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Metallic Butterfly Wing Scales

Superstructures
with High Surface-
Enhancement
Properties for Optical
Applications

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Preface

By a long-term evolution, biological species have developed numerous powerful structures and functions to survive the natural selection process. These natural designs always present inspirations for solving complex human problems. Early imitations of biological structures can be traced back to six centuries ago, when Leonardo da Vinci tried to fabricate a “flying machine” by studying the anatomy and flight of birds. However, although scientists have never stopped artificially imitating nature (*biomimetics*), many natural designs still surpass the most advanced human products in complexity and functionality.

Over a decade ago, however, a group of new materials, morphology genetic materials, was developed (Cook et al., *Angew Chem Int Ed* 2003, 42, p. 557). Using a great variety of chemical and physical methods, scientists directly replicated the bio-structures in functional components. These materials not only preserve the original biological morphologies, but also have a broad range of manually endowed functions.

As a part of these studies, this book mainly demonstrates how natural butterfly wing scales can be used to produce advanced SERS substrates. These scales feature 3D sub-micrometer structures that are superior to many human designs in terms of structural complexity, reproducibility, and cost. Moreover, there are globally over 174,500 species of butterflies and moths and each bears various types of scales. This fact presents much freedom for researchers to select appropriate structures according to different applications.

This book presents three approaches for replicating natural butterfly wing scales using a variety of metals required by state-of-the-art science and technology. Among these methods, a single versatile chemical route (Chap. 3) can be used to produce butterfly scales in seven different metals (Ag, Au, Cu, Co, Ni, Pd, and Pt). Significantly, the Au scales such as SERS substrates have ten times the analyte detection sensitivity and are one tenth the cost of their human-designed commercial counterparts (Klarite™). Since some species of butterflies and moths (e.g., silk moth) have been farmed for thousands of years and one wing usually bears over 100,000 scales, these materials are promising in SERS applications. In addition, preliminary mechanisms of these surface-enhancement phenomena are also included in this book, which have been applied in designing artificial arrays with high SERS performance (Jeon et al., *Small* 2014, 10, p. 1490).

The main contents of this book are based on the studies conducted in the past 5 years in the Morphology Genetic Lab established by Prof. Di Zhang at Shanghai Jiao Tong University. These replications of butterfly scales to metals were carried out after the first metal butterfly made via PVD in the Vukusic group at the University of Exeter (Garrett et al., *J Biophoton* 2009, 2, p. 157). We greatly appreciate Mr. Xiang Ding, Mrs. Jing Fang, Mrs. Guofen Song, and Mr. Wenshu Chen for editing the drafts. We would also like to thank the financial support from the Natural Science Foundation of China (No. 51202145, No. 51171110, No. 51271116, and No. 91333115), Shanghai Science and Technology Committee (No. 14JC1403300 and No. 14520710100), and Research Fund for the Doctoral Program of Higher Education of China (20120073120006 and 20120073130001). In addition, I appreciate the support provided by the Program for New Century Excellent Talents in University, Ministry of Education, China.

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Chapter 1

Background

In the twentieth century, the understandings of materials' properties deepened to an electronic level. Present technologies have realized the control of the electron motion in media based on the advances in semiconductor physics. This in turn leads to a rapid development in electronics and information technologies (Moore's law). However, an information processor needs high speed and capacity while the capacity of an electronic device is limited. As Moore's law might be approaching its limits, scientists are seeking for alternative strategies to satisfy the rapidly increased application demands. One of the most promising solutions is to use photons as information carriers to replace electrons. Over the past decades, great efforts have been spent in seeking ways to effectively control light propagation within materials. These studies have opened up a new research field; nanophotonics.

Currently, photonic crystals and plasmonic devices are two of the most promising solutions for the manipulation of light at a submicrometer level. Photonic crystals (or photonic band gap materials) refer to a group of artificial dielectric structures with photonic band gaps [1]. Radiations with specific wavelength can propagate in these structures while others are prohibited. This is achieved by a periodic modulation in dielectric coefficients by materials and environments. Analogous to semiconductors with electronic band gaps, photonic crystals are critical to optical integrated circuits. Optical components like photonic crystal fibers, photonic crystal optical waveguides, photonic crystal couplers, and photonic crystal beam splitters have been developed so far [2].

However, typical photonic structures are of hundreds of nanometers in dimension. Though photonic devices have high speeds and broad bandwidths, their size is comparable to light wavelength and the energy loss will rapidly increase with the decrease in device dimension. Thus, it is difficult to interconnect photonic structures with conventional nanosized electronic devices. To solve this problem, plasmonic devices were recently developed [3–7]. Since the dielectric coefficients of *metals* are *negative*, metallic nanostructures can generate surface plasmon polaritons (SPPs) or localized surface plasmons (LSPs) under the excitation of electromagnetic waves [8]. These SPPs or LSPs within a subwavelength region can carry information instead of mere electrons or photons, thus bridging the structural gap