1-1-10. Time-Resolved Microspectroscopy

Overview

Time-resolved microspectroscopy is an advanced technique that combines the temporal resolution of time-resolved spectroscopy with the spatial resolution of optical microscopy, enabling the visualization and analysis of ultrafast photophysical and photochemical phenomena in materials ranging from the microscale to the nanoscale. This approach is widely applied in diverse fields such as chemistry, physics, biology, materials science, and nanotechnology.

Current Status and Frontiers

A comprehensive understanding of complex and heterogeneous systems in materials science and life sciences requires the analysis of dynamic behaviors across a wide range of temporal and spatial scales. In particular, to observe relaxation processes involving photoexcited states, photochemical reactions, and structural changes at the nanoscale, the integration of time-resolved spectroscopy with microscopic techniques is essential. Time-resolved microspectroscopy and single-molecule/single-particle spectroscopy have rapidly advanced in recent years, and their integration is driving new frontiers in photochemistry.

Time-resolved microspectroscopy is a technique that combines ultrashort pulsed lasers in the femtosecond and picosecond regimes with optical microscopy. For example, time-resolved fluorescence microscopy allows for the analysis of spatial distributions of excited-state lifetimes and intermolecular interactions within living cells. In recent years, the integration with super-resolution techniques (such as STED and SMLM), which were recognized with the 2014 Nobel Prize in Chemistry, has pushed the limits of this method to achieve spatial resolutions below 100 nm.

In addition to fluorescence detection, advancements are being made in femtosecond transient absorption microspectroscopy, which employs pump-probe techniques to capture changes in light absorption by materials. This approach has revealed how local structures affect charge carrier dynamics in photofunctional materials such as solar cells and photocatalysts, and the insights gained are being utilized as guidelines for material design (e.g., Katayama, Miyasaka, and others). Furthermore, combining this technique with scanning near-field optical microscopy (SNOM) enables the observation of exciton dynamics in semiconductor materials with spatial resolutions beyond the diffraction limit of light (approximately half the wavelength). More recently, time-resolved microspectroscopy techniques utilizing stimulated Raman scattering and photoemission have emerged, accelerating the diversification of spectroscopic methodologies.

These time-resolved microspectroscopic techniques enable the visualization and analysis of how local composition, defects, crystallinity, and heterointerfaces in thin films and powder samples influence photophysical and photochemical processes (Fig. 1). By taking advantage of the high sensitivity and throughput of fluorescence detection, ultrafast phenomena such as the diffusion and reactions of excitons and charge carriers within individual particles can be directly observed. The range of target materials is broad, including solar-cell materials such as organic semiconductors and hybrid organic-inorganic perovskites, as well as photocatalysts. For example, spatiotemporal analyses at the single-molecule and single-particle levels have uncovered structure-activity correlations in heterogeneous photocatalytic reactions, such as facet- and defect-specific redox behaviors (e.g., Tachikawa, Majima, and others).

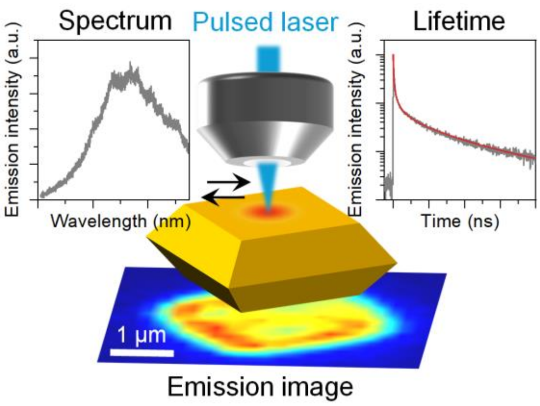

Figure 1. An example of time-resolved microspectroscopic measurements on a single photocatalyst particle.

References

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Future Perspectives and Directions

Challenges to be addressed and goals to be achieved within the next decade include: the integration of multimodal and multiscale measurement methodologies, the further development of in situ/operando measurement techniques at higher spatiotemporal resolutions, and the fusion with big data analysis and artificial intelligence (AI) for advanced data interpretation.

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