

Multiple-dimensional micro/nano structural models for hydrophobicity of butterfly wing surfaces and coupling mechanism

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Abstract The microstructure, wettability and chemical composition of the butterfly wing surfaces were investigated by a scanning electron microscope, a contact angle meter and a Fourier transform infrared spectrometer. The micro/nano structural models for hydrophobicity of the butterfly wing surfaces were established on the basis of the Cassie equation. The hydrophobicity mechanisms were discussed from the perspective of biological coupling. The butterfly wing surfaces are composed of naturally hydrophobic material and possess micro/nano hierarchical structures, including primary structure (micrometric scales), secondary structure (nano longitudinal ridges and lateral bridges) and tertiary structure (nano stripes). The wing surfaces exhibit high hydrophobicity (contact angle 138° – 157°) and low adhesion (sliding angle 1° – 3°). The micromorphology and self-cleaning performance of the wing surfaces demonstrate remarkable anisotropism. The special complex wettability ascribes to a coupling effect of the material element and the structure element. In micro-dimension, the smaller the width and the bigger the spacing of the scale, the stronger the hydrophobicity of the wing surfaces. In nano-dimension, the smaller the height and the smaller the width and the bigger the spacing of the longitudinal ridge, the stronger the hydrophobicity of the wing

surfaces. This work promotes our understanding of the hydrophobicity mechanism of bio-surfaces and may bring inspiration for biomimetic design and preparation of smart interfacial materials.

Keywords Micro/nano structure · Hydrophobicity model · Superhydrophobicity · Adhesion · Biological coupling · Butterfly

1 Introduction

Wettability (e.g., hydrophobicity, hydrophilicity, oleophobicity, lipophilicity, adhesion, etc.) is one of the important properties of solid surface, which is basically determined by chemical composition (free energy) and microstructure (roughness) of the surface. In the last few years, the interfacial materials with desirable properties and functions have attracted tremendous interest due to valuable theoretical importance and a wide variety of applications in industrial, military, biomedical and domestic fields. The earliest wetting theories were proposed by Young [1], Cassie and Baxter [2], Cassie [3], and Wenzel [4, 5]. The Young equation describes quantitatively the contact angle (CA) of a liquid droplet by thermodynamic parameters. The Cassie approach assumes that the droplet settles on the peaks of the roughness geometry does not fill up the grooves (depressions) but instead traps air under it, forming a composite contact. The Wenzel approach assumes that the liquid sinks into the grooves of the rough surface, forming a wetted contact. The Cassie and Wenzel theories present two possible equilibrium states of a droplet on a rough substrate. The geometric parameters of the rough surface determine which of these two states have relatively lower free energy [6, 7].

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Hydrophobicity models include mainly microstructure models [8, 9] and free energy models [10, 11].

After millions of years of natural selection, various creatures have evolved peculiar macro-/microstructures, forms and functions to adapt to the environment. Many animals and plants possess distinctive body surfaces which are hydrophobic, self-cleaning, anti-adhesive, anti-corrosive, anti-fouling, anti-icing, drag reducing, self-healing, fatigue resistant, anti-wearing and so on [12–18]. Insect is the unique flying invertebrate, which has the most species, the largest population and the widest distribution throughout the world. The butterfly wing surface is one of the most complicated three-dimensional periodical substrates in nature. It has become a popular bio-template because of its excellent characteristics such as attractive iridescence, superhydrophobic property and quick heat dissipation ability [19–23]. In this work, the multiple-dimensional micro/nano structural models for hydrophobicity of butterfly wing surface were established on the basis of the Cassie equation. Additionally, the wettability mechanisms were discussed from the perspective of biological coupling. The results provide enlightenment for artificial manipulation of surface wettability and biomimetic preparation of smart functional materials, novel microfluidic devices and easy-cleaning coatings.

2 Materials and methods

2.1 Materials

The butterfly specimens, belonging to seven families, 23 genera, 27 species, were collected from June through August, 2013, in Changchun City (the Nanhu Park, Zoo & Plant Park, Jingyuetan National Forest Park), Jilin City (Zuojia Special Zone), Dalian City (Lüshunkou District) and were identified by systematic taxonomy. The butterfly wings were cleaned, desiccated and flattened, then cut into 5 mm × 5 mm pieces from discal cell (Fig. 1a). The distilled water for CA and sliding angle (SA) measurements was purchased from Tianjin

Pharmaceuticals Group Co. Ltd., China. The volume of water droplets for CA and SA measurements was 5 μL . The CaCO_3 particle was purchased from Shanghai Aibi Chemistry Preparation Co. Ltd., China. The particle size distribution was 5–10 μm .

2.2 Characterization of microstructure

After gold coating by an ion splash instrument (SBC-12, Beijing Instrument Research and Manufacture Center of CAS, China), the wing pieces were observed and photographed under a SEM (JSM-5500LV, Japan). Using Photoshop software, the microstructural parameters of the butterfly wing surfaces were measured in SEM images.

2.3 Measurements of wetting angles

Using an optical contact angle measuring system (Data-Physics OCA20, Germany), the CA of water droplets on the butterfly wing surfaces was measured via sessile drop method at ambient conditions of $(25 \pm 1)^\circ\text{C}$ and relative humidity of approximately 80 %. The SA of water droplets was measured along three different directions, including forward SA (FSA, the SA of droplets from wing base to wing terminal end), backward SA (BSA, the SA of droplets from wing terminal end to wing base) and perpendicular SA (PSA, the SA of droplets perpendicular to the major axis of wing) (Fig. 1b). The water droplets were dripped on the sample table in a horizontal position, then the inclination degree of the table was raised 1° each time until the droplets rolled off freely. The inclination degree of the table was recorded as the SA value.

2.4 FT-IR measurement

After grinding finely, 5–8 mg of wing samples were mixed homogeneously with 200 mg of KBr and pressed into a thin slice. The absorbance was measured by means of FT-IR (Nicolet FT-IR200, USA). The chemical composition of the wing surface was analyzed by the FT-IR spectra.

2.5 Removal of CaCO_3 particles

The wing pieces were affixed to glass slides with double-sided adhesive tape and put on the sample table of OCA20. Five milligrams of CaCO_3 particles were evenly spread on the discal cell of the wing. A water droplet from an injector fell on the CaCO_3 area. The sample table was inclined 3° , and the droplet flowed through the contaminated area. A stereo microscope (Zeiss SteREO Discovery V12, Germany) was used to observe the removal of CaCO_3 particles.

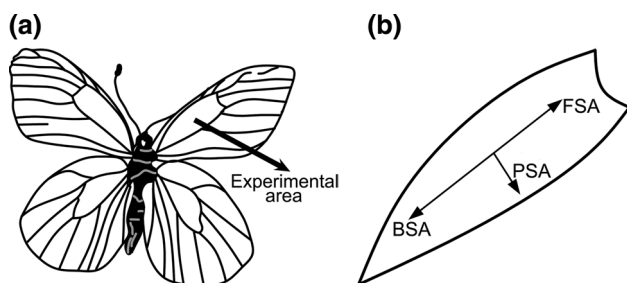


Fig. 1 The experimental area (a) and the sliding angles in different directions (b) on the butterfly wing surface

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