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Rebounding Droplet-Droplet Collisions on Superhydrophobic Surfaces: from the Phenomenon to Droplet Logic

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Collisions between water droplets classically lead to uncontrolled coalescence into larger droplets, as observed for falling droplets.[1] Thus, it would contrast common experiences to find two impacting water droplets to bounce like billiard balls, and to control whether they bounce or coalesce by using simple methods. Here we show this can be achieved for droplets moving on a superhydrophobic surface, and we also present the conditions for bouncing and coalescence. Utilizing rebounding droplets, we demonstrate AND/OR and NOT/FANOUT Boolean operators and a flip-flop memory as elements for superhydrophobic droplet logic. Additionally incorporating coalescence, the droplet logic concept can be generalized to droplet-logic controlled chemistry. Thus, we also demonstrate a model elementary operation, where a chemical reaction is triggered by droplet coalescence, whereas upon rebounding no reaction occurs. In summary, we show that ordinary collisions between water droplets can be simply controlled and converted to informed matter.

Collisions between liquid droplets have been classically studied for droplets moving in air or in other gas, in the context of rainfall, inkjet printing or spraying.[1,2] The studies have revealed five distinct regimes of collision: (I) coalescence after minor deformation, (II) bouncing, (III) coalescence after substantial deformation, (IV) coalescence followed by separation for near head-on collisions, and (V) coalescence followed by separation for off-center collisions. In free-fall studies, bouncing, i.e., rebounding is commonly observed for hydrocarbon droplets,[1,3] but bouncing of equal-sized water droplets at atmospheric pressure is observed only at near-grazing collisions.[1] Recently, Nilsson and Rothstein reported also on droplet-droplet collisions on superhydrophobic surfaces (with an advancing contact angle of 150° over a broad range of contact angle hysteresis) and resulting droplet mixing upon coalescence, as illustrated in **Figure 1** (top panel). However, they did not observe rebounding collisions,[4] illustrated in Figure 1 (bottom). Beyond the grazing collisions of droplets in free fall, bouncing has only been observed for a water droplet falling on a second droplet that wets a solid surface,[5] in a similar fashion as a droplet can bounce when falling on a large pool of water.[6,7] Here we present the first demonstration of rebounding droplet-droplet collisions of water droplets colliding at all impact angles, by using a superhydrophobic surface to support moving water droplets, as illustrated in Figure 1. In contrast to the previous reports on rebounding collisions in air, the superhydrophobic surface enables bouncing or coalescence in controlled, reproducible conditions, for example by selecting well-defined collision geometries, potentially enabling technological applications for bouncing droplets.

Colliding droplets coalesce if the air gap between them is diminished to the dimension of molecular interaction.[1,8] Thus, due to the low velocity of a collision in regime I, there is enough time for the gas between the two droplets to drain out, and the collision results in coalescence. Conversely, in regime II, the gas layer between the droplets remains sufficiently thick during the collision, because of the non-negligible viscosity of air, and coalescence is prevented.[2] In regime III, liquid surfaces are forced to approach each other by the inertia of the colliding droplets, and coalescence occurs. During a collision of regime II, resulting in a bounce, the colliding droplets lose all their impact inertia before the air layer between the droplets has drained out. Part of the kinetic energy is converted to surface energy through an increase in surface area of the deforming droplets, and part is lost through viscous dissipation. Bouncing is promoted by droplets using the energy stored as surface energy for restoring their spherical shape.[1]

By definition, a surface is superhydrophobic if the contact angle between a water droplet and the surface at the solid/liquid/air interface is larger than 150° and the contact angle hysteresis is small, i.e., droplets easily slide or roll off when the surface is tilted even slightly.[9–11] Superhydrophobicity requires a suitable microstructure, typically in combination with hydrophobic surface chemistry, and is known to lead to properties including self-cleaning and drag reduction.[12–15] Recently, we introduced superhydrophobic tracks for low-friction guided transport of water droplets, allowing facile transport of droplets by electric fields or gravity.[16] In the current study, such tracks are employed for directing droplet motion in designed geometrical trajectories to perform controlled bouncing and coalescing collisions for droplet logic gates.

Different concepts for storing and manipulating information beyond the mainstream electronics have been previously

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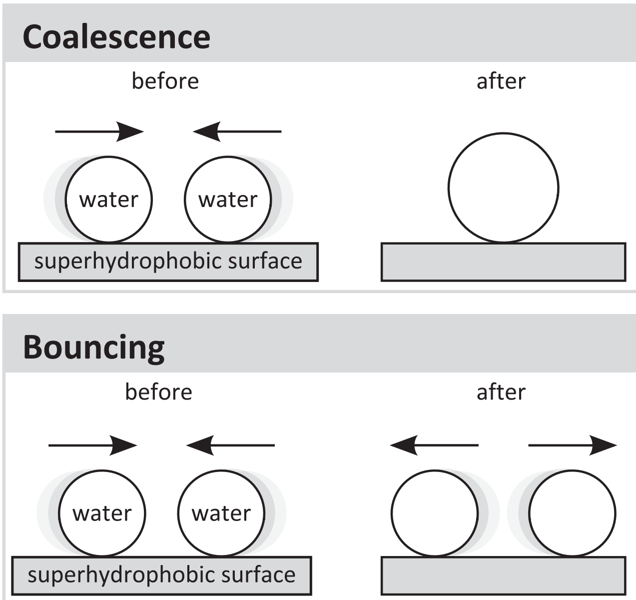

Figure 1. Two scenarios for a water droplet impacting a second droplet while moving over a superhydrophobic surface. Coalescence: two droplets collide with each other and merge (top). Bouncing: two droplets collide with each other and rebound like billiard balls (bottom).

explored. Alternatives to the common silicon-based logic include implementations using organic electronics,[17,18] microelectromechanics,[19] optics,[20] electrochemistry,[21] molecular interactions,[22] iontronics,[23] and even swarming crabs.[24] Also logic functions based on microfluidic systems have been implemented,[25] using droplets or bubbles as bits of information.[26–30] The conventional approach concerns droplets or bubbles transported in a liquid medium, like water droplets in oil or air bubbles in aqueous surfactant solutions, where surfactants were required to stabilize the interfaces during bubble-bubble interaction. To enable logic also with the two most common fluids (namely pure water and air), we propose the new concept of droplet logic in a gas medium, where droplets interact via rebounding collisions.

First, we show a conceptual finding that on a superhydrophobic surface, the collisions of pure water droplets can be controlled to undergo either bouncing or coalescence. We describe the "phase diagram" for the collision processes, based on the Weber number, which is a measure of kinetic energy, and the collision geometry. Having described the physical phenomenon, we construct the relevant droplet logic gates. Finally, the droplet logic is combined with chemistry, incorporating chemical cargo within the droplets. This is enabled in the presented approach, since parameters like velocity and collision geometry can be controlled in order to determine whether coalescence or bouncing occurs, and thus whether reaction occurs or not. This sets foundation for droplet-logic controlled programmable chemistry.

Droplet collisions are usually classified using two parameters: Weber number and impact parameter. The Weber number, *We*, is defined as $We = 2R\rho v^2/\gamma$, where R is the droplet radius, v the relative velocity of droplets, and ρ and γ density and surface tension of the liquid, respectively. In a collision of two similarly-sized water droplets, the Weber number is a dimensionless measure of kinetic energy. The impact parameter, B, is defined as $B = \chi/2R$, where χ is the projection of the distance between droplet centers in the plane perpendicular to v. The impact parameter ranges from $B = 0$ for a head-on collision to $B = 1$ corresponding to a grazing collision.

Letting a water droplet move on a superhydrophobic surface and collide with a stationary second droplet, unconventional bouncing collisions were observed in the entire range of impact parameter values from zero to one, as shown in the B vs. *We* diagram in **Figure 2**a together with a series of images presenting head-on and mid-angle collisions both in the bouncing and coalescing regimes. The corresponding video is available in Supporting Information (Video S1). Coalescence of colliding water droplets was observed in region I, region III and region III*. In contrast, rebounding water droplets were reproducibly observed in region II. We speculate that the mechanism of the rebounding droplet-droplet collisions on superhydrophobic surfaces is analogous to the classic rebounding droplet-droplet collisions in air, i.e., the air layer between the colliding droplets does not have sufficient time to drain out.[1,2] However, further experiments and/or simulations would be needed to confirm this and to characterize the shape of the region boundaries.

The complex shapes of the collision/bouncing regions in Figure 2a open rich possibilities for tuning collision outcomes. Especially, the Weber number range from 2 to 5 allows controlling of bouncing and coalescence by adjusting the impact parameter. Next, we demonstrate incorporation of additional functionalities in the collision by showing that control over droplet bouncing and coalescence allows suppression or triggering of chemical reactions between reactants or analytes confined within the droplets. Shown in Figure 2b, a collision-controlled model chemical reaction is demonstrated using silver nanoclusters[31] and the quenching of their fluorescence by reaction with cysteine. When the collision results in a bounce, the chemicals do not mix (Figure 2b left). Thus, no reaction occurs and the fluorescence is not affected. However, when the collision results in coalescence, the chemicals mix and a chemical reaction rapidly quenches the fluorescence of the silver nanoclusters (Figure 2b right). The corresponding video is available in Supporting Information (Video S2).

In the following paragraphs, we illustrate how the diagram in Figure 2a allows the designing of programmable fluid handling operations. Employing water droplets, there are several possibilities to represent the logical bits. Here, we will consider the presence of a droplet at a certain time and location on the substrate as representing the logical value "1". The absence of a droplet at that location and time represents "0". The presented droplet logic concept can be viewed as the liquid analogue of the well-known theoretical billiard ball logic. However, whereas billiard ball logic is a theoretical model based on elastic collisions between solid balls,[32] the collisions in real systems and also in our droplet logic are inelastic of nature.

In order to implement droplet logic components, superhydrophobic tracks were prepared on a copper plate to allow droplet transport guided along a trajectory using designed impact parameters (see Experimental for further details). **Figure 3** demonstrates the operation of superhydrophobic droplet logic gates.

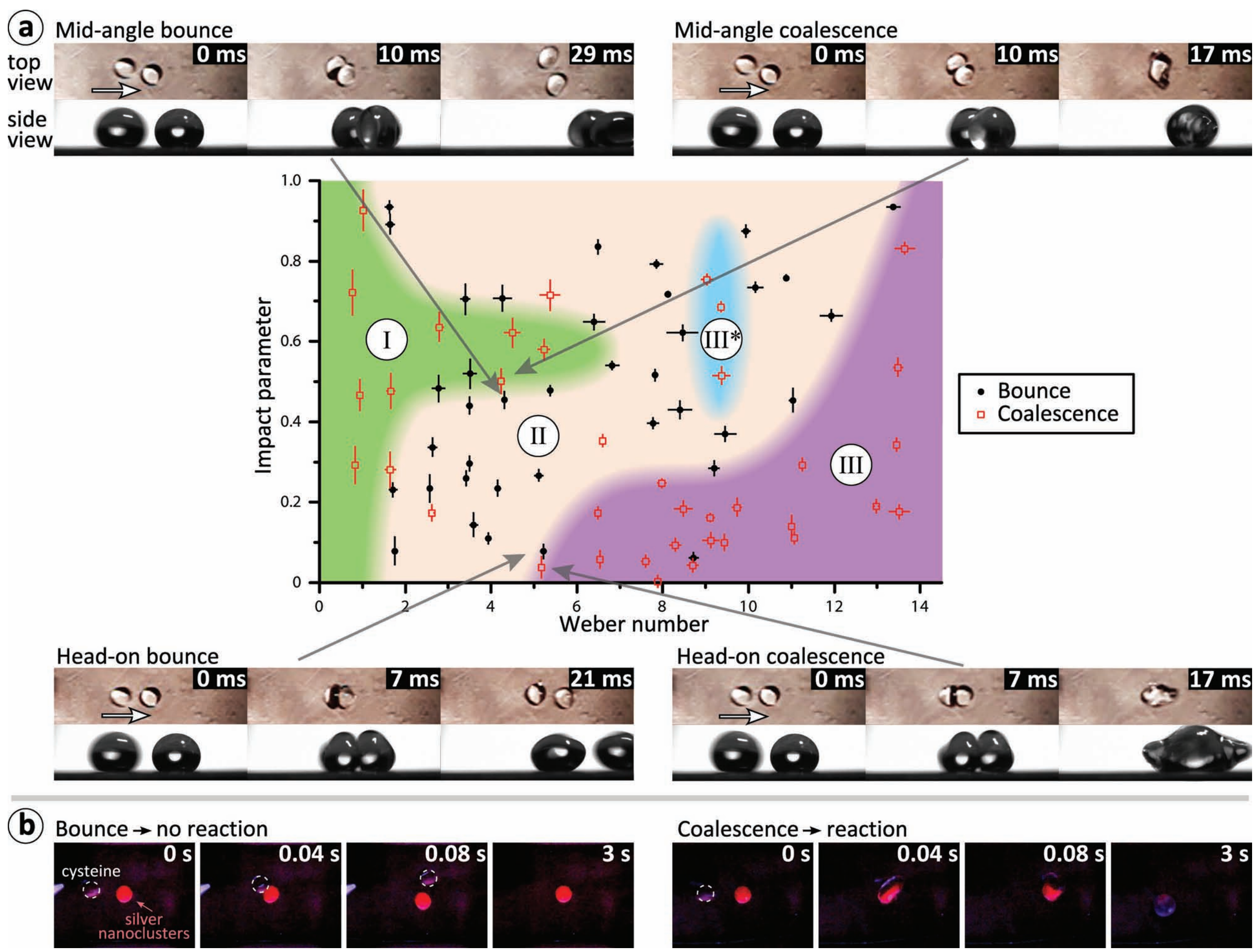

Figure 2. a) Collision regimes of water droplets moving on a superhydrophobic surface. Top-left panel: a mid-angle collision viewed from top and from side. A moving droplet (left) hits the droplet at rest, and droplets (diameter 3 mm) bounce without coalescence. Top-right panel: a mid-angle collision resulting in coalescence. Bottom-left panel: a head-on collision with droplets bouncing without coalescence. Bottom-right panel: A head-on collision resulting in coalescence. In the middle: experimentally determined regimes of bouncing and coalescence of water droplets colliding on a superhydrophobic surface. The error bars show the experimental standard error, calculated as described in detail in the Methods section. The corresponding video is available in Supporting Information (Video S1). b) A collision-controlled chemical reaction. A moving water droplet containing cysteine collides with a water droplet containing fluorescent silver nanoclusters (droplet diameters 5 mm). Right panel: when the collision results in a bounce, the chemicals do not mix. Thus, no reaction occurs and the fluorescence is not affected. Left panel: When the collision results in coalescence, the chemicals mix and a chemical reaction rapidly quenches the fluorescence of the silver nanoclusters. The corresponding video is available in Supporting Information (Video S2).

Figures 3a-c present the NOT/FANOUT gate. A source (1) is connected to the top-left input. Thus, if there is no input from the synchronized signal channel (A) at the top-right, a signal in the middle output channel ($\bar{A}$) results. However, if there is an input droplet from A, it collides with the source droplet coming from 1, and output is triggered not in the middle but both in the leftmost and rightmost output channels. Thus, this droplet logic gate performs the logical NOT operation and additionally duplicates the input signal. In Figures 3d-f, the AND/OR logic gate is presented. A single droplet, arriving to the logic gate from either input A or input B, leaves the gate through the bottom-left output (A+B). However, simultaneous input from both A and B results in a collision and an output in both output channels (A+B and $A\cdot B$). The corresponding videos, showing the NOT/FANOUT and AND/OR gates in operation, are available in Supporting Information (Videos S3 and S4). A toggle flip-flop memory based on droplet collisions is presented in **Figure 4**. A flip-flop is a device able to store a binary bit, i.e., to remember in which of the two states the device was last set up. A toggle flip-flop changes its state every time it is addressed. In the toggle flip-flop device presented in Figure 4, the memory bit is represented by a droplet sitting in one of the bistable positions in an infinity-symbol-shaped depression in the middle of the device. The incoming droplet collides with the droplet in the bistable position, thereby triggering output in one of the two output channels depending on the initial position of the middle drop. After collision, the incoming droplet lands to the other position in the bistable depression. Thus, the incoming

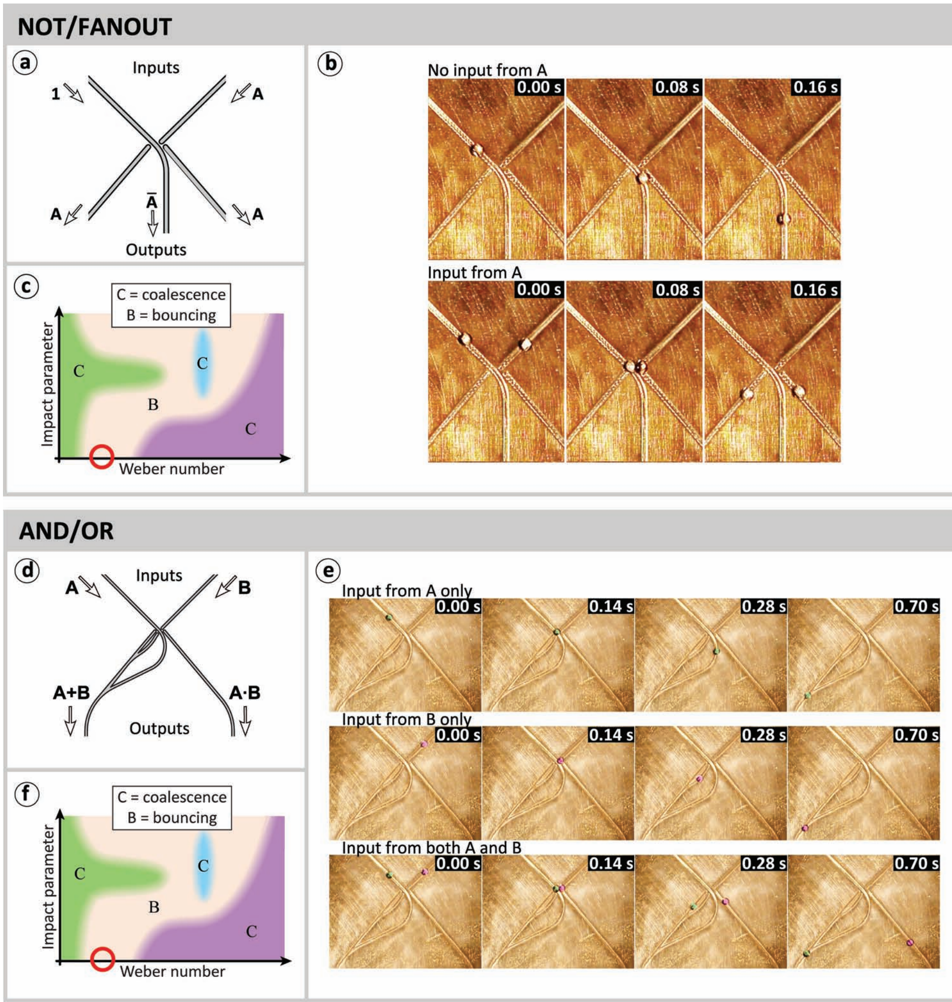

Figure 3. Superhydrophobic droplet logic gates. a) A schematic showing the NOT/FANOUT logic gate connections. The two inputs of the gate are located at the top of the image, and the three outputs at the bottom. b) A series of images demonstrating the NOT/FANOUT gate operation. The corresponding video is available in Supporting Information (Video S3). c) The selected collision conditions (red circle) are shown qualitatively in the Weber number/impact parameter diagram. d) A schematic showing the AND/OR logic gate connections. The two inputs are situated at the top of the image and outputs at the bottom. e) A series of images demonstrating the AND/OR gate operation. The droplets have been colored via image editing for clarity. The corresponding video is available in Supporting Information (Video S4). f) The selected collision conditions (red circle) are shown qualitatively in the Weber number/impact parameter diagram.

droplets trigger alternating output between the two outputs. A video showing the memory in operation is available in Supporting Information (Video S5).

We have shown that, unlike two colliding water droplets that commonly coalesce under classic conditions, two water droplets colliding with each other while moving over a superhydrophobic surface can reproducibly bounce or coalesce depending on the collision conditions. The underlying Weber number/impact parameter diagram allows designing the outcome of collisions. Furthermore, we have demonstrated that the phenomenon opens functionalities–by designing proper bouncing conditions, we presented elementary logic operations and a flip-flop memory, using water droplets in superhydrophobic tracks as bits of binary data. The droplet collisions were found to be reliably reproducible: as a proof of concept, we demonstrated 100 subsequent operations in the flip-flop memory without error (Video S5).

In contrast to previous droplet or fluid logic implementations,[26–30] pure water droplets could be used without need for stabilizing surfactants or oils, owing to the superhydrophobic surface. Therefore, the pure water within the droplets can host water-soluble chemical reactants, importantly without surfactant additives that potentially disturb for example in biochemical analysis. In the presented concept, control between coalescence and bouncing determines whether a given chemical reaction occurs or not. Thus, incorporating coalescence as an additional operation within the superhydrophobic droplet logic, we demonstrated droplet-logic controlled chemistry.

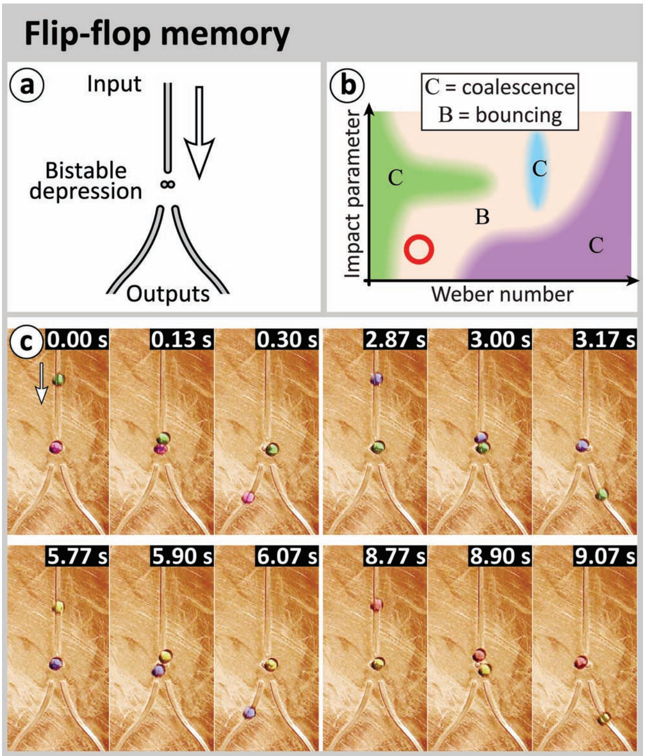

Figure 4. Superhydrophobic flip-flop memory. a) A schematic describing the flip-flop memory. The memory bit is represented by a droplet sitting in one of the bistable positions in an infinity-symbol-shaped depression in the middle of the image. b) The selected collision conditions are shown in the Weber number/impact parameter diagram. c) A series of images demonstrating the flip-flop memory operation. The droplets have been colored via image editing for clarity. The corresponding video is available in Supporting Information (Video S5).

In summary, it is fascinating to observe a novel and easily accessible phenomenon concerning one of the most ordinary objects existing, i.e., water droplets. When impacting each other while traveling on a superhydrophobic surface, water droplets are able to rebound like billiard balls. We show that bouncing or coalescence can be easily controlled by selecting proper collision parameters, and present elementary logic operations based on this concept. We foresee that the present work opens a route for superhydrophobic droplet-logic based devices, such as autonomous simple logic devices not requiring electricity, and in programmed biochemical analysis.

Experimental Section

The Geometry for Droplet Collisions: A copper plate (109 × 27 mm) was bent to a U-shape with a flat portion of about 20 mm in the middle. For the measurements presented in this work, a side slope of approximately 70° was used. A shallow depression was forged to the center of the plate for enabling a well-defined position of the target drop.

Cutting the Tracks: Superhydrophobic tracks were prepared on copper plates with a size of about 120 × 100 × 5 mm. Track geometries were cut by milling (Elekmerk Oy). Tracks had a depth of approximately 0.4 mm and a width of 1 mm.

The Superhydrophobic Coating: Subsequent to creating the required geometries, a superhydrophobic coating was applied to the copper plates. First, the plates were polished with sandpaper (P180). Second, the plates were washed with ethanol and acetone. Subsequently, a superhydrophobic coating was applied employing the procedure by Larmour et al.[33]. Silver nitrate (Riedel-de Haën, 99%), dichloromethane (Sigma-Aldrich, 99.5%) and 1*H*,1*H*,2*H*,2*H*-perfluorodecanethiol (Aldrich, 97%) were used as received.

Droplet Collisions: Droplet collisions were performed in a contact angle measurement device (CAM 200, KSV Instruments). First, a water droplet was placed to the depression on the curved superhydrophobic plate using a Finnpipette (Thermo Scientific). Next, a second droplet of similar volume was released on the side slope using the software-controlled dispenser of the CAM 200, and the droplets were let to collide. The event was recorded from side with the software-triggered camera of the CAM 200, and from above using a manually triggered Casio Exilim FH-25 digital camera. Both cameras recorded at 420 fps. Videos were analyzed using the ImageJ software, where droplet positions were determined manually. For analysis, ten frames before impact were used from the top camera and five frames from the side camera. A line was fitted in three dimensions to the coordinates obtained from the videos to obtain the impact parameter value. The vertical error bars in Figure 2a show the standard errors of this fitting. In order to determine the Weber number, the separation between droplet coordinates in two subsequent frames was used for calculating the velocity at that instant. Subsequently, an average over all frames was calculated, and this value was used to determine the Weber number. The horizontal error bars in Figure 2a show the standard error of this averaging.

Collision-Controlled Chemical Reaction: An aqueous dispersion of fluorescent silver nanoclusters[31] stabilized with 0.5 mg cm^{-3} poly(methacrylic acid) (ratio silver/carboxylic acid = 6) and a 20 mM aqueous solution of L-cysteine (Fluka, 99.5%) were used. Collisions were performed on the curved superhydrophobic plate under UV illumination. The events were recorded using a Canon EOS 550D digital camera at 50 fps.

Droplet Generation for Logic Operations: For applying multiple subsequent droplets to a superhydrophobic track, a flat-tipped 25-gauge needle was connected to a 50-cm plastic tube filled with water. The hydrostatic pressure of the water inside the vertical tube resulted in a flow with a relatively constant droplet rate from the needle. The droplets had a diameter of approximately 3 mm, determined from video recordings.

Video Recording from Logic Operations: Videos from logic operations were recorded using a Canon EOS 550D digital camera at 50 fps.

Supporting Information

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

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