remarkable performance, achieving an onset voltage for oxygen evolution as low as 1.47 V vs. reversible hydrogen electrode (RHE). More significantly, the (AlCoCrFeMnNi)O HEC successfully operated stably in seawater for 1,000 hours under a constant current density of 100 mA/cm^2, demonstrating extraordinary stability in the salt-rich environment. *In situ* XAS carried out during OER with varying applied voltages at **TPS 44A** beamline revealed that Co and Mn underwent OER-dependent oxidation (valence changes), evidenced by shifts in their edge-jump regions toward higher photon energy, as shown in **Fig. 3**. This mechanism is known as the adsorbate evolution mechanism, where the active metal binds to the reaction intermediate, resulting in an increased negative charge. Meanwhile, a decrease in coordination number for both Co and Ni occurs without a corresponding increase in oxidation state, where oxygen atoms detach from the lattice to form an oxygen vacancy. The stabilizing elements Al, Cr, and Fe did not show significant valence changes during the OER. Their roles are critical for ensuring longevity. The absence of Fe, for example, leads to the loss of synergistic influence of the spinel phase.

These spinel HECs are being explored for CO_2 reduction, water splitting, and next-generation catalysts, offering potential pathways to cleaner energy technologies. Yet, without tools like XAS, their true potential would remain hidden behind a fog of atomic disorder. In CO_2 conversion, *in situ* XAS revealed that redox-flexible cations like Fe^{3+} enable a reversible "breathing" mechanism that enhances performance. For seawater splitting, XAS showed that active metals (Co and Mn) switch oxidation states while stabilizing elements (Al, Cr, Fe) maintain the high-entropy structure. This insight transforms HECs from randomness into a balanced atomic ensemble for a cleaner, more efficient future. (Reported by Chi-Liang Chen of the NSRRC and Yu-Chuan Lin of National Cheng Kung University)

This report features the work of Yu-Chuan Lin and his collaborators published in ACS Appl. Mater. Interfaces ***17****, 52315 (2025); and the work of Wei Hsuan Hung and his collaborators published in Sustain. Mater. Technol.* ***45****, e01515 (2025).*

TPS 32A Tender X-ray Absorption Spectroscopy
TPS 44A Quick-scanning X-ray Absorption Spectroscopy

- XAS
- Spinel, Materials Science, Green Sustainable Chemical Process, Water Splitting

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(Photo)electrochemical H_2O_2 Sensing Platform for Future Application in Cancer Diagnosis

The controllable synthesis of anatase–rutile TiO_2 has been developed, which exhibits enhanced (photo)electrocatalytic activity for the monitoring of hydrogen peroxide under visible light, presenting potential applications in cancer diagnosis.

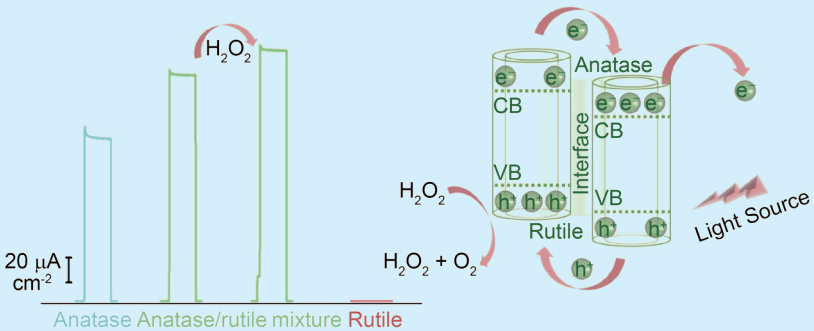

Fig. 1: Schematic illustration of photoelectrochemical H_2O_2 sensing based on the anatase–rutile phase transformation on TiO_2 supports. [Reproduced from Ref. 1]

Reactive oxygen species (ROS), such as superoxide ($O_2^{\cdot-}$), hydroxyl radicals (OH·), and hydrogen peroxide (H_2O_2), play essential roles in metabolic regulation and immune responses *via* nicotinamide adenine dinucleotide phosphate (NADPH) oxidase activation. While ROS are necessary for cellular homeostasis, excessive levels lead to protein

and lipid oxidation, DNA damage, and oxidative stress, all of which contribute to carcinogenesis. Among ROS, H_2O_2 is moderately reactive yet sufficiently stable to diffuse across membranes and reach the nucleus, where it can cause oxidative DNA damage. Its strong association with tumor initiation and progression highlights the need for sensitive and reliable H_2O_2 detection strategies.

Multiple analytical methods—including fluorescence, chemiluminescence, colorimetry, electrochemistry, and photoelectrochemistry (PEC)—have been developed for H_2O_2 sensing. PEC has attracted significant interest because of its high sensitivity, low background noise, and the separation of optical excitation from electrical detection. In PEC systems, photoactive materials generate electron–hole pairs under illumination, which drive redox reactions with probe molecules and produce measurable photocurrents. Therefore, optimizing photoactive materials is crucial for achieving high PEC performance.

Titanium dioxide (TiO_2) is one of the most widely used photoelectrode materials due to its stability, low cost, and environmental friendliness. However, its wide bandgap and limited charge transport hinder performance. Mixed-phase TiO_2, particularly anatase–rutile heterostructures, enhances charge separation through stable phase boundaries and defect-rich interfaces with oxygen vacancies and Ti^{3+} states. These characteristics improve carrier mobility and suppress recombination, significantly increasing PEC activity (**Fig. 1**).

Nanostructured TiO_2 significantly improves performance by increasing the active surface area and enhancing mass transport. One-dimensional (1D) TiO_2 architectures, such as nanotubes, are particularly beneficial due to their efficient electron pathways. Electrochemical anodization is widely used to fabricate ordered TiO_2 nanotubes. To mitigate environmental concerns related to fluoride electrolytes, recent studies have utilized fluoride-free phosphate, sulfate, and nitrate electrolytes, in which nanotube growth is controlled by the oxygen bubble mold mechanism.

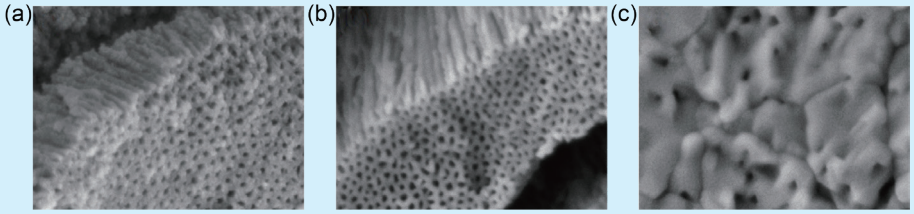

Fig. 2: FESEM images of (a) anatase, (b) anatase–rutile mixture, and (c) rutile TiO_2 supports. [Reproduced from Ref. 1]

To fully understand sensing behavior, synchrotron-based X-ray spectroscopies—including X-ray absorption spectroscopy (XAS) at **TLS 20A1**, wide-angle X-ray scattering (WAXS) at **TLS 23A1**, and X-ray excited optical luminescence (XEOL) at **TPS 23A**—analyze morphological, chemical, and electronic changes, offering key insights into structure–reactivity relationships in PEC systems for H_2O_2 detection.

Han-Wei Chang (National United University) demonstrated that 1D TiO_2 nanotubes—anatase (400 °C), anatase–rutile mixture (600 °C), and rutile (800 °C) TiO_2 supports—synthesized *via* fluoride-free electrochemical anodization and subsequent thermal annealing, show strong potential as PEC catalysts for H_2O_2 sensing in human serum. The TiO_2 supports were extensively characterized using Field Emission Scanning Electron Microscopy (FESEM) and synchrotron-based techniques, including XAS, WAXS, and XEOL, at the NSRRC, Taiwan. These analyses revealed that annealing enables precise control over the anatase–rutile phase composition, Ti^{3+}/Ti^{4+} distribution, and oxygen vacancy concentration, all of which significantly influence PEC activity. FESEM images (**Fig. 2**) show well-aligned, vertically oriented nanotube arrays several micrometers long with nanometer-scale inner diameters. The nanotubes form through the oxygen bubble mold mechanism, governed by the interplay of ionic and electronic currents during anodization. Heat treatment at increasing temperatures transformed the TiO_2 crystalline structures and tailored their surface properties. The optimized nanotube arrays, featuring enhanced charge transport and abundant active sites, exhibited superior PEC performance for H_2O_2 detection.

To investigate the structural evolution of anodized Ti-based samples annealed at different temperatures, WAXS (**TLS 23A1**), XEOL (**TPS 23A**), and XAS (**TLS 20A1**) analyses were performed. WAXS was used to examine phase transitions and crystal structure development. Grain sizes were estimated using the Scherrer equation. As shown in **Fig. 3(a)**, reference patterns for anatase and rutile TiO_2 were included for peak identification. All samples exhibited diffraction peaks corresponding to metallic Ti, reflecting the underlying Ti substrate. Additional peaks appearing between 400 and 600 °C indicate the formation of crystalline anatase TiO_2, with peak intensities increasing with temperature, confirming enhanced crystallinity and phase stability. Weak rutile peaks emerge at 600 °C, demonstrating the onset of the anatase–rutile transformation. At 800 °C, the complete disappearance

of anatase peaks and the dominance of rutile reflections confirm a full phase transition, consistent with morphological changes observed in FESEM.

XEOL was used to analyze defect-related optical emissions during phase transformation. XEOL detects luminescence generated by X-ray excitation, providing sensitivity to deep-level defects. As shown in **Fig. 3(b)**, anatase and mixed-phase TiO_2 samples exhibit a green emission at ~501 nm (2.48 eV), attributed to oxygen vacancies and hydroxyl-related defect states. Mixed anatase–rutile samples also show a broad near-infrared emission centered at 855 nm (1.45 eV), associated with deep traps—likely originating from Ti interstitials or oxygen vacancies that reduce Ti ions. Multiple resonances in this band suggest strong exciton–phonon coupling. At 800 °C, where rutile is predominant, defect-related emissions are greatly suppressed, indicating a lower defect density and the absence of anatase-related luminescence.

XAS at the Ti L-edge and O K-edge was performed to investigate annealing-induced changes in surface electronic structure. **Figure 3(c)** presents Ti $L_{2,3}$-edge spectra, where the L_3–eg doublet (peaks 4a and 4b) is a sensitive indicator of crystal phase. Anatase samples exhibit a strong low-energy 4a peak and a weaker 4b shoulder. As annealing temperature increases, the relative intensities shift, indicating a gradual transformation from anatase to rutile. At 600 °C, mixed-phase samples maintain an anatase-dominant profile, while at 800 °C, the inversion of the 4a/4b intensity ratio confirms a rutile-dominant surface.

Figure 3(d) shows the O K-edge XAS spectra. Anatase samples display characteristic pre-edge peaks (4c and 4d) corresponding to O 2p–Ti 3d hybridized states. Rutile samples exhibit clear splitting of the 4f peak into two components ($4f_1$ and $4f_2$), along with a blue shift of the 4e peak, enabling reliable differentiation between phases. Mixed anatase–rutile samples annealed at ~600 °C display partial splitting and shifting, confirming the coexistence of both phases. At 800 °C, the absence of anatase features indicates complete conversion to rutile, consistent with Ti $L_{2,3}$-edge results.

Collectively, WAXS, XEOL, and XAS show that anodized TiO_2 remains mainly anatase up to ~600 °C, partially transforms into an anatase–rutile mixture at 600 °C, and fully converts to rutile at 800 °C. This controllable phase evolution directly affects the electronic structure and defect landscape of TiO_2, offering tunable properties essential for optimizing its performance in photoelectrochemical sensing applications. (Reported by Han-Wei Chang, National United University)

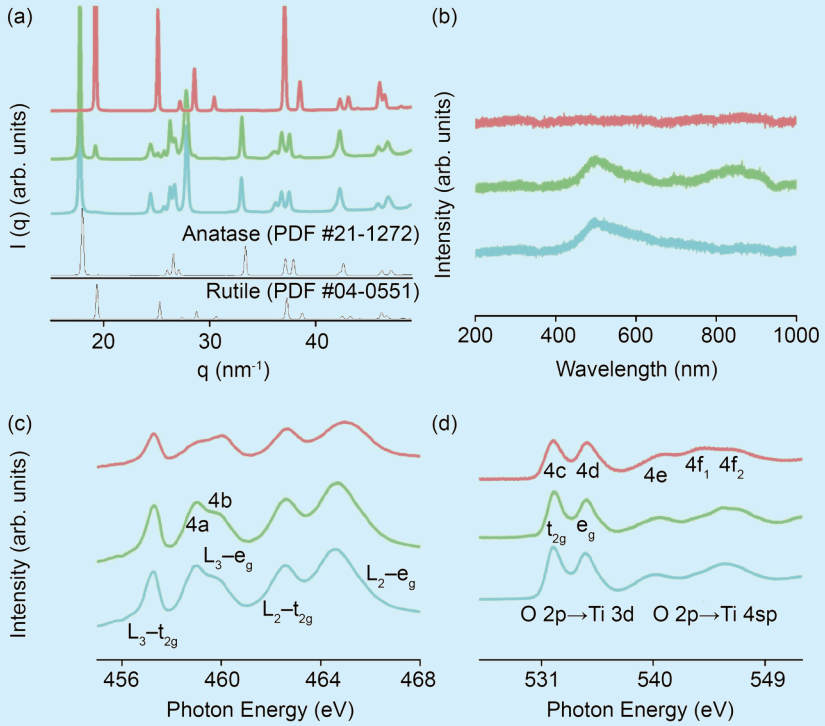

Fig. 3: (a) WAXS profiles, (b) XEOL spectra, (c) Ti L-edge XAS spectra, and (d) O K-edge XAS spectra of anatase (blue line), anatase–rutile mixture (green line), and rutile TiO_2 supports (red line). [Reproduced from Ref. 1]

This report features the work of Han-Wei Chang and his collaborators published in Surf. Interf. ***74****, 107719 (2025).*

TPS 23A X-ray Nanoprobe
- XEOL
- Materials Science, Chemistry

TLS 20A1 XAS
- XAS
- Materials Science, Chemistry

TLS 23A1 Small/Wide Angle X-ray Scattering
- WAXS
- Materials Science, Chemistry

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