'\text{OH}$ group can be determined based on these coupling constants.
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High-Temperature Wetting Transition on Micro- and Nanostructured Surfaces**

Tong Zhang, Jingming Wang,* Li Chen, Jin Zhai, Yanlin Song, and Lei Jiang*

With the discovery of novel wetting phenomena in nature, such as the self-cleaning effect of lotus leaves and the effortless stand and quick waterborne movement of water striders’ legs, surfaces with special wettability have recently attracted significant attention and have become increasingly important in our daily lives.[1] Moreover, surface wettability at non-ambient temperature, especially at high temperature (above 100 °C), is of great importance in many industrial processes, including water transportation and metal processing, among others.[2] Recently, several advances have been made, such as the fabrication of thermally responsive materials with controllable wettability,[3] the repellent characteristics of different superhydrophobic surfaces to hot water,[4] application of hydrophobic surfaces on heat exchangers at low temperature,[5] evaporation-triggered wetting transition for water droplets on hydrophobic microstructures,[6] and enhancement of boiling by nanostructured interfaces.[7] The theory and applications of a liquid droplet bouncing on a hot surface in a solid–liquid heat transfer system, a very important phenomenon, have also been reported.[8] However, the effect of chemical composition and surface morphology on the wetting behavior at high temperature (above 100 °C) has not been studied systematically.

Herein, we report the investigation of the wetting behavior of surfaces with different chemical compositions and structures from 20 to 200 °C. Four kinds of micro- and nanostructured surfaces with different wettabilities were successfully fabricated. The wetting behavior of a water droplet was observed to be different on the surfaces, and the wetting transition (from spreading to bouncing) occurred at a specific temperature (i.e., the bouncing temperature, T_b) on hydrophilic, hydrophobic, and superhydrophobic surfaces. Surface wettability was crucial to the wetting-transition behavior, and surface roughness also affected the bouncing temperature of a surface (T_b). When surfaces with the same chemical composition got flatter, T_b decreased at the superhydrophilic surfaces and hydrophobic surfaces, while it increased at the hydrophilic surfaces. However, the spreading–bouncing transition did not take place on superhydrophobic surfaces.

Silicon wafers with various structures were fabricated to investigate wettability at different temperatures. Wafers with micropillars and nanowire arrays (SiNWA) were obtained by lithography etching and chemical etching, respectively.[9] The samples were coated with fluorooalkylsilane (FAS) to obtain hydrophobic substrates.[10] Figure 1 shows the top-view scanning electron microscope (SEM) images and the static contact angle (CA) images of a water droplet before and after chemical modification with FAS at 25 °C. As shown in Figure 1 a,b, the unmodified flat silicon and microstructured silicon surfaces (MSis) exhibited hydrophilic characteristics, and the FAS-modified MSis (FAS-MSis) were hydrophobic. Correspondingly, in Figure 1 c,d, the unmodified nanostruc-

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tured silicon and micro- and nanostructured silicon surfaces (MNSis) were superhydrophilic, with contact angles near 0°, while the FAS-modified MNSis (FAS-MNSis) were superhydrophobic (CA > 160°), such that the 2 μL water droplet could not descend but was stuck to the pinhead instead. The effect of the micropillar side length \( D \) (\( D = \infty \) represents surfaces without any microstructure) of the four different substrates on the water contact angle at 25°C are shown in Figure S1 in the Supporting Information.

Subsequently, the wetting behavior of the four groups of surfaces (MSis, FAS-MSis, MNSis, and FAS-MNSis) at various temperatures was investigated. The schematic diagram of the experimental device is shown in Figure S5 in the Supporting Information. A heating stage with controllable temperature was used. The surface temperature and the water spreading or bouncing were recorded with a precise thermocouple and a CCD, respectively. The injector was kept 200 mm higher than the heating stage to preserve the droplet from heat. Only when the stage temperature reached the test temperature was the injector rotated down, and a 3.5 μL water droplet was pushed out. After the water droplet left the needle of the injector, it was rotated again to the high position. The water droplet was well preserved before coming into contact with the high-temperature surfaces (see the Supporting Information for details).

Figure 2 shows the typical spreading and bouncing behavior of water droplets on surfaces with different wettabilities at temperatures above 100°C. The droplet did not wet the surface but instead bounced on the surface at a certain temperature, which was called the bouncing temperature (\( T_b \)). For the hydrophilic smooth silicon surface (Figure 2a), the water droplet stood on the surface with a contact angle smaller than 60° before the surface temperature reached its \( T_b \). at 183°C and then evaporated quickly. When the surface was heated to 183°C or above, the water droplet wetted the surface and then bounced up with a contact time of about 0.16 s. Similarly, \( T_b \) of the hydrophobic surface was 164°C. The droplet stood on the hydrophobic smooth silicon surface modified with FAS with a contact angle larger than 100° and evaporated slowly when the surface temperature was lower than its \( T_b \) at 164°C (Figure 2b), but bounced up slightly with a longer contact time of about 0.4 s when the temperature reached or exceeded 164°C. In comparison, the droplet evaporated and disappeared immediately when the temperature of the superhydrophilic surface was lower than its \( T_b \) at 152°C (Figure 2c). In cases when the surface temperature was higher than 152°C, the droplet on the superhydrophilic surface bounced so strongly and quickly that the contact time between the droplet and the surface was less than 0.04 s. No bouncing occurred on the FAS-modified superhydrophobic surface with SiNWA (Figure 2d). At lower temperatures (e.g., 60°C), the droplet pinned on the surface and evaporated very slowly, but at higher temperature (80°C), below the boiling point of water, the droplet rolled away after being dropped on the surface.

At a given temperature, the vaporizing velocity of a droplet clearly depends on the heat-transfer ability of the surface. The more heat is transferred through the solid–liquid interface, the faster the droplet vaporizes. Hence, the wetting and bouncing processes both indicated that the superhydrophilic surface had excellent heat-transfer ability. The drop evaporated very fast below \( T_b \) and above \( T_b \), the bottom part of the droplet evaporated faster and formed a vapor film to bounce the droplet up in less than 0.04 s, which was much faster than on the hydrophilic and hydrophobic surfaces. In comparison, the droplet stood on the superhydrophobic surface with a contact angle larger than 150° and evaporated very slowly at lower temperature and did not wet but rolled away at 80°C. The small velocity of vaporization demonstrated the poor heat-transfer ability of the superhydrophobic surface.

Although substrates with similar structures, such as the MSis, exhibited similar high-temperature spreading and bouncing and had similar contact times in the bouncing process, \( T_b \) of surfaces with similar contact angles varied with the change of surface roughness. Figure 3 shows the relationship between surface roughness and \( T_b \) for MSis, MNSis, and FAS-MSis. With an increase in \( D \) (from 10 μm to infinity), \( T_b \) increased for the hydrophilic MSis (from 157 to 183°C) while it decreased for the hydrophobic FAS-MSis (from 186 to 164°C).
and superhydrophilic MNSis (from 168 to 152°C). The bouncing temperature \( T_b \) of the hydrophilic MSis was higher than the superhydrophilic MNSis for \( D \geq 20 \mu m \).

The comparisons between the \( T_b \) of different surfaces remind us that, although the superhydrophilic MNSis could enhance heat transfer between solid and water, the droplet would bounce on them at a lower temperature compared with the hydrophilic MSis. Furthermore, if the surface temperature is above \( T_b \), a vapor film would be generated. Therefore, for equipment with strict and high working temperature, the surface with a higher \( T_b \) should be chosen.

Two theoretical models of the wetting state at high temperature have been proposed to explain the change in \( T_b \) (Figure 4). It is understood that a set volume of vapor film has to be produced by phase transition to bounce a given droplet. Throughout the bouncing process, the internal temperature of the water droplets changed little. Therefore, the vaporization velocity and the vapor film formation could only be influenced by the change of surface conditions (Supporting Information S6). As shown in Figure 4, the volume of vapor film can be expressed as in Equation (1): \( V = A(v_v - v_w)t \) where \( V \) is the volume of vapor film, \( A \) is the wetting area between solid and liquid, \( v_v \) is the vaporizing velocity that changes with surface temperature, \( v_w \) is the rewetting velocity controlled by the contacting solid and liquid, and \( t \) is the time of wetting before bouncing. When the droplet made contact with the unmodified MSis and the MNSis with high surface energy, it was in a Wenzel state, in which the liquid completely fills the grooves of the rough surface. According to Figure 4a and Equation (1), if \( V \) and \( v_v \) are invariable and \( t \) changes little on similar surfaces, then \( v_v \) must decrease with the increase in \( A \), and \( T_b \) would decrease as well. For the hydrophilic MSis, the wetting area between silicon and water decreases when \( D \) increases (see the Supporting Information). Hence, \( T_b \) exhibits the same change as \( D \). For the MNSis, \( A \) decreases with a decrease in \( D \), so \( T_b \) decreases when \( D \) increased. Furthermore, nanostructured surfaces have far larger specific surface areas than microstructured surfaces, so the value of \( A \) for MNSis is much larger than that of MSis, which makes \( t \) for MNSis much shorter than the other bounced series of surfaces. In contrast, FAS-MSis and FAS-MNSis exhibited the Cassie state when drops made contact with them. In the Cassie state, \( A \) becomes larger as the surface gets flatter, because air remains in the micro- and nanogrooves. For FAS-MSis, the longer \( D \) is, the larger \( A \) becomes, and \( T_b \) decreases accordingly. However, according to the Cassie equation, if a surface exhibits excellent superhydrophobic characteristics with a contact angle near 180°, the droplet cannot wet the surface but would be separated from the solid by an almost continuous air film. The Cassie equation is defined as in Equation (2): \( \cos \theta_c = f_s (\cos \theta + 1) - 1 \) where \( f_s \) is the area fraction of the solid. If \( \theta_c \) is close to 180°, then \( f_s \) would be quite tiny as it approaches 0. As a result, \( v_v \) would be near 0, too. Thus, the droplet could not bounce on the superhydrophobic FAS-MSis but rolled away with a slight imbalance. More evidence can be seen in Supporting Information.

In summary, the typical wetting transition on micro- and nanostructured surfaces with different wettabilities at high
temperature has been investigated. Experimental results indicate that both surface wettability and surface roughness are crucial to the wetting transition behavior. The spreading–bouncing transition occurred on hydrophilic, hydrophobic, and superhydrophobic surfaces above 100 °C. When the side length of micropillars on substrates increased from 10 μm to infinity (i.e., no micropillars), $T_s$ decreased for the superhydrophobic MNSis and hydrophobic FAS-MSis, while it increased for the hydrophilic MSis. However, the spreading–bouncing transition could not take place on superhydrophobic FAS-MNSis. The two proposed mechanisms of wetting at high temperature explained the transition phenomena well. Moreover, the high-temperature wetting transition could be potentially valuable in water transportation and other industrial applications, such as material choice in liquid–solid systems working at non-ambient temperature.

**Experimental Section**

Instruments and characterization: SEM images of the samples were obtained using a field-emission scanning electron microscope (JSM-6700F, Japan). Contact angles were measured on an OCA20 instrument (DataPhysics, Germany) at 25 °C. Deionized water droplets (about 2 μL) were dropped carefully onto the surface. The average contact angle value was obtained by measuring at five different positions of the same sample.

Fabrication of SiNWAs: Cut silicon wafers were soaked in H2SO4/H2O2 (H2SO4 97%)/H2O2 (30%) 3:1) for 30 min at 80 °C, then rinsed with deionized water four or five times. Cleaned silicon strips were put into the etching solution (HF 5.0 mol L$^{-1}$ and AgNO3 0.015 mol L$^{-1}$), sealed at 50 °C for 25 min, then immersed in 20% nitric acid for 30 s and finally rinsed with deionized water four or five times.

Modification with FAS: Cleaned silicon strips with microstructures were put into a sealed container together with a piece of glass coated with about 0.5 mL FAS. Then the container was then evacuated with a vacuum pump, and the vacuum was maintained vacuum for 12 h.

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**Keywords:** high-temperature chemistry · hydrophobic effect · microstructure · surface chemistry · wettability


