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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.

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

$$\gamma_{SG} - \gamma_{SL} - \gamma_{LG}\cos\theta = 0 \tag{1}$$

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 $< 10^\circ$ or $> 150^\circ$ are considered to be superhydrophilic or superhydrophobic surfaces, while surfaces with oil CAs $< 10^\circ$ or $> 150^\circ$ 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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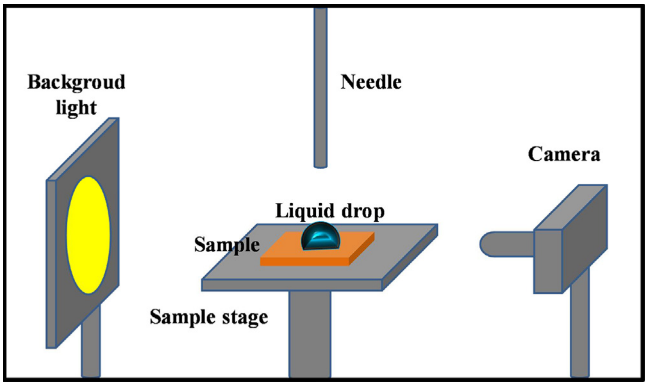

Fig. 1. The CA measurement equipment based on the droplet image analyzing method.

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 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