Ultrastructure and Self-cleaning Function of Moth (Notodontidae) and Butterfly (Lycaenidae) Wings

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Abstract. The microstructure, hydrophobicity, adhesion and chemical composition of the butterfly and moth wing surfaces were investigated by a scanning electron microscope (SEM), a contact angle meter, and a Fourier transform infrared spectrometer (FT-IR). Using ground calcium carbonate (heavy $CaCO_3$) as contaminating particle, the self-cleaning performance of the wing surface was evaluated. The wing surfaces, composed of naturally hydrophobic material (chitin, protein, fat, etc.), possess complicated hierarchical micro/nano structures. According to the large contact angle (CA, 148.3~156.2 ° for butterfly, 150.4~154.7 ° for moth) and small sliding angle (SA, 1~3 ° for butterfly, 1~4 ° for moth), the wing surface is of low adhesion and superhydrophobicity. The removal rate of contaminating particle from the wing surface is averagely 88.0% (butterfly wing) and 87.7% (moth wing). There is a good positive correlation (R^2 =0.8385 for butterfly, 0.8155 for moth) between particle removal rate and roughness index of the wing surface. The coupling effect of material element and structural element contributes to the outstanding superhydrophobicity and self-cleaning performance of the wing surface. The wings of flying insect can be potentially used as templates for biomimetic preparation of biomedical interfacial material with multi-functions.

Introduction

Wettability is basically determined by chemical composition (free energy) and microstructure (roughness) of the surface [1~3]. The interfacial material with special properties and functions is attracting more and more attention due to the wide application in industrial, agricultural, military and biomedical fields. After long-term natural evolution and selection, many plants and animals have possessed special (anti-adhesive, anti-corrosive, anti-wetting, anti-icing, anti-wearing, etc.) body surfaces to adapt to the environment. Inspired by the wettability of various bio-surfaces, lots of biomimetic materials have been artificially prepared [4~6]. Insect is not only the unique flying invertebrate, but the animal with the most species, the largest number and the most widespread distribution on the earth. As one of the most complicated three-dimensional periodical substrates in nature, insect body surface has been employed as a popular fabrication template because of its superior characteristics [7]. Using ground calcium carbonate as contaminating particle, in this work the self-cleaning performance of insect in Lepidoptera (butterfly and moth) was evaluated. The mechanism of wettability and self-cleaning property was discussed from the perspective of biological coupling. The results can bring insight for design and preparation of novel interfacial material and biomedical self-cleaning surface.

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Materials and Methods

Materials

The specimens of butterfly (ten species in Lycaenidae) and moth (ten species in Notodontidae) were collected in Changchun City, Dalian City, Harbin City and Jilin City of Northeast China. The wings were cleaned, desiccated and flattened, then cut into 5 mm × 5 mm pieces from the discal cell (Fig. 1). The distilled water for CA and SA measurements was purchased from Tianjin Pharmaceuticals Group Co. Ltd., China. The volume of droplet for CA and SA measurement was 5.0 μl, the volume of droplet for measurement of $CaCO_3$ removal rate was 9.0 μl. The average diameter of $CaCO_3$ particle was 5~10 μm.

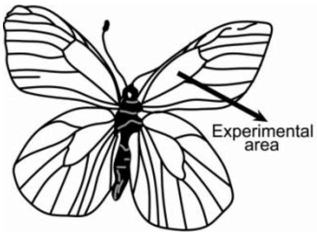

Figure 1. The experimental area of the wing surface

Methods

Characterization of the Micro/nano Structure

After gold coating by an ion sputter coater (Hitachi E-1045, Japan), the wing pieces were observed and photographed by a SEM (Hitachi SU8010, Japan). Using Photoshop software, the microstructural parameters of the wing were measured in SEM images.

Measurements of the Wetting Angles

Using an optical CA measuring system (DataPhysics OCA20, Germany), the CA of water droplet on the wing was measured by sessile drop method at room conditions of 25±1 ^{o}C and relative humidity of approximately 80%. The sliding angle (SA) of water droplet was measured along the direction from base to terminal end of the wing. The water droplet was dripped on the sample table in a horizontal position, then the inclination degree of the table was raised 1 °each time until the droplet rolled off freely. The inclination degree of the table was recorded as the SA value.

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.

Evaluation of the Self-cleaning Performance

The wing pieces were affixed to a glass slide with double-sided adhesive tape, and put on the sample table of OCA20. Five mg of $CaCO_3$ particle was 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 °, the droplet flowed through the contaminated area. Using an electronic analytical balance (Shimadzu AUX-120, Japan), the mass of $CaCO_3$ residual was measured, and the removal rate was calculated.

Results and Discussion

The Self-cleaning Performance of the Wing Surface

Both the butterfly and the moth wing surface display outstanding self-cleaning performance. When the droplet flows over the wing surface, most $CaCO_3$ particles are taken away. The removal rates are all over 80.0%. The average removal rate is 88.0% (butterfly wing) and 87.7% (moth wing), respectively (Table 1).

Table 1. The CA, SA, removal rate of $CaCO_3$ particle, roughness index (*RI*) on the wing surfaces

Species		CA (°)	SA (°)	Removal rate of $CaCO_3$ particle (%)	Roughness index (*RI*) of wing surface
Butterfly	*Antigius attilia*	152.4	2	85.4	2.1
	Araragi enthea	153.1	2	83.6	2.1
	Artopoetes pryeri	155.5	2	86.7	2.7
	Favonius aurorinus	156.2	1	90.5	3.8
	Favonius orientalis	148.3	3	88.3	2.8
	Japonica saepestriata	152.6	1	91.8	3.5
	Neozephyrus japonicus	150.7	3	88.2	2.8
	Neozephyrus taxila	154.2	2	91.4	3.6
	Shirozua jonasi	154.5	1	86.6	2.2
	Thecla betulae	150.8	2	87.0	3.0
Moth	*Cerura menciana*	153.6	1	92.5	3.5
	Clostera anachoreta	152.3	2	87.8	2.6
	Hybocampa umbrosa	154.7	1	91.6	3.6
	Lampronadata cristata	150.4	2	90.3	3.2
	Lophocosma atriplaga	152.9	4	82.4	1.7
	Nericoides davidi	153.3	3	85.8	2.5
	Nericoides leechi	152.8	4	82.7	2.6
	Paranerice hoenei	154.5	2	88.1	2.8
	Peridea lativitta	153.2	2	87.2	2.6
	Phalera assimilis	151.6	2	88.9	3.0

$$RI = \sqrt{\frac{4d^2}{e^2} + 1},$$

where d and e represent height and width of the longitudinal ridge, respectively [8].

The Low Adhesive Superhydrophobicity of the Wing Surface

The wing surfaces of the butterfly and moth exhibit superhydrophobicity. All the water CAs are over 150 °, except *Favonius orientalis* (148.3 °) (Table 1). Meanwhile, the wing surfaces have low adhesion, the water SA is so small (SA 1~3 ° for butterfly, 1~4 ° for moth) that even a very slight tilting of the wing is sufficient to cause the droplet to roll off. The wing surfaces are of low adhesive superhydrophobicity. The butterfly and moth wings have perfect superhydrophobic and self-cleaning surfaces.

The Micro/nano Structure of the Wing Surface

The butterfly and moth wing surfaces display similar micro/nano structures (Fig. 2). The micrometric scales constitute the primary structure. For the butterfly wing, the length of the scale is 57~124 μm, the width is 32~65 μm, the spacing is 56~90 μm [Fig. 2(a)]. For the moth wing, the length of scale is 186~328 μm, the width is 64~125 μm, the spacing is 103~172 μm [Fig. 2(d)]. The submicrometric longitudinal ridges and lateral bridges on the scales constitute the secondary structure [Fig. 2(b), 2(e)]. The nano stripes on the longitudinal ridges and lateral bridges constitute the tertiary structure [Fig. 2(c), 2(f)].

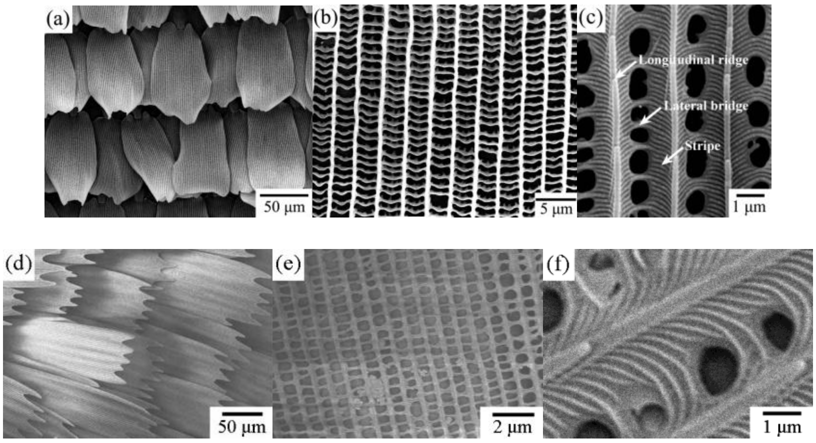

Figure 2. The hierarchical microstructure of the butterfly and moth wing surfaces (SEM)

(a) Primary structure (butterfly); (b) Secondary structure (butterfly); (c) Tertiary structure (butterfly); (d) Primary structure (moth); (e) Secondary structure (moth); (f) Tertiary structure (moth).

The Self-cleaning Mechanism of the Wing Surface

The wing surfaces of butterfly and moth exhibit highly similar absorption characteristic of FT-IR spectra (Fig. 3).

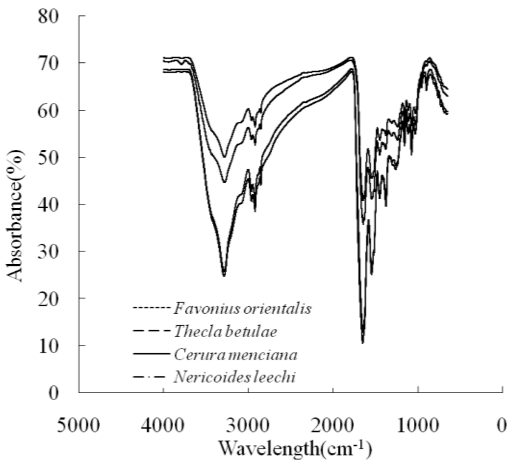

Figure 3. FT-IR spectra of moth and butterfly wing surfaces

For the butterfly wing, the absorption peaks are at 3261, 2944, 2876, 1650, 1534, 1383, 1227, 1147, 1055 cm^{-1}. For the moth wing, the absorption peaks are at 3294, 2942, 2881, 1652, 1531, 1381, 1230, 1176, 1071 cm^{-1} (Table 2). These absorption bands result from the stretching vibration, skeletal vibration, deformation vibration and in-plane bending vibration of the bases (e.g. $-CH_3$, $-CH_2$, $-C-CH_3$, C-H, O-H, C=O, C-O, N-H) in chitin, protein or fat [9]. Owing to the existence of hydrogen bond (H-bond), O-H peak is always rather wide. The absorption bands around 3294, 3261, 2944, 2942, 2881, 2876 cm^{-1} result from stretching vibration of $-CH_3$, $-CH_2$, C-H bases in chitin, protein or fat. The absorption band around 1652, 1650 cm^{-1} results from symmetrical stretching vibration of C=O, C-H, N-H bases in chitin or protein. The absorption band around 1534, 1531 cm^{-1} results from skeletal vibration of C-C in chitin and deformation vibration of C=O, C-H, $-C-CH_3$, $-CH_2$ bases in protein or fat. The absorption bands around 1383, 1381, 1230, 1227 cm^{-1} result from in-plane bending vibration of C-H base in chitin, protein or fat. The absorption bands around 1176, 1147, 1071, 1055 cm^{-1} arise from stretching vibration of C-O base in chitin, protein or fat. The butterfly and moth wing surfaces are composed mainly of naturally hydrophobic material (intrinsic CA 95~100°), which is the chemical foundation of the superhydrophobicity and self-cleaning property on the wing surfaces. However, much higher hydrophobicity can not be induced by the chemical composition alone.

Table 2. The characteristic peaks in FT-IR spectra of butterfly and moth wings

Species		4000~2500 cm^{-1}			2500~1500 cm^{-1}		1500~1000 cm^{-1}			
Butterfly	*Antigius attilia*	3264	2944	2876	1648	1535	1379	1227	1152	1057
	Araragi enthea	3265	2943	2876	1653	1532	1385	1221	1145	1058
	Artopoetes pryeri	3262	2944	2877	1651	1536	1383	1227	1148	1050
	Favonius aurorinus	3261	2947	2875	1654	1535	1384	1224	1146	1051
	Favonius orientalis	3255	2945	2877	1650	1532	1380	1228	1145	1058
	Japonica saepestriata	3257	2945	2878	1650	1537	1387	1225	1154	1057
	Neozephyrus japonicus	3259	2938	2872	1645	1535	1382	1229	1143	1052
	Neozephyrus taxila	3268	2943	2869	1652	1528	1384	1227	1144	1050
	Shirozua jonasi	3261	2946	2874	1648	1530	1386	1226	1145	1059
	Thecla betulae	3256	2942	2881	1651	1538	1378	1231	1145	1053
	Average	3261	2944	2876	1650	1534	1383	1227	1147	1055
Moth	*Cerura menciana*	3301	2945	2884	1652	1530	1382	1231	1175	1073
	Clostera anachoreta	3286	2939	2878	1647	1528	1384	1236	1176	1071
	Hybocampa umbrosa	3295	2944	2882	1657	1532	1383	1229	1175	1068
	Lampronadata cristata	3287	2940	2884	1654	1525	1383	1233	1181	1072
	Lophocosma atriplaga	3294	2948	2878	1653	1537	1380	1228	1174	1075
	Nericoides davidi	3306	2937	2881	1651	1532	1381	1227	1175	1069
	Nericoides leechi	3291	2946	2879	1650	1534	1382	1232	1176	1072
	Paranerice hoenei	3299	2939	2880	1649	1530	1380	1229	1177	1071
	Peridea lativitta	3289	2941	2879	1650	1529	1379	1230	1176	1067
	Phalera assimilis	3292	2942	2883	1652	1531	1378	1226	1173	1070
	Average	3294	2942	2881	1652	1531	1381	1230	1176	1071

Due to the rough structures on the wing surface, most contaminating particles settle on the tips of microtextures, the actual contact area between particle and microstructure is very small. The adhesive force between particles and water droplet is much larger than that between particles and microstructure, thus the particles can be “trapped” and taken away easily by the rolling droplet. The removal rate of contaminating particle has no significant correlation (R^2<0.1) with the scale parameters (length, width, spacing) or the longitudinal ridge parameters (height, width, spacing), but has significant correlation (R^2=0.8385 for butterfly, 0.8155 for moth) with roughness index (*RI*) of the wing surface (Fig. 4). *RI*, the magnitude of surface roughness, is the ratio of the real area to the geometry projection area. The superhydrophobicity and self-cleaning characteristic of the wing surface ascribes to the coupling effect of hydrophobic material and rough structure. The self-cleaning function endows butterfly and moth with the ability to lighten body burden, decrease drag, increase flight efficiency and optimize energy budget. Thus, they can get more opportunities to survive.

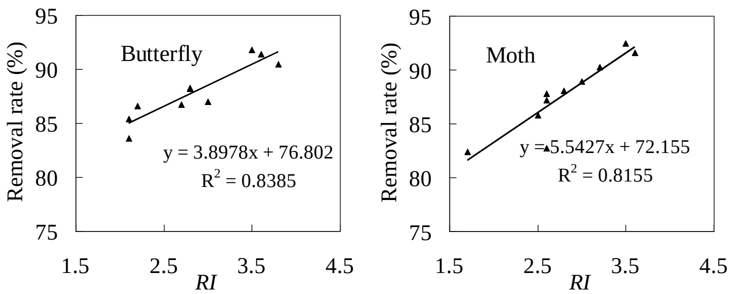

Figure 4. Relationship between the removal rate of $CaCO_3$ particle and roughness index (RI) of the wing

Summary

The wing surfaces of butterfly and moth in Lepidoptera have similar chemical composition, multiple-dimensional microstructure, wettability and self-cleaning characteristic, despite the different taxonomic positions, morphological features and living habits. The wing surface is of low adhesion (SA 1~4°) and superhydrophobicity (CA 148.3~156.2°). The removal rate of $CaCO_3$ contaminating particle from the wing surface is averagely 88.0% (butterfly wing) and 87.7% (moth wing). There is a good positive correlation (R^2=0.8385 for butterfly, 0.8155 for moth) between particle removal rate and roughness index of the wing surface. The excellent self-cleaning property of the wing surface ascribes to the coupling effect of material element and structural element. The wings of Lepidoptera insect can be used as biomimetic templates for preparation of biomedical functional material.

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