PRESS RELEASE

May 19, 2026
High Energy Accelerator Research Organization (KEK)
Institute of Science Tokyo

Direct Observation of Photoexcited Hole-Injection Dynamics in Cocatalysts for Water Splitting

— Co-Doping Acts as a “Latch”, Extending the Lifetime of Holes Transferred to the Cocatalyst by ~16-fold —

Executive Summary

- We directly observed, using time-resolved X-ray absorption spectroscopy, photoexcited hole-injection dynamics from a semiconductor photocatalyst (titanium dioxide) to a cocatalyst (iridium oxide), which drive the light-induced water-oxidation reaction.
- When nitrogen- and fluorine-co-doped titanium dioxide was used, the hole lifetime in the iridium oxide cocatalyst was extended by approximately 16-fold on the nanosecond timescale (1 ns = one billionth of a second). This prolonged lifetime was correlated with enhanced water-oxidation activity.
- While N,F co-doping was originally established as a treatment for imparting visible-light responsiveness to semiconductor photocatalysts, this study experimentally revealed that the same co-doping treatment also acts as a “latch” at the semiconductor/cocatalyst interface, suppressing the back-transfer of holes from the cocatalyst to the semiconductor.

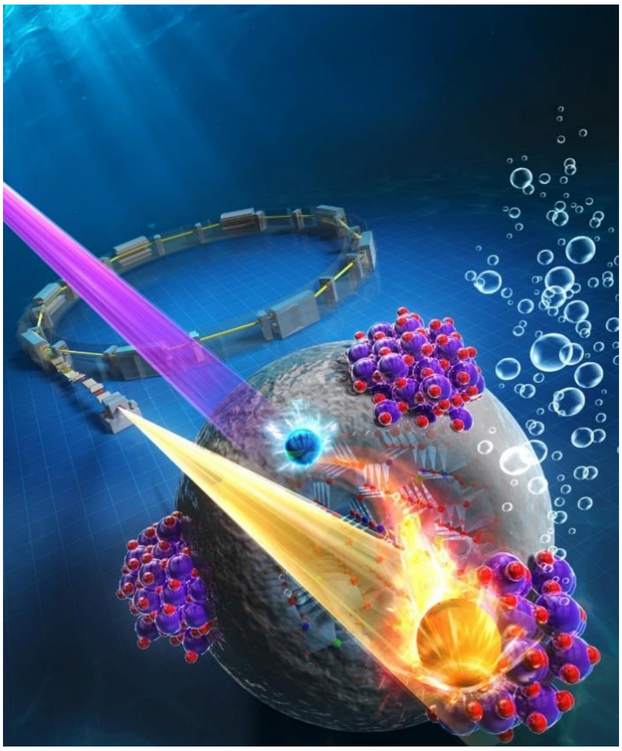

Figure 1. Conceptual illustration of this study. When ultraviolet (UV) light (purple) irradiates a semiconductor photocatalyst (sphere), photoexcited holes are generated and injected into the iridium oxide cocatalyst (purple + red) loaded on the surface. Using time-resolved X-ray absorption spectroscopy with synchrotron X-ray pulses (yellow), we directly observed hole dynamics in the cocatalyst on the nanosecond timescale.

Summary

The High Energy Accelerator Research Organization (KEK) and the Institute of Science Tokyo have succeeded in directly observing the photoexcited hole-injection dynamics — which drive the light-induced water-oxidation reaction — from a semiconductor photocatalyst to a cocatalyst, using time-resolved X-ray absorption spectroscopy at the Photon Factory Advanced Ring (PF-AR), KEK's synchrotron radiation facility.

In photocatalytic water splitting, it is well known that loading a small amount of metal oxide called a "cocatalyst" onto a semiconductor photocatalyst alters the dynamics of photogenerated charge carriers and thereby enhances activity. However, charge-carrier dynamics within the cocatalyst itself had remained unclear due to limitations of conventional experimental techniques.

In this study, we focused on iridium oxide (IrO_x) cocatalysts loaded on nitrogen- and fluorine-co-doped titanium dioxide (IrO_x/TiO_2:N,F), and by exploiting the element selectivity of X-rays, we succeeded in extracting the behavior of holes within the IrO_x under ultraviolet (UV) light excitation. We further demonstrated that longer hole lifetimes in the cocatalyst correlate with higher water-oxidation activity.

Interestingly, although N,F co-doping was originally developed and used to render photocatalytic materials responsive to visible light, we found that this treatment also has another important effect — substantially extending the hole lifetime within the cocatalyst.

These results were obtained by a collaborative research group led by Researcher Tomoki Kanazawa (KEK Institute of Materials Structure Science), Associate Professor Shunsuke Nozawa (KEK), and Professor Kazuhiko Maeda (Institute of Science Tokyo). The experiments were carried out using the time-resolved X-ray experimental station AR-NW14A at KEK PF-AR.

These findings were published online in ACS Catalysis (American Chemical Society) on May 13, 2026.

Background

“Solar water splitting,” which decomposes water into hydrogen and oxygen using sunlight, is a promising option for renewable energy. Semiconductor photocatalysts absorb the energy of sunlight to generate electrons and positive holes, which then reduce and oxidize water to produce hydrogen and oxygen, respectively. However, with semiconductor photocatalysts alone, electron–hole recombination occurs frequently, resulting in low water-splitting efficiency.

A widely used strategy to overcome this issue is to load small amounts of metal oxide called a “cocatalyst” on the semiconductor surface. For example, iridium oxide (IrO_x) is widely used as an excellent cocatalyst for the water-oxidation reaction. The cocatalyst receives electrons or holes from the semiconductor and separates the two, suppressing recombination, and also serves as a reaction site, thereby substantially improving water-splitting efficiency.

Furthermore, to make use of a broad solar spectrum that includes visible light, the semiconductor photocatalyst must be rendered responsive to visible light. To this end, strategies have been established that co-dope titanium dioxide (TiO_2) with anions such as nitrogen and fluorine — while maintaining charge neutrality and modulating the band structure — to enable visible-light absorption. The IrO_x/TiO_2:N,F used in this study is also a visible-light-responsive photocatalytic material developed using this strategy.

To clarify the role of the cocatalyst, it is essential to directly observe the dynamics of electrons and holes within the cocatalyst. With conventional experimental techniques, however, it has been difficult to separate signals originating from the semiconductor from those originating from the cocatalyst, and the charge-carrier dynamics within the cocatalyst had remained unclear.

Research and Results

Focusing on the excellent element specificity of synchrotron X-rays, our research group aimed to directly observe the hole dynamics within the cocatalyst using time-resolved X-ray absorption fine structure spectroscopy (TR-XAFS). We selected nitrogen- and fluorine-co-doped rutile-type titanium dioxide loaded with an IrO_x cocatalyst (IrO_x/TiO_2:N,F) — which exhibits high photocatalytic activity — as the sample, and also measured undoped titanium dioxide (IrO_x/TiO_2) for comparison.

At the AR-NW14A beamline of PF-AR, we photoexcited the TiO_2 semiconductor with a UV pulsed laser (wavelength: 343 nm) and probed the electronic state of the Ir atoms in IrO_x using X-ray pulses with a duration of approximately 100 picoseconds (100 trillionths of a second). By acquiring difference spectra of the X-ray absorption near-edge structure (XANES) at the Ir L_{III} edge before and after UV excitation, we succeeded in directly visualizing hole injection into IrO_x through changes in the electronic state of the Ir atoms.

The measurements revealed that both IrO_x/TiO_2 and IrO_x/TiO_2:N,F exhibited, after UV excitation, characteristic changes in the Ir L_{III} XANES spectrum — a chemical shift of the absorption edge and a spectral feature associated with hole formation in the Ir 5d orbital — confirming that holes are injected from the semiconductor into the cocatalyst (Figure 2).

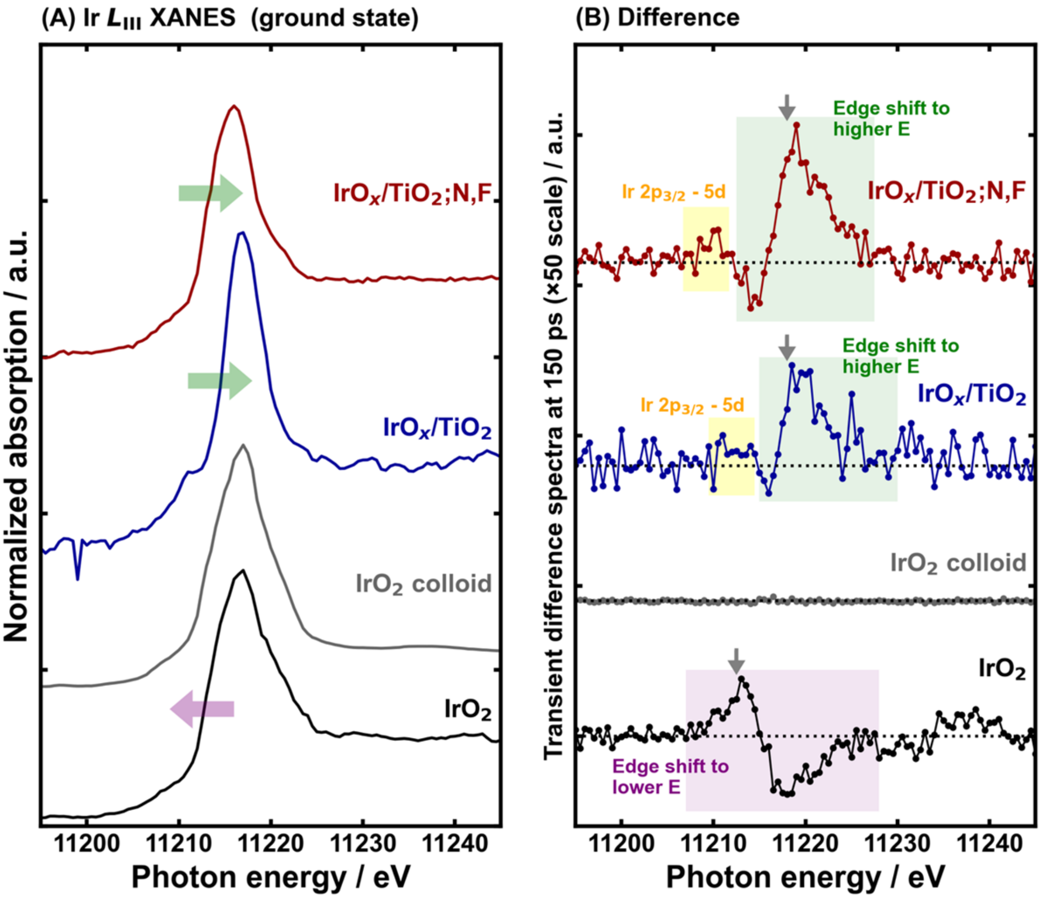

Figure 2. XANES spectra at the Ir L_{III} edge (A: ground state) and time-resolved difference spectra at 150 ps after UV excitation (B: magnified ×50). The green (purple) shaded regions correspond to the shift of the absorption edge toward higher (lower) photon energy, and the yellow shaded region corresponds to hole generation in the Ir 5d orbital. For samples in which IrO_x nanoparticles are loaded on a semiconductor surface (IrO_x/TiO_2:N,F and IrO_x/TiO_2), signals attributable to hole injection from the semiconductor into the Ir 5d orbital of IrO_x are observed after UV excitation. By contrast, no UV-excitation-induced signal is observed for IrO_x nanoparticles that are not loaded on a semiconductor (IrO_2 colloid), whereas for crystalline IrO_2, signals attributable to electron transfer from the O 2p orbital to the Ir 5d orbital induced by direct UV excitation of IrO_2 itself are observed.

Analysis of the hole lifetime within the cocatalyst revealed approximately 27 nanoseconds (1 ns = one billionth of a second) for IrO_x/TiO_2, compared with approximately 420 nanoseconds for IrO_x/TiO_2:N,F — corresponding to an approximately 16-fold increase. Correspondingly, IrO_x/TiO_2:N,F exhibited approximately three times higher photocatalytic water-oxidation activity (O_2 evolution) than IrO_x/TiO_2, demonstrating a clear correlation between the hole lifetime within the cocatalyst and the water-oxidation activity.

This extension of the hole lifetime is explained by the fact that N,F co-doping of TiO_2 shifts the valence-band edge of TiO_2 to lower energy, thereby raising the energy barrier for back-transfer of holes from IrO_x to TiO_2 (Figure 3). A small barrier is already present in undoped IrO_x/TiO_2, but co-doping deepens this barrier substantially. In other words, the band-structure change brought about by co-doping also functions as a "latch" at the semiconductor/cocatalyst interface that confines holes on the cocatalyst side, strongly suppressing hole back-transfer.

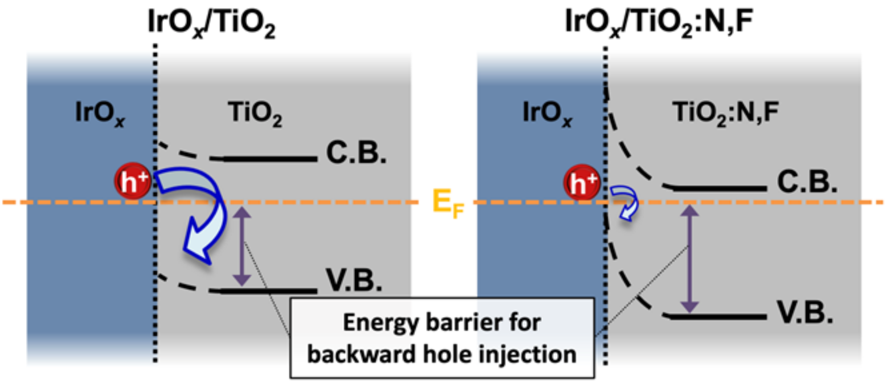

Figure 3. Schematic of the band alignment at the IrO_x/semiconductor interface. N,F co-doping of TiO_2 shifts the valence-band edge to lower energy, which raises the barrier against back-transfer of holes from IrO_x into the semiconductor. As a result, the hole lifetime within the cocatalyst is extended.

Significance and Future Prospects

Co-doping semiconductors with nitrogen and fluorine has long been widely used as a strategy for creating photocatalytic materials capable of absorbing sunlight, especially visible light. The present study experimentally revealed that the band-structure change resulting from this co-doping has yet another distinct effect at the semiconductor/cocatalyst interface: it acts as a "latch" for the holes transferred to the cocatalyst — suppressing their return to the semiconductor and extending their lifetime by approximately 16-fold. In other words, what had been understood as a "treatment for visible-light activity" turns out also to function as a "treatment that suppresses the return of holes transferred to the cocatalyst."

In addition, this work demonstrates that time-resolved X-ray absorption spectroscopy is a powerful tool for directly observing the charge dynamics at the semiconductor/cocatalyst interface. This provides a new design guideline for evaluating and tailoring semiconductor/cocatalyst combinations for solar water splitting on the basis of a microscopic physical quantity — the interfacial energy alignment between the semiconductor and cocatalyst.

Going forward, by applying this technique to a variety of semiconductor/cocatalyst systems, we expect this approach to contribute to the development of more efficient photocatalytic materials — not only for solar water splitting but also for CO_2 reduction, NH_3 synthesis, and other applications aimed at the efficient use of renewable energy.

This work was supported by the Japan Science and Technology Agency (JST) Strategic Basic Research Programs, CREST "Materials Science with Anomalous Structures" (JPMJCR20R2); the Japan Society for the Promotion of Science (JSPS) KAKENHI Grants-in-Aid for Scientific Research (JP25H00899, JP22H05148, JP22KJ3125; Specially Promoted Research JP21H04974); and the Ministry of Education, Culture, Sports, Science and Technology (MEXT) Advanced Research Infrastructure for Materials and Nanotechnology (ARIM) program (JPMXP1225KU1050, JPMXP1225KU1053).

Paper Information

Time-Resolved X-ray Absorption Fine Structure Reveals Hole-Injection Dynamics and Charge-Carrier Kinetics in Cocatalysts for Water Oxidation

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Journal: ACS Catalysis (published online on May 13, 2026)

DOI: https://doi.org/10.1021/acscatal.6c02061

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