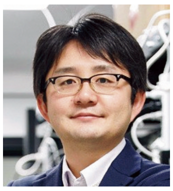
Plasmon–molecule remote coupling for enhanced optical spectroscopy



Department of Systems Innovation, Graduate School of Engineering Science

Professor Takeo Minamikawa

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Abstract

In conventional understanding, strong interactions between the collective electron oscillations (plasmons) in metallic nanoparticles and target molecules occur only when the molecules are located within an extremely short distance, typically less than 10 nm, from the metal surface. In this study, we experimentally demonstrated, for the first time in the world, a remote plasmonic enhancement phenomenon in which optical signals are strongly amplified even when the metal and molecules are separated by more than 100 nm. This was achieved by forming a columnar-structured silica overlayer on silver nanoparticles. The phenomenon is applicable to both fluorescence and Raman spectroscopy, achieving detection sensitivities higher by 10^2–10^7 times compared with conventional approaches. Because the analyte molecules are not in direct contact with the metal surface, the structure prevents molecular degradation induced by catalytic effects and suppresses deterioration of the metallic substrate, thereby enabling molecular spectroscopic measurements with excellent chemical stability and mechanical durability.

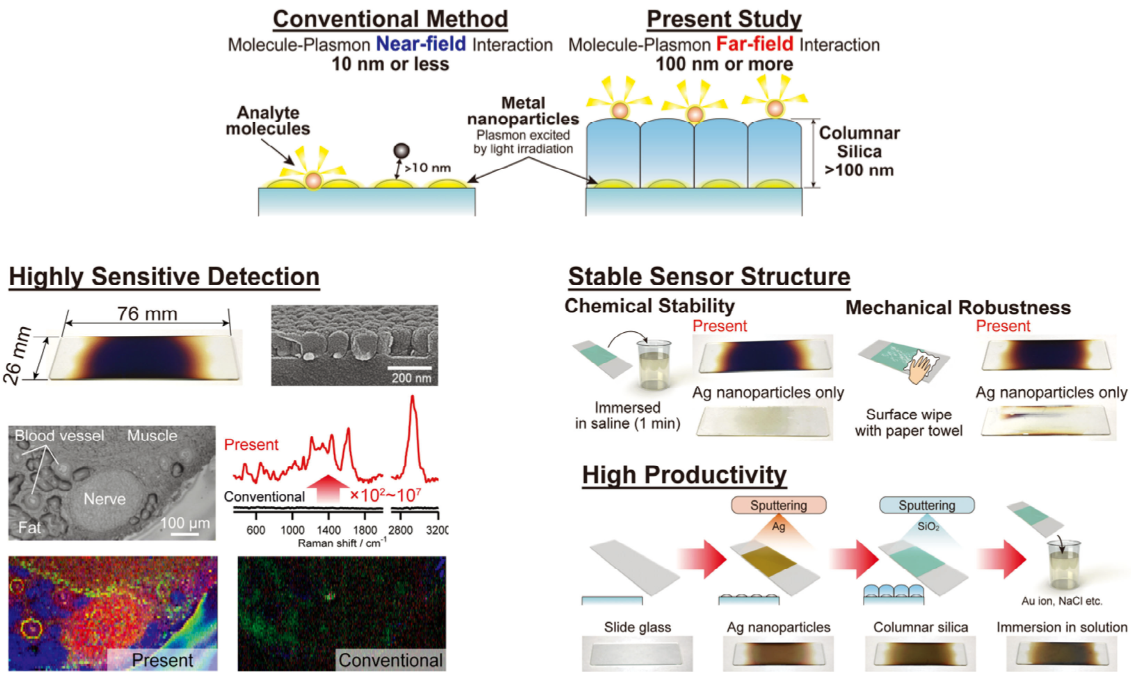
Background & Results

Plasmonics, which exploits the interaction between light and collective electron oscillations in metallic nanostructures, has attracted great attention as a key technique for realizing highly sensitive molecular analysis and biosensing. However, conventional plasmonic sensing requires that the target molecules be positioned within 10 nm of the metal surface to experience strong enhancement, inevitably causing direct metal-molecule contact. Such contact can induce catalytic reactions, degradation of analytes, or surface modification of the metal, leading to reduced chemical stability and poor mechanical robustness, major obstacles to practical plasmon-based ultrasensitive sensing.

To address these challenges, we developed a new approach in which a columnar-structured silica layer was formed on silver nanoparticles. We demonstrated that plasmon–molecule coupling can occur even at distances exceeding 100 nm, allowing substantial enhancement of optical signals without direct contact. When applied to Raman and fluorescence spectroscopy, this phenomenon produced up to 10^7-fold and 10^2-fold signal enhancements, respectively. Moreover, the silica layer protects the metal nanoparticles, providing both chemical stability and mechanical robustness. This configuration enables long-term, reliable measurements under chemically or physically demanding conditions and establishes a robust platform for high-sensitivity spectroscopy.

Significance of the research and Future perspective

This achievement is significant from both scientific and technological viewpoints. Scientifically, it provides the first experimental evidence of long-range plasmon–molecule interactions beyond 100 nm, extending the conventional limits of light–matter coupling and initiating a new concept of “Remote Plasmonics”. Technologically, it delivers a reliable and durable plasmon-enhanced sensing platform capable of high-sensitivity detection for previously difficult targets such as corrosive or biological samples. The synergy of stability, robustness, and sensitivity offers strong potential for real-world deployment. Looking ahead, this technology is expected to find wide applications in environmental monitoring, materials evaluation, and medical diagnostics, contributing to next-generation optical sensing systems that unite high performance with durability.



Patent

Treatise Minamikawa, Takeo; Sakaguchi, Reiko; Harada, Yoshinori et al. Long-range enhancement for fluorescence and Raman spectroscopy using Ag nanoislands protected with column-structured silica overlayer. Light: Science & Applications. 2024, 13, 299. doi: 10.1038/s41377-024-01655-3

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Keyword plasmon, molecular sensing, biosensing, Raman spectroscopy, fluorescence spectroscopy