Fabrication of biomimetic SERS substrates based on the nanostructures of lepidoptera

M. Yamazaki[1] and H. Takei[2,3]

[1]Graduate School of Life Sciences, [2]Faculty of Life Sciences, Toyo University, Itakura, Gunma 374-0193, Japan, [3]Bio-Nano Electronics Research Centre, Toyo University, Kawagoe, Saitama 350-8585, Japan

Objective

In order to employ surface-enhanced Raman spectroscopy (SERS) for industrial applications, further improvements in the fabrication method of noble metal nanostructures are required. The method of using structures existing in the biological world is known as biomimetics. In SERS, the use of submicron structures of butterfly scales has been reported recently. In this paper, we not only report the latest findings on scale structures but also introduce for the first time an effective submicron structure other than the wing. The shape of scales is typically an oval, approximately 100 microns long and 50 microns wide. In the direction of the long axis, ridges are formed at intervals of several microns. This would not be useful as SERS structures, but the surface and lower parts of the ridges have submicron structures. A submicron structure other than those originating from the wings is the antennae of moths. Advanced species of moths can detect female sex pheromones (smell molecules) even from a distance of more than several kilometers, and their receptors exist in the antennae. So, we thought it would be possible to detect VOCs with high sensitivity by using this antenna. Based on the knowledge of ideal nanostructures obtained from lepidopteran structures, it would be possible to artificially fabricate SERS substrates. It could be useful for SERS. However, the size and shape of the noble metal nanostructures need to be optimized in order to effectively utilize the enhancement effect of the scale substrate. In addition, it was necessary to consider not only the species of butterfly but also the region and the back, front of the scales. We selected *S. charonda* and *A. yamamai* for evaluation of their suitability as SERS substrates.

Methods

The scales of butterflies have a periodic and hierarchical submicron structure, and the SERS effect can be obtained by covering the scales with noble metals using a vapor deposition method. In particular we will examine (1) the optimal structure by comparing the signals of substrates using various butterfly scales, (2) substrates that selectively use specific parts of the scales (scaffold-like structures that support three-dimensional structures), and (3) detection of VOCs by a substrate using the antenna of *A. yamamai*. In these studies, volatile methyl mercaptan was used in addition to the standard reagents R6G and β-carotene.

Results

(1) The scales of *Ornithoptera priams* have a wavy cloud−like structure in the white and purple scales of *S. charonda*, effective as a SERS substrate. (2) The scaffold structure is more effective than the structure seen from the front side. (3) It may have a higher enhancement than scales. The three-dimensional structures of these samples were observed by SEM.

Reference:

[1] Z. Zhang, W. Yu, J. Wang, D. Luo, X. Qiao, X. Qin, T. Wang, *Anal. Chem.,* **89**, 1416-1420 (2017).