



Protocol Article

Contact angle measurement of natural materials

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ABSTRACT

Contact angle (CA) is the most important parameter used to quantify the wettability of solid surfaces. In order to evaluate wettability performance, numerous methods have been developed to measure the CA of solid surfaces. Recent years have seen increased focus on the special wettability performance of various biological materials. Biomimetic wettability has become one of the most popular research fields, and novel CA measurements have been invented accordingly. In this protocol, we introduce several CA measurement techniques mainly based on the image capture method, which is commonly to investigate the wettability of natural materials. According to the solid/liquid/gas context, we classify CA measurements into three types: in air, under liquid, and air bubble measurements, and describe methods for each. The precise measurement of CA together with study of surface structure can reveal the mechanisms of special wettability, thus accelerating the investigation of biomaterials.

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1. Introduction

Wetting is a universal physical phenomenon with important effects in nature and in human life. Wetting occurs when a liquid contacts a solid, and a liquid layer extends along the surface of the solid. Different intermolecular interactions between the liquid and the solid cause materials to have different wetting properties [1–3]. In 1805, Thomas Young was the first to describe the concepts of contact angle (CA) and wettability [4]. During the following two hundred years, many researchers have conducted theoretical studies and developed analytical techniques in the field of wettability. Great progress has been achieved in many aspects, such as the relationship between roughness and hydrophobicity [5,6], the relationship between roughness, air and superhydrophobicity [7], the hysteresis of CA [8–10], and micro- and nano-scale hierarchical structure-induced superhydrophobicity [11].

The main index used to evaluate the wettability of a solid surface is CA. Conventionally, it describes the behavior of a liquid droplet on a solid surface in air, and is defined as the angle between the tangent at the three phase point and the solid surface. Generally,

solid surfaces with CAs < 90° are considered hydrophilic, while surfaces with CAs > 90° are considered hydrophobic. The relationship between CA and interface tensions can be described by Young's equation [12]:

$$\gamma_{SG} - \gamma_{SL} - \gamma_{LG} \cos \theta = 0 \quad (1)$$

where θ represents CA, and γ_{SG} , γ_{SL} , and γ_{LG} represent the solid/gas, solid/liquid, and liquid/gas interface tensions, respectively. However, recent studies investigating the chemical and structural states of water droplets have determined that the boundary between hydrophilicity and hydrophobicity for a smooth solid surface actually occurs at a CA of 65° [13–17].

In the past several decades, bioinspired surfaces with special wettability properties have emerged from intensive investigations of wettability phenomena. Several extreme superwettability states have been established, including superhydrophilic (SHL), superhydrophobic (SHB), superoleophilic (SOL), and superoleophobic (SOB) states. Specifically, solid surfaces with water CAs < 10° or > 150° are considered to be superhydrophilic or superhydrophobic surfaces, while surfaces with oil CAs < 10° or > 150° are considered as superoleophilic or superoleophobic surfaces. When using water or oil to replace air, other possible extreme superwettability states will be obtained: underwater superoleophobic (WSOB), underwater superoleophilic (WSOL), underoil superhydrophobic (OSHB), and underoil superhydrophilic (OSHL) [1]. With the establishment of these terms, theoretical principles of wettability have

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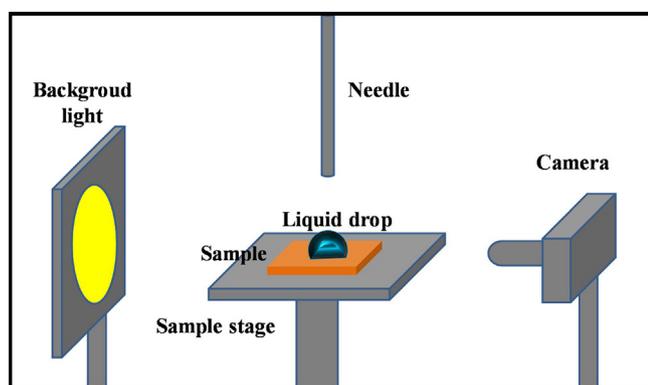


Fig. 1. The CA measurement equipment based on the droplet image analyzing method.

deepened, and various CA measurement methods have been developed to evaluate wetting abilities in different solid-liquid-gas systems. There are several well-developed conventional methods for measuring CA, such as confocal microscopy techniques [18], the Wilhelmy method [19], and atomic force microscopy (AFM) [20,21]. With the concurrent development of image analysis techniques during these years, the droplet image analysis method has become the most commonly used [22]. It has the advantages of an easy operating process, suitability for various materials, and low liquid requirements. Droplet image analysis can directly measure CA from the image capture of the droplet. It can be easily performed using a goniometer, which is usually composed of three parts: a background light, a sample stage and a camera (Fig. 1). After the liquid droplet has been carefully placed onto the sample, an image of the droplet is captured and analyzed to determine a CA value. In this process, the background light, sample stage and camera should be aligned to ensure accurate CA measurement.

Recently, “special wettability” or “superwetting” phenomena have been discovered to be widespread in nature. Many plants and animals have adaptations that exploit natural materials with special wettability [23–26], such as self-cleaning lotus leaves [27], water-walking insects [28], water-collecting desert beetles [29] and spider silk [30], water-transporting cactus [31], and water-filled pitcher plants [32]. Intensive exploration of these biomaterials has further accelerated the investigation of bioinspired surfaces with extreme wetting states. With demand for manufactured biomimetic superwetting systems, researchers have constructed a series of bioinspired, complex, solid-liquid-gas systems. However, wettability testing methods remain lacking and are urgently needed. In this protocol, a detailed process for wettability measurement is proposed, with particular applicability to natural materials and synthetic biomimetic materials. The main method for testing CA is based on droplet image analysis, and various processes are introduced to adapt it to different solid-liquid-gas systems.

2. Materials

2.1. Natural materials

To investigate wettability performance, the upper surfaces of natural materials are usually examined. Wettability is governed by both the chemical composition and the surface structure of a material. For example, surfactant wax is the key factor determining the superhydrophobic properties of lotus leaves. Therefore, in order to investigate wettability properly, samples should be pre-cleaned very carefully to ensure that the surface's chemical composition is not modified or damaged. Normally, natural materials can be ultrasonically cleaned with deionized water for several minutes

and then dried under nitrogen. Ethanol or other organic solvents are not recommended for cleaning as they may affect the surface's chemical composition. Cleaning times should be kept as short as possible to retain the surface structure. On the other hand, live plants and animals exhibit different wettability properties than dead ones. Therefore, natural organic samples should be tested alive or immediately after death. In this case, all samples should be taken from living organisms just before the experiments in order to maintain freshness and real-world performance [33]. Additionally, freeze fractures of natural organic samples were often used. These samples were frozen with liquid nitrogen and then broken using forceps.

2.2. Liquids

All water used in CA measurements should be deionized. Any kind of oil, such as heavy oil, vegetable oil or gasoline, etc., can be used depending on the situation. Sometimes, typical organic solvents such as hexane and 1,2-dichloroethane can also be used as the oil phase, as convenient.

3. Measurements of contact angle

Different measurement techniques were applied to different solid-liquid-gas systems. Generally, depending on the solid-liquid-gas system, CA measurements can be classified into three types (Fig. 2): 1) liquid droplet measurements in an air atmosphere, which can be divided into water contact angle (WCA) in air and oil contact angle (OCA) in air (Fig. 2a); 2) liquid droplet measurements in liquid conditions, including underwater OCA and under-oil WCA (Fig. 2b); and 3) air bubble measurements under liquid conditions, such as underwater or under-oil air bubble measurements (Fig. 2c). Here, we will discuss the detailed process of CA measurement in different solid-liquid-gas systems.

3.1. CA measurements in an air atmosphere

3.1.1. Static contact angle measurements

Static CA measurement is often used to characterize the wettability properties of a solid surface. As shown in Fig. 3a, the general process is as follows: a certain volume of water droplet should be carefully injected onto the solid surface, then an image of the droplet is captured from which a CA measurement can be obtained. Generally, five different locations on each sample should be tested and the mean taken as the static CA. In this approach, three steps are crucial, as described below.

3.1.1.1. Droplet volume. According to previous literature, the volume of the drop (drop size) should be within 0.5–10 μL . In general, use of small drops avoids water droplet deformation caused by gravity. When comparing the wetting phenomena of different surfaces, CAs must be measured with water droplets of the same volume. Otherwise, the effect of the drop size must be considered, as CA measurement is affected by water droplet volume and gravity. Therefore, 2 or 3 μL might be a suitable volume for measuring the CA of water droplets on solid surfaces. However, because of the low water adhesion of many superhydrophobic surfaces, it is very difficult to place water droplets of <4 μL on them. [34] Zhang et al. [35] proposed a new method for measuring the CAs of superhydrophobic surfaces in which a 5 μL water droplet is placed on the sample, then CA is measured once the droplet decreases in volume to 0.3 μL after evaporation for 40 min under ambient conditions [36].

3.1.1.2. Settling time. The CA should be measured shortly after droplet deposition on the solid surface, to ensure that evaporation is

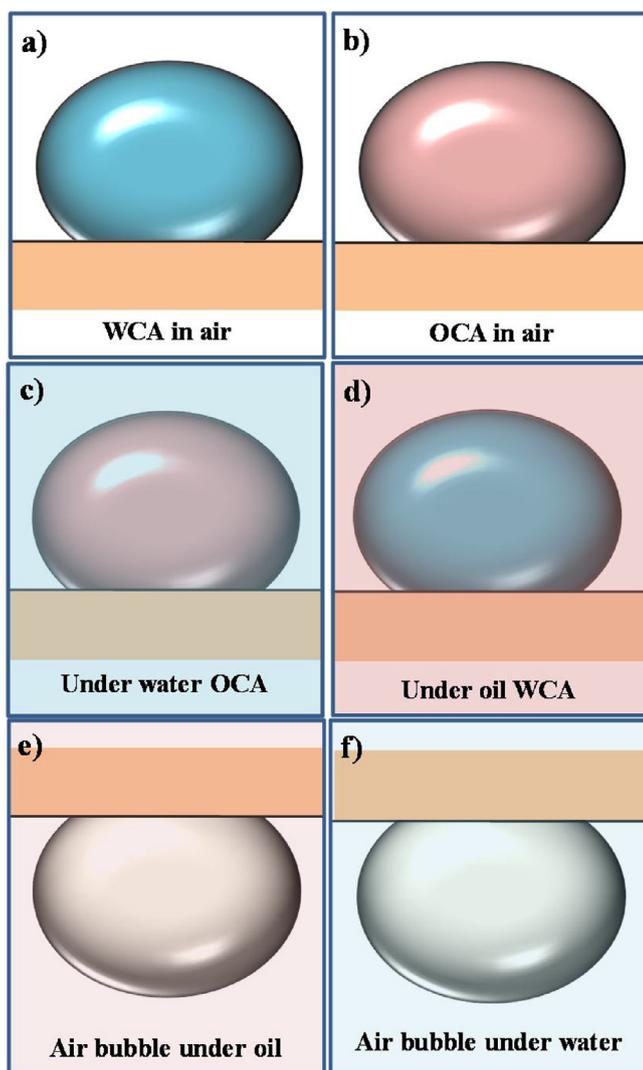


Fig. 2. The three type CA measurements: first, liquid droplet measurements in air atmosphere which can be divided into a) WCA in air and b) OCA in air; second, liquid droplet measurements in liquid conditions including c) under water OCA and d) under oil WCA; third, the air bubble measurements under liquid conditions which are e) under water air bubble measurements and f) under oil air bubble measurements, respectively.

minimized. However, enough time must be allowed for the droplet to spread on the surface and, possibly, react with it. Therefore, the time between deposition and measurement has to be properly determined, then replicated for each droplet during measurement of CA.

3.1.1.3. Fitting modes. Importantly, water droplet shapes can be fitted with various modes, such as ellipse fitting, circle fitting, tangent searching, and Laplace–Young fitting. Different fitting modes always result in different observed values of CA, even as much as 150° – 179° with similar shapes. [35,37–39] Therefore, for the accurate determination of solid surface wettability, the fitting mode should be clearly noted and be consistent with static CA values.

3.1.2. Dynamic contact angle measurements

As Young's equation describes (Eq. (1)), a unique CA is expected for a drop on an ideally smooth surface. However, for a real surface, a drop placed on it has a spectrum of CAs. As shown in Fig. 3b, the highest possible apparent CA is the advancing contact angle (θ_a), and the lowest possible apparent CA is the receding contact angle (θ_r). The difference between the advancing and receding contact angles is known as the contact angle hysteresis (CAH). Usually, measurement of a dynamic contact angle includes the advancing contact angle (θ_a), receding contact angle (θ_r) and rolling off contact angle (θ_s).

3.1.2.1. Contact angle hysteresis measurements. Contact angle hysteresis (CAH) can be used to reflect differences between different superhydrophobic states. Based on the sessile drop method, there are two main methods of measuring CAH:

1) Adding/removing liquid: This involves putting droplets onto a solid surface and gradually adding liquid to them to increase their volume. At the beginning, the contact area of the droplets and solid surface is consistent, while the CA gradually increases with the addition of liquids. As the volume of the liquid droplets increases to a certain critical value, a three-phase contact line begins to move forward. The CA, measured just before the three-phase contact line starts to move forward, is known as the advancing contact angle (θ_a). Conversely, if liquid is gradually removed from the droplets at a very low rate to reduce their volume to a certain value, the three-phase contact line of the droplets begins to move backward. The CA determined before this movement is the receding contact angle. There are several points that should be noted.

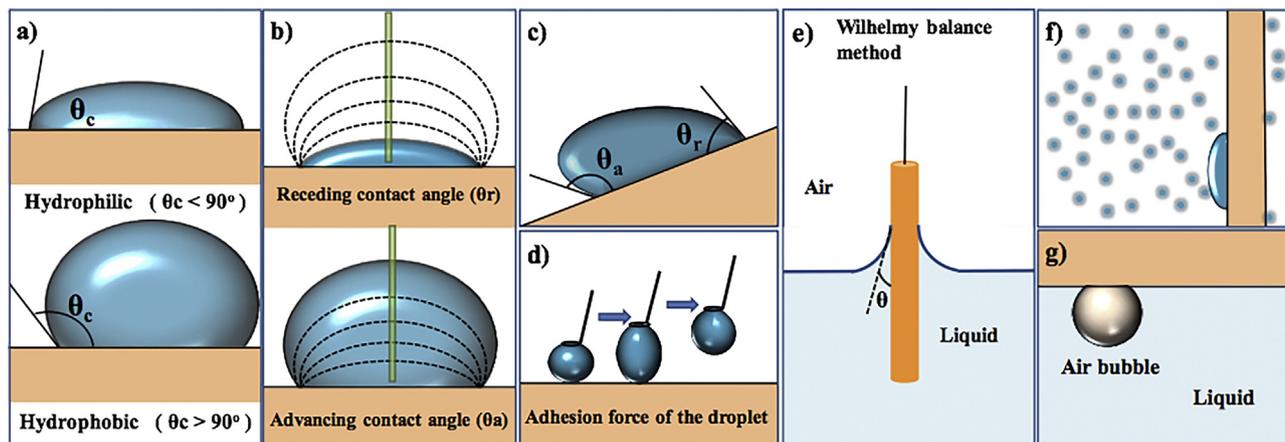


Fig. 3. The CA measurements, including: a) the static contact angle measurements; b) the CA hysteresis measurements; c) sliding angle measurements; d) adhesion force measurements; e) CA measurements of fibers (Wilhelmy balance method); f) collection and driven tiny liquid drops measurements; g) air bubble measurements. In these Figures, the orange parts represent for the samples and the blue or yellow parts represent for the water or oil droplets. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Rate of liquid addition/removal. The rate of increasing or decreasing the volume of liquid droplets should be low enough to ensure that the droplets have sufficient time to relax. This allows measurements to be carried out under quasi-equilibrium conditions.

Diameter of the needle/capillary tube. Needles or capillary tubes are used during this process to add or withdraw liquid. Their diameter must be small enough (relative to the droplet) to reduce wetting effects on the wall of the needle/capillary tube. This is especially important for the accurate measurement of receding angles.

Calculation equation. Due to the involvement of a needle or capillary tube, the droplet is usually not axisymmetric, and therefore cannot be approximated as part of a circle or ellipse. Therefore, use of Young-Laplace or other circle/ellipse-based equations will result in errors. In this case, the tangent method can be used, although it is often affected by background noise.

2) Tilting plate method: This involves placing a large volume liquid droplet on a sample surface, then gradually inclining the sample. The liquid droplet will not move at the beginning, but the contact angle of the front gradually increases while that of the rear gradually decreases as the liquid transfers from the rear to the front. Prior to the liquid droplet sliding, the CA determined at its advancing edge is the advancing angle (θ_a), while the CA determined at its receding edge is the receding angle (θ_r). Also at this moment, the sliding angle (θ_s) can be measured (as shown in Fig. 3c). The sliding angle is the critical angle at which a liquid droplet with a certain weight begins to slide down the inclined surface. It is another parameter of CAH used to describe the relative ease with which a liquid moves on a solid surface.

Crucial step. It should be noted that in order to obtain a better sliding angle, the volume of the liquid should be properly controlled in the range of 5–10 μL . The droplet should not be too large (which affects the CA) or too small (which influences the sliding movement).

3.1.2.2. Adhesion force measurements. Adhesion is one of the most important physical characteristics of superhydrophobic surfaces. The superhydrophobic surfaces of natural materials can be categorized as having low or high surface adhesion, depending on their properties. Typical low adhesion surfaces include lotus leaves and cicada wings [40], which exhibit a self-cleaning effect whereby dust is easily removed from their surfaces due to the low adhesion of water droplets. High adhesion surfaces include gecko foot-hair [41], rose petals [42], and peanut leaves [43], where water droplets do not easily roll off, even if the surfaces are inclined 90 or 180°. With further research into superwetting surfaces, special adhesion surfaces have potential applications in many fields, such as microfluidic channels [44,45] and self-cleaning [46,47] surfaces.

The adhesion properties at a solid-liquid interface is directly related to the dynamic process of the liquid droplet on the solid surface. Accordingly, the adhesion force needs to be determined through the dynamic process of the solid's wettability. Usually, a smaller sliding angle results in lower adhesion force, and vice versa. Therefore, the sliding angle is the most commonly used qualitative characterization of adhesion properties. McCarthy first proposed a method to qualitatively analyze the adhesion strength of solid surfaces by analyzing the dynamic process of CA measurement. [48] In addition, some researchers used a high-speed video system to record bouncing liquid droplets to qualitatively analyze the adhesion properties of superhydrophobic surfaces [49–51]. However, when superhydrophobic surfaces are in a Wenzel/Gecko state, it is difficult for water droplets to roll off a solid surface under gravity, so sliding angle cannot truly reflect surface adhesion. Therefore, the most commonly used approach to quantitatively characterize adhesion is to use a high-sensitivity microelectromechanical balance system to measure the separation forces of the liquid con-

tacting the solid surface. In this approach (as shown in Fig. 3d), a liquid droplet is suspended with a metal cap and programmed to make contact with the solid surface at a constant speed (not too fast, perhaps 0.005 mm s^{-1}), and then is removed. As soon as the droplet contacts the surface, it leaves the surface in the opposite direction. The forces are continuously recorded during this process, and the adhesion force equals the maximum force minus the force when the droplet left the solid surface.

3.1.2.2.1. Crucial step. This method encounters problems when testing high adhesion surfaces, such as those with a Cassie-Wenzel transition state or Wenzel state. The high adhesion force of these states will lead to stretching, deformation and separation of water droplets, such that tiny amounts of water remain on the solid surface, which further affects the quantitative characterization of adhesion force. So far, there are no more effective methods or standard evaluations used to measure the adhesion force between solid-liquid interfaces.

3.1.3. Contact angle measurements of fibers (Wilhelmy balance method)

Biological materials have a variety of peculiar structures, including smooth, fibrous and needle-like. Versatile methods of CA measurement have been applied to various structures. For example, when examining the wettability performance of water strider legs, CA was measured by the Wilhelmy balance method, which is probably the most reliable technique for measuring CAs on individual or single fibers of known diameter (Fig. 3e). Indeed, the Wilhelmy balance method has already been used for several decades [52–56], since it was first described by Ludwig Wilhelmy in 1863 [19]. This technique is based on the measurement of the total force acting on the sample [52]:

$$F = F_W + F_B + F_C = mg + \rho gV + \rho \gamma \cos\theta \quad (2)$$

where F_W is the weight of the dry fiber, which equals the sample mass (m) times the acceleration of gravity (g); F_B is the buoyancy force, which depends on the density of the liquid (ρ) and the immersed sample volume (V); and F_C is the capillary force, which depends on the sample perimeter (p), the liquid surface tension (γ) and the contact angle (θ).

3.1.3.1. Crucial step. In using the above equation, fibers or rods with known perimeters are ideal samples, although it is sometimes difficult to measure the perimeter and wetted length precisely. In addition, this technique is quite useful for studying dynamic CAs and contact angle hysteresis if the solid sample can be produced with a uniform cross-section in the submersion direction. The Wilhelmy balance method can be also used to measure the CA of capillary tubes if both the inside and outside surfaces are made of the exact same material. In this case, the perimeter should be the sum of the inner and outer perimeters of the capillary tube. In general, the Wilhelmy balance method can be applied to samples with various geometric shapes, such as plates, rods, wires, tubes, and capillaries.

3.1.4. Collection and driven ultra-small droplet measurements

In the past decade, bio-inspired structures exhibiting wetting phenomena have been extensively investigated due to their potential applications in industrial fields, such as flotation for mineral recovery [57] and wastewater treatment [58]. Although numerous advancements have been made and mechanisms are well understood at the macroscale (millimeters), many issues remain unresolved at the micro- or nanoscales (micro- or nanometers). Measurements of ultra-small droplets on solid surfaces have allowed the study of wetting theories down to the nanoscale.

When droplet sizes become very small and approach the micro- or even nanoscale, wetting behavior is no longer significantly influ-

enced by surface tension, but more so by line tension and liquid evaporation (both are usually negligible in macroscale studies) [59]. On the other hand, such droplets can be approximated as part of a sphere, because the influence of gravity is negligible compared to that of surface tension [60]. Therefore, at micro- and nanoscales, Young's classic equation must be modified to include the line tension effect [59,61,62].

$$\cos \theta = \frac{\gamma_{sv} - \gamma_{sl}}{\gamma_{lv}} - \frac{\sigma\gamma_{lv}}{R} \quad (3)$$

where θ is the contact angle, γ is the surface tension, σ is the line tension of the three-phase system, and R indicates the radius of the droplet's surface. The subscripts s , l , and v represent the solid, liquid and vapor phases, respectively.

With the recent rapid development of advanced imaging techniques, several methods have been developed to establish droplet profiles for measuring the CAs of ultra-small droplets. Methods such as interference microscopy, confocal microscopy, environmental scanning electron microscopy (ESEM), and AFM have been used to establish droplet profiles [63–69]. However, due to the micro- or nanoscale of ultra-small droplets, the effect of evaporation also plays a significant role when measuring CA. Therefore, methods requiring long times to determine micro- and nano-droplet profiles are impractical. Meanwhile, a number of methods have also been developed to deposit ultra-small liquid droplets on surfaces. The simplest way is by using an air sprayer [70], which mixes macroscale droplets with compressed air to generate ultra-fine droplets with a wide range of sizes. However, controlling the size of the droplets remains a challenging problem [71].

Recent research has indicated that many natural organisms have the ability to drive ultra-small droplets in a certain direction. Testing the driving performance can reflect the CAH of the surface. The behavior of the water drops can be recorded by an optical contact angle meter system with a charge-coupled device camera in time-lapse mode. The collection rates of water droplets and micron-sized oil droplets can be measured with various similar approaches.

When testing the ultra-small droplet collection and driving ability of solid samples, experiments should be carried out in a sampling room or directly in an air atmosphere (Fig. 3f). First, a solid sample should be carefully fixed on a sampling frame, and then numerous tiny water droplets are generated by an ultrasonic humidifier and introduced into the sampling room or onto the sample at a velocity of 20–30 cm s⁻¹. The directional motion of the tiny water droplets is recorded in every picture from condensing on the sample to visually appearance.

3.1.4.1. Crucial step. The size of the droplets has a very important influence on the Laplace pressure, which drives droplet movement. Therefore, the size of the droplet should be measured from the frame just before the drop begins to move. Other antifogging and droplet movement tests are carried out via condensation experiments; for example, by exposing solid samples to humid air after cooling in a refrigerator for several hours, or putting samples in a cooling chamber and introducing a humidified airflow.

3.1.4.2. Crucial step. The collection and driving performance of micron-sized oil droplets can also be measured by a similar approach. In this case, a specimen chamber should be used to hold water. The testing sample should be fixed on a sample frame and immersed in deionized water carefully to avoid air bubbles. The micron-sized oil droplets are generated by stirring and ultrasonically treating the mixture of oil and deionized water, then the mixture is sprayed through a syringe and needle onto the test sample. The entire process can also be recorded by an optical microscope-equipped contact angle meter system.

3.2. Contact angle measurements under liquid

While wetting performance in air atmospheres has been well studied, wetting underwater, underoil and in other liquid environments is becoming increasingly important in numerous applications, such as oil/water separation, and the recovery of coal and valuable minerals from ores. Various kinds of solid-liquid-gas systems have been constructed with the development of super-wetting systems. As shown in Fig. 2, there are three typical environment conditions according to solid-liquid-gas systems: air, underwater and underoil. The measurement of underwater oil contact angle (OCA) and oil sliding angle (OSA) are important for many natural materials with special wettability.

3.2.1. Crucial step

Before measuring OCA and OSA, samples should be carefully immersed in deionized water to make sure that no air bubbles exist on the test surfaces. During measurements of oil wettability, a syringe is immersed in water and 2–3 μ L of oil is injected under the water. Thus, oil droplets are suspended on the top of the syringe. After lightly shaking down the oil droplets onto the sample surface, the OCA or OSA can be measured. Liquids with higher densities than water (for example, 1,2-dichloroethane) can be used to facilitate the testing of underwater sliding angles. Then, the OCA and OSA are calculated as the mean of measurements taken at five different locations on the tested surface.

3.3. Captive bubble methods

As mentioned above, according to the different types of solid/liquid/air systems, there are three major classifications of CAs on solid surfaces: 1) water/oil CA in air (Fig. 2a); 2) oil CA in water or water CA in oil (Fig. 2b); and 3) air bubble CA under water/oil (Fig. 2c). Similar to the CA of liquid on a solid surface, air bubble CA can be defined as the equilibrium CA of the pinned bubbles on a solid surface, where the air/liquid interface meets the solid surface. The sessile drop method is commonly used to measure the former two kinds of CAs, but is not suitable for testing air bubble CA under water/oil because the air bubbles tend to move toward the surface of the liquid. Consequently, captive bubble methods are used instead. In this approach, a square quartz cuvette is used as the sample room, which is filled with water or oil and fixed onto the optical contact angle measurement device. Then, solid samples are laid horizontally in the liquid. Before testing, all of the samples are immersed in the liquid for about 30 min to achieve a redistributed, well-proportioned air layer. A bent needle is used to generate air bubbles beneath the solid samples. The behavior of the air bubbles (such as bursting, pinning, etc.) is recorded by a high-speed camera.

3.3.1. Crucial step

In order to make sure the air bubbles leave the needle orifice, the pumping speed should be controlled to be greater than a proper value. The volume of the exiting air bubble is usually about 3 μ L, and the distance between the solid surface and the needle orifice must be controlled throughout the experiment.

4. Examples of CA measurement of biomaterials

Recently, biomimetic research on organisms with special wettability properties has received tremendous interest from both theoretical and applied points of view. During the investigation of wetting performance, various measurement methods can be used and even combined to better reflect true CA values. Here are some examples.

Initial studies focused on plant leaves, such as those from lotus, rose, rice and taro. They have been extended to various other

biological materials such as spider silk, cactus, and insect body parts (e.g. water striders, desert beetles). In these cases, static CAs are usually measured as the primary data. However, there are some points that are worth noting before testing is conducted. First, as explained in the Materials section, all samples should be as fresh as possible, as wetting behavior may change as samples become stale. Second, sample surfaces should be carefully cleaned so that they are free of dust and have undisturbed chemical compositions. Third, to obtain an even surface, whole leaves or parts of a leaf should be affixed to glass slides with double-sided adhesive tape. With more complicated surface structures or plant shapes, several sorts of CA measurements are usually used in combination. For example, to test the droplet adhesion property of rose petals, static and dynamic CA measurements are used in combination. To measure the anti-fogging property of mosquito compound eyes or the water collection properties of spider silk and cactus, ultra-small droplet measurements are used. To evaluate the direction-dependent adhesion property of water strider legs, measurements employing the Wilhelmy balance method are utilized [72]. To examine the underwater oleophobicity of fish skin, underwater measurements are taken and compared with CA measurements in air. In addition, to further reveal the mechanisms of special wettability performance, wettability should be investigated alongside surface structure and surface chemical composition.

5. Expected results

Contact angle measurements generally pertain to a liquid droplet (or air bubble) making contact with a solid surface. Such CA values are indispensable for evaluating the special wettability performance of natural materials. Sometimes, however, CAs do not precisely reflect the real wettability properties of animals because it is difficult to measure live samples, which may exhibit different CAs to those of non-living samples. Therefore, CA measurements should be performed on live samples where possible, or very soon after death. Furthermore, since the wettability performance of biological materials (anisotropy, droplet driving, etc.) is largely dependent on surface structure, CA measurement methods must be carefully designed if they are to be accurate. Combinations of CA measurement and SEM imaging can be used to investigate the mechanisms of special wettability.

6. Future prospects

Contact angle is one of the best indicators of surface wettability. While CA measurements have been developed for more than one hundred years, recent years have seen accelerated progress in the discovery of the special wettability properties of organisms. In addition to the well-established methods of investigation, many new ones have been developed, such as underwater oil micro-droplet collection, fog collection, and liquid droplet driving. All these methods have their own applications, advantages and disadvantages, and should be selected according to practical purposes. In the future, new CA measurement technology, such as novel instruments equipped with specialized sample rooms or injection needles, is urgently needed for the precise quantification of the properties of natural materials. Furthermore, CA measurement methods should aim for improvements in accuracy, multi-functionality, and online analysis.

Competing interests

The authors declare no potential conflicts of interest with respect to authorship and/or publication of this article. Opinions and assertions contained herein are those of the authors and are not

construed as necessarily representing the views of their respective employers.

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