

Reactive-Intermediate Channelling from Interfacial Hydrogen Peroxide Generation to Confined Catalysis for Water Decontamination

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Abstract

Improving hydrogen peroxide (H_2O_2) utilization remains a challenge in advanced oxidation processes (AOPs), because increasing H_2O_2 generation or catalytic activity does not control the fate of newly generated H_2O_2 before activation. H_2O_2 can diffuse into bulk water, decompose, or undergo competing reactions before reaching catalytic sites. Here, we extend reactive-intermediate channelling to heterogeneous AOPs, whereby interfacially generated H_2O_2 is preferentially transferred from its formation domain to connected catalytic domains for capture and activation before equilibration with bulk water. This concept is implemented using a polytetrafluoroethylene-coated Cu-containing titanium silicalite-1 catalyst (PTFE@Cu/TS-1). Contact-electro-catalysis at the PTFE–water interface generates H_2O_2 , while the hierarchical MFI framework directs it toward confined Ti–Cu domains. Framework Ti sites capture H_2O_2 , and neighbouring Cu centres regulate its electronic structure during formation of a Ti–O–O–Cu intermediate, enabling localized contaminant oxidation. The apparent rate constant over PTFE@Cu/TS-1 is 2.2, 2.6 and 12.3 times those obtained over PTFE@TS-1, a physical mixture of PTFE and Cu/TS-1, and pristine PTFE, respectively. H_2O_2 fate analysis further shows lower bulk accumulation, greater pollutant-coupled consumption and a higher apparent utilization index. These results establish reactive-intermediate channelling as a strategy for controlling the fate and utilization of in situ generated oxidants in heterogeneous AOPs.

Introduction

Hydrogen peroxide (H_2O_2)-based advanced oxidation processes (AOPs) are widely used to remove organic contaminants from water, yet their efficiency depends on whether H_2O_2 can be delivered to catalytic sites and converted into productive oxidation.^{1–4} Although increasing H_2O_2 supply or catalytic activity can accelerate apparent reaction rates, these approaches do not control the fate of H_2O_2 during transport to active sites. Externally supplied H_2O_2 must traverse the aqueous phase before activation. During this transport, it can decompose or react with water-matrix constituents (Fig. 1A).^{5,6} H_2O_2 utilization is therefore governed by how effectively available H_2O_2 is directed into catalytic consumption instead of bulk-phase redistribution or loss.

In situ H_2O_2 generation shortens the transport pathway associated with external dosing and can reduce bulk-phase mass-transfer limitations.⁴ Photochemical,⁷ electrochemical,⁸ and mechanically⁹ driven processes have therefore been developed to produce H_2O_2 from water and oxygen under mild conditions. Contact-electro-catalysis (CEC), for example, generates H_2O_2 at a dynamic solid–water interface through mechanical contact between dielectric materials and water without external electrical or light input.^{10,11} Interfacial generation places H_2O_2 close to catalytic surfaces, but physical proximity alone does not ensure efficient utilization. Newly generated H_2O_2 can still desorb, redistribute into bulk water or undergo competing reactions before catalytic interception.^{12,13} Spatial and kinetic mismatches between H_2O_2 formation and consumption can therefore persist even when both functions coexist within

the same heterogeneous system (Fig. 1B).¹⁴ Interfacially generated H_2O_2 may also transiently experience local solvation and electrostatic environments distinct from bulk water, providing an opportunity for interception before equilibration with the surrounding solution.^{15–20}

Intermediate channelling offers a framework for controlling the fate of reaction intermediates between sequential catalytic steps. In biological and synthetic cascade reactions, reactive intermediates can be preferentially transferred between catalytic sites before equilibrating with the bulk phase, thereby coupling consecutive reactions and limiting diffusional loss.²¹ H_2O_2 is a common reactive intermediate in multistep catalytic cascades, where spatial organization of H_2O_2 -generating and H_2O_2 -consuming components can enhance overall cascade efficiency.²² Applied to heterogeneous AOPs, this principle provides a means of addressing the spatial and kinetic disconnect between reactive-intermediate formation and downstream utilization. We therefore introduce reactive-intermediate channelling, whereby a newly generated reactive intermediate is preferentially transferred from its formation domain to connected catalytic domains before equilibration with bulk water. Importantly, physical proximity alone does not constitute channelling, because rapidly diffusing intermediates such as H_2O_2 can still equilibrate with the bulk phase before downstream consumption.²³

Here, we demonstrate reactive-intermediate channelling using interfacially generated H_2O_2 as the model intermediate in a polytetrafluoroethylene-coated, Cu-containing titanium silicalite-1 catalyst (PTFE@Cu/TS-1) (Fig. 1C). The PTFE–water interface generates H_2O_2 through contact electrification, while the hierarchical MFI framework directs the newly generated H_2O_2 toward internal catalytic domains. Framework Ti sites intercept and coordinate H_2O_2 , and neighbouring Cu centres subsequently regulate the electronic structure of the coordinated peroxide through a Ti–O–O–Cu intermediate, enabling localized contaminant oxidation. Pore-accessibility modulation and comparison with physically mixed PTFE and Cu/TS-1 distinguish this connected pathway from simple coexistence of H_2O_2 generation and activation components. H_2O_2 fate analysis further shows that PTFE@Cu/TS-1 combines lower bulk H_2O_2 accumulation with greater pollutant-coupled consumption and enhanced contaminant transformation. These results demonstrate how reactive-intermediate channelling controls the post-formation fate of H_2O_2 by connecting interfacial oxidant generation with confined catalytic utilization.

Results and Discussion

Construction and Structural Characterization of PTFE@Cu/TS-1

To construct the catalytic architecture required for H_2O_2 channelling, we integrated a dielectric PTFE interface with a Cu-containing hierarchical TS-1 framework. The PTFE layer provides the contact-electrification interface for H_2O_2 generation, while the accessible MFI framework connects this interface

with Ti-containing domains and neighbouring Cu sites for subsequent peroxide capture and activation.^{24,25}

Cu species were incorporated into TS-1 via an in situ crystallization method using mercapto-functionalized organosilane ligands as coordination mediators (Fig. 2A, **Supplementary Text S2**).²⁶ This synthesis promotes incorporation of dispersed Cu species during framework growth while retaining access to the internal zeolitic domains. A PTFE overlayer was then introduced by thermal immobilization of a PTFE suspension.¹⁰ The MFI framework remained well preserved following Cu incorporation and PTFE deposition. TEM images show that Cu/TS-1 and PTFE@Cu/TS-1 retain the hierarchical morphology of the parent TS-1 (Fig. 2B, C, F, G).²⁷ Powder XRD patterns display the characteristic MFI reflections without detectable crystalline CuO_x phases at the investigated PTFE loadings (Fig. 2M).²⁸ N₂ adsorption–desorption measurements further show that the microporous structure is largely retained after PTFE incorporation, with only minor changes in total pore volume and pore-size distribution (**Supplementary Fig. S1 and Table S1**). These results indicate that PTFE deposition preserves the zeolitic transport network required for access to internal catalytic domains.

Elemental mapping reveals homogeneous distributions of Si, Ti and Cu throughout the zeolite particles, together with distinct C and F signals after PTFE deposition (Fig. 2E, I and **Supplementary Fig. S2**). Because of the limited atomic-number contrast between Cu and the Ti/Si framework, local Cu configurations were further examined by integrated differential phase-contrast STEM (iDPC-STEM). iDPC-STEM images of Cu/TS-1 show localized contrast features consistent with atomically dispersed Cu species and ultrasmall Cu clusters within the MFI domains (Fig. 2D). The zeolitic lattice remains intact after PTFE deposition (Fig. 2H and **Supplementary Fig. S3**). ICP–MS gives a Cu loading of approximately 0.91 wt% (**Supplementary Fig. S4**). Together with the absence of crystalline CuO_x reflections and the microscopic observations, these results support a highly dispersed Cu population within the zeolitic architecture.

Cu K-edge XAS further resolved the local coordination environment of the Cu species. The XANES edge position lies between those of Cu₂O and CuO, indicating an average Cu valence state between Cu(I) and Cu(II) (Fig. 2J). Fourier-transformed EXAFS spectra show a dominant Cu–O contribution at ~ 1.5 Å and a weaker Cu–Cu contribution near 2.5 Å (Fig. 2K). Wavelet transform analysis in k- and R-space supports the coexistence of isolated Cu sites and ultrasmall Cu-containing clusters, while the absence of pronounced long-range Cu–Cu scattering argues against the formation of extended CuO_x domains (Fig. 2L and **Supplementary Table S2**).²⁹ These local Cu environments place electronically accessible Cu centres within the Ti-containing MFI domains, providing the structural basis for the Ti–Cu cooperation examined below.

FTIR and XPS analyses further verify PTFE incorporation while confirming preservation of the zeolitic framework. FTIR spectra retain the characteristic MFI vibrations at ~ 1220, 1100, and 800 cm⁻¹ (T–O–T, T = Si or Ti), while characteristic –CF₂– vibrations emerge after PTFE deposition (**Supplementary Fig.**

S5).³⁰ Small spectral shifts indicate perturbation at the PTFE–zeolite interface, whereas the absence of additional bands attributable to M–F or C–O–Si bonding is consistent with physical immobilization rather than covalent grafting.³¹ High-resolution C 1s and F 1s XPS spectra retain the characteristic chemical states of PTFE, while Ti 2p remains characteristic of framework Ti(IV) (**Supplementary Figs. S6, S7**), indicating that PTFE deposition does not substantially alter the Ti coordination environment.³²

Together, these structural analyses establish an integrated architecture comprising a PTFE interfacial layer, an accessible Ti-containing MFI transport network and highly dispersed internal Cu species. This architecture provides the structural basis for examining whether interfacially generated H₂O₂ can be channelled toward confined Ti–Cu catalytic domains.

Interfacial HO Channelling to Confined Ti Domains

We next examined whether newly generated H₂O₂ could be intercepted before bulk equilibration and directed toward internal catalytic domains. Efficient channelling requires an interfacial generation site that remains accessible to water while retaining the contact-electrification characteristics needed for H₂O₂ formation. Water contact-angle measurements identified 2.5 wt% PTFE as providing an appropriate balance between aqueous accessibility and surface hydrophobicity (**Supplementary Fig. S8**). Under ultrasonic excitation, the PTFE interface exhibited a pronounced zeta-potential shift from – 16.1 mV to – 32.1 mV (Fig. 3A), consistent with interfacial charge separation during contact electrification.¹⁰ Comparable electrokinetic responses were observed for PTFE, PTFE@TS-1 and PTFE@Cu/TS-1 (**Supplementary Fig. S9**), indicating that incorporation of the zeolitic component does not substantially alter the interfacial charging behaviour responsible for CEC.

To determine the environment experienced by H₂O₂ immediately after formation, DFT calculations compared HOOH interactions at the PTFE interface with solvation in bulk water. The calculated HOOH–PTFE interaction energy was weaker than the corresponding stabilization in water (– 1.48 versus – 1.86 eV), suggesting no strong thermodynamic preference for H₂O₂ retention at the PTFE surface and therefore a tendency toward subsequent redistribution into the aqueous phase (Fig. 3B; **Supplementary Fig. S10**).^{33, 34} Molecular dynamics (MD) simulations further show that the presence of HOOH perturbs the hydrogen-bonding structure at the PTFE–water boundary. The O–H radial distribution function of the PTFE–H₂O–HOOH system differs from that of PTFE–H₂O, indicating that H₂O₂ initially experiences an interfacial solvation environment distinct from bulk water (Fig. 3C; **Supplementary Figs. S11, S12**).³⁵ Differential charge-density and work-function analyses further support polarization at the PTFE–water interface (**Supplementary Figs. S13, S14**). Together, these results suggest that newly generated H₂O₂ occupies a transient interfacial environment before redistribution, providing a finite window for catalytic interception.

In situ ultrasonic ATR–FTIR spectroscopy was used to monitor peroxide-associated species during contact electrification. A transient band at ~ 835 cm^{–1}, assigned to peroxide-associated O–O vibrations,

appeared under ultrasonic excitation and rapidly diminished after the stimulus was stopped (**Supplementary Fig. S15**). This reversible response is consistent with continuous peroxide formation followed by consumption or redistribution rather than persistent accumulation.³⁶ Similar peroxide-associated features were observed for Ti-free PTFE@S-1 and Ti-containing PTFE@TS-1, supporting the assignment of H₂O₂ generation to the PTFE-mediated contact-electrification interface rather than framework Ti. Ti-containing samples additionally exhibited perturbations in framework vibrations, consistent with interaction between generated H₂O₂ and Ti-containing domains. Further spectral changes in PTFE@Cu/TS-1 suggest that neighbouring Cu species modify the local environment of the coordinated peroxide. These observations are consistent with a sequential process in which H₂O₂ is generated at the PTFE–water interface and subsequently intercepted within the zeolitic framework.

To test whether this interception depends on access to the internal pore network, the microporosity of Cu/TS-1 was reversibly modulated before PTFE deposition. TPABr molecules were introduced to partially occupy MFI micropores and restrict access to internal Ti–Cu domains, whereas subsequent thermal removal of confined TPABr restored pore accessibility. Parent, pore-blocked and regenerated samples were then coated with identical PTFE loadings to maintain comparable interfacial generation conditions. N₂ adsorption–desorption measurements showed a substantial decrease in micropore volume after TPABr treatment and recovery after thermal regeneration (**Supplementary Fig. S16**). XRD confirmed preservation of the MFI framework, while XPS showed no substantial changes in the Cu and Ti chemical states following pore modulation (**Supplementary Figs. S17–S19**). These results indicate that TPABr treatment predominantly alters molecular accessibility to internal domains rather than the underlying framework structure.

The effect of pore accessibility on peroxide interception was then examined by quasi-operando UV–vis diffuse reflectance spectroscopy of wet catalysts after ultrasonic activation. PTFE@Cu/TS-1 displayed a pronounced peroxide-associated absorption feature in the 300–400 nm region together with a colour change from white to pale yellow (Fig. 3D).³⁷ This feature was markedly weakened after TPABr occupation and recovered following thermal regeneration (**Supplementary Fig. S20**), linking framework accessibility with peroxide accommodation within the catalyst. Comparison of PTFE@S-1 and PTFE@Cu/S-1 with their Ti-containing counterparts further showed that framework Ti contributes to peroxide retention within the MFI channels (**Supplementary Fig. S21**).

Solution-phase H₂O₂ measurements provide an independent measure of how pore accessibility affects peroxide partitioning after interfacial generation. Increasing the TPABr treatment time led to progressively higher bulk H₂O₂ concentrations, consistent with reduced interception by Ti-containing micropores (**Supplementary Fig. S22**).³⁸ Thermal regeneration returned the bulk H₂O₂ concentration toward that of the parent catalyst (Fig. 3E). The inverse relationship between framework-associated peroxide signals and bulk H₂O₂ accumulation therefore indicates that accessible Ti-containing domains alter the partitioning of newly generated H₂O₂ between confined regions and the surrounding solution. Correspondingly, 2-fluorophenol (2-FP) degradation decreased after pore occupation and recovered after

regeneration (Fig. 3E). Because the samples retained comparable PTFE loadings and contact-electrification responses, these changes are consistent with altered peroxide interception and utilization rather than changes in H_2O_2 generation.

MD simulations were further used to separate the contribution of framework Ti from physical confinement by the MFI topology. In structurally comparable Cu/TS-1 and Ti-free Cu/S-1 models, H_2O_2 remained associated with the Ti-containing framework for substantially longer periods, whereas it more readily diffused toward the surrounding phase in Cu/S-1 (Fig. 3G; **Supplementary Fig. S23**). Quantitative retention analysis confirmed stronger peroxide association in the presence of framework Ti, indicating that Ti sites provide specific interactions with H_2O_2 beyond geometric confinement alone.

Together, these results support a channelling process in which CEC-generated H_2O_2 occupies a transient interfacial state and is preferentially intercepted by accessible Ti-containing micropores before complete equilibration with bulk water. Restricting access to these domains shifts H_2O_2 toward bulk accumulation and suppresses contaminant oxidation, whereas restoring pore accessibility reverses both effects. Framework Ti therefore provides a chemical interception site within the MFI transport network, linking interfacial H_2O_2 generation to downstream confined activation.

HO Channelling Enables Productive Contaminant Oxidation

We next examined whether the H_2O_2 channelling established above translates into productive contaminant oxidation. During the dark adsorption stage, all catalyst systems exhibited limited 2-FP removal, with adsorption contributions below 15% (Fig. 4A), indicating that the subsequent concentration decrease under ultrasonic excitation predominantly arose from oxidation.

Control experiments were then used to distinguish a connected channelling architecture from simple coexistence of H_2O_2 -generating and H_2O_2 -activating components. PTFE alone generated interfacial H_2O_2 through contact electrification but showed negligible 2-FP degradation, demonstrating that H_2O_2 generation alone was insufficient for effective oxidation. PTFE@TS-1 exhibited higher activity than PTFE, consistent with the contribution of framework Ti sites to the interception and utilization of interfacially generated H_2O_2 . A physical mixture of PTFE and Cu/TS-1, which contains both H_2O_2 -generating and Cu-containing catalytic components but lacks a connected transport pathway between them, remained substantially less active than PTFE@Cu/TS-1. This comparison distinguishes H_2O_2 channelling from simple functional co-location. PTFE@Cu/TS-1 exhibited the highest apparent rate constant ($4.56 \times 10^{-2} \text{ min}^{-1}$), corresponding to 2.2, 2.6 and 12.3 times the values obtained with PTFE@TS-1, the PTFE + Cu/TS-1 physical mixture and pristine PTFE, respectively (Fig. 4B). Variations in catalyst loading, ultrasonic power and pollutant concentration changed the absolute reaction rates but preserved the relative activity trends (**Supplementary Figs. S24–S26**), supporting the contribution of the integrated generation–transport–capture–activation pathway to the observed enhancement.

The extent of contaminant transformation was further evaluated by defluorination, total organic carbon (TOC) removal and product analysis. Defluorination increased concurrently with TOC removal (Fig. 4C), indicating C–F bond cleavage accompanied by progressive breakdown of the organic carbon framework. Time-resolved LC–TOF–MS analysis showed sequential transformation of fluorinated intermediates and gradual disappearance of detectable fluorocarbon fragments (**Supplementary Fig. S27**). No major accumulation of fluorinated intermediates was observed during the reaction, consistent with continued transformation of partially oxidized products. Proposed substrate-dependent transformation pathways and toxicity predictions are provided in **Supplementary Figs. S28–S30**. A qualitative bean-germination and early-growth assay further showed improved plant growth in treated water relative to untreated 2-FP wastewater (**Supplementary Fig. S31**), providing complementary biological evidence of reduced phytotoxic effects after treatment.

PTFE@Cu/TS-1 retained high degradation efficiency over eight successive oxidation cycles (Fig. 4D). ICP–MS detected low Ti and Cu leaching (Fig. 4E), while post-reaction SEM and XRD analyses showed preservation of the zeolitic morphology and crystalline framework (**Supplementary Figs. S32–S33**). These results indicate that the coupled oxidation pathway operates without substantial deterioration of the catalyst structure under the tested conditions. PTFE@Cu/TS-1 also maintained oxidation activity toward representative fluorinated compounds, phenolics, dyes, nitroaromatics and antibiotics (Fig. 4F), showing that the catalytic architecture is applicable to contaminants with diverse molecular structures.

The relationship between H_2O_2 accumulation and productive oxidation was then examined directly. In the absence of 2-FP, PTFE exhibited the highest measurable bulk H_2O_2 concentration during CEC operation, followed by PTFE@TS-1 and PTFE@Cu/TS-1 (Fig. 4G), opposite to their oxidation activity. Bulk H_2O_2 accumulation therefore does not directly describe productive H_2O_2 utilization. Instead, the lower accumulation observed for PTFE@Cu/TS-1 is consistent with more rapid transfer of newly generated H_2O_2 into downstream catalytic pathways.

To quantify this behaviour independently of the in situ generation rate, paired experiments with externally supplied H_2O_2 were conducted in the absence and presence of 2-FP. The initial H_2O_2 concentration was operationally partitioned into residual H_2O_2 , background H_2O_2 loss and pollutant-coupled H_2O_2 consumption (Fig. 4H, **Supplementary Fig. S34**). PTFE@Cu/TS-1 showed the greatest pollutant-coupled H_2O_2 consumption among the tested systems, indicating stronger coupling between H_2O_2 consumption and contaminant transformation. An apparent H_2O_2 utilization index, defined as the moles of 2-FP transformed per mole of pollutant-coupled H_2O_2 consumed, was consequently highest for PTFE@Cu/TS-1 (Fig. 4I). Together with the lower bulk H_2O_2 accumulation under CEC conditions, these results show that enhanced oxidation arises from more effective routing of available H_2O_2 into contaminant-associated catalytic consumption rather than accumulation in the aqueous phase.

To further examine the coupling between substrate localization and confined H_2O_2 activation, the adsorption period was varied before ultrasonic excitation. Extending the pre-adsorption time from 0 to

30 min increased the apparent rate constant by approximately 3.5-fold (**Supplementary Fig. S35**), although adsorption itself accounted for less than 15% of 2-FP removal. The increase in oxidation rate when substrate molecules were pre-enriched within accessible catalytic domains is consistent with localized oxidation involving channelled H_2O_2 rather than reaction dominated by freely diffusing oxidants.

Collectively, these results show that H_2O_2 channelling affects both the location and the fate of peroxide after interfacial generation. Connecting H_2O_2 formation with pore-directed transport, Ti-mediated interception and downstream activation suppresses bulk accumulation while increasing pollutant-coupled H_2O_2 consumption and contaminant transformation. Productive H_2O_2 utilization therefore depends on the organization of the pathway between oxidant formation and catalytic consumption, rather than on H_2O_2 generation or bulk concentration alone.

Ti–Cu Electronic Coupling Enables Confined HO Activation

We next examined how the intercepted H_2O_2 is activated within the confined Ti–Cu domains. In conventional AOPs, H_2O_2 activation commonly proceeds via O–O homolysis to generate diffusible radicals or through heterolytic pathways involving terminal high-valent metal–oxo species.^{39,40} The limited contribution of these pathways in PTFE@Cu/TS-1 suggests that H_2O_2 is activated through a coordinated intermediate whose electronic structure is regulated by the neighbouring Ti–Cu environment.

Radical-scavenging and oxygen-transfer probe experiments first examined the nature of the reactive species involved in 2-FP oxidation. Addition of tert-butanol (TBA), an efficient $\cdot\text{OH}$ scavenger, caused only modest inhibition of 2-FP degradation (Fig. 5A), indicating that freely diffusing $\cdot\text{OH}$ is not the dominant oxidant under these conditions.⁴¹ Methyl phenyl sulfoxide (PMSO), commonly used to probe oxygen-transfer reactivity of high-valent metal–oxo species, showed negligible conversion to methyl phenyl sulfone (PMSO₂), arguing against a dominant terminal metal–oxo pathway (Fig. 5A;

Supplementary Fig. S36).⁴² DMPO spin-trapping EPR likewise showed no substantial accumulation of freely diffusing radical species (**Supplementary Fig. S37**). Scavenger experiments targeting other reactive oxygen species produced only limited or pathway-dependent effects. Collectively, these observations indicate that 2-FP oxidation is not dominated by a single freely diffusing ROS and are consistent with H_2O_2 activation within a coordinated Ti–Cu environment.

The participation of Cu in this activation process was examined by continuous-wave X-band EPR spectroscopy (Fig. 5B). The pristine catalyst exhibited the characteristic anisotropic features of EPR-active Cu(II) centres. Following H_2O_2 activation, broadening of the $g_{\parallel}$ feature and changes in the $g_{\perp}$ envelope were observed, indicating perturbation of the local coordination and electronic environment of Cu.⁴³ Post-reaction Ti 2p, O 1s and Cu 2p XPS spectra further showed changes in the local electronic

environment (**Supplementary Figs. S38 and S39**). These reversible electronic changes support direct involvement of Cu centres in the interaction with peroxide-derived species.

DFT calculations were then used to resolve the evolution of H_2O_2 after interception by framework Ti (Fig. 5C; **Supplementary Fig. S40**). Free H_2O_2 is a closed-shell singlet, and initial coordination to d^0 Ti(IV) preserves this closed-shell electronic configuration. Ti coordination nevertheless redistributes electron density within the bound H_2O_2 and polarizes the O–O unit.⁴⁴ Interaction with a neighbouring Cu centre produces a substantially different electronic state. Structural reorganization toward the Ti–O–O–Cu configuration is accompanied by the emergence of spin polarization, showing that the open-shell character develops during Ti–Cu coupling rather than during the initial Ti-mediated capture step.⁴⁵ This sequence separates two functions within the confined domain: Ti provides initial H_2O_2 coordination, whereas Cu promotes subsequent electronic activation.

Spin-density calculations, together with spin-resolved PDOS and atomic magnetic-moment analyses, further resolved the nature of this activated state (Fig. 5D; **Supplementary Figs. S41-S43 and Table S3**). The calculated unpaired density is distributed across the coupled O–O–Cu region instead of being localized on an isolated oxygen atom. Atomic magnetic moments and integrated spin-density analysis show the same delocalized character. The resulting state is therefore better described as a spin-polarized, metal-coupled peroxide-derived configuration than as a freely dissociated oxygen-centred radical.

The electronic origin of this behaviour was examined using orbital and projected density-of-states analyses (Fig. 5C, F). Ti(IV), with an empty 3d manifold, accepts electron density from the oxygen lone pairs and stabilizes the initially coordinated H_2O_2 . Neighbouring Cu introduces occupied and partially occupied 3d states that overlap with peroxide-derived O 2p states near the Fermi level. This interaction redistributes electron density across the Cu–O–O region and increases the antibonding contribution along the O–O coordinate. Projected density of states (PDOS) analysis corroborates this interaction (Fig. 5E, **Supplementary Figs. S44, S45**). Cu 3d states overlap with peroxide O 2p states near the Fermi level, indicating direct electronic communication between Cu and the coordinated peroxide. Differential charge-density maps provide a corresponding real-space representation of this redistribution (Fig. 5G, **Supplementary Fig. S46**). The accompanying change in O–O distance confirms substantial reorganization of the O–O unit upon formation of the Ti–O–O–Cu state.

Energetic calculations further distinguished H_2O_2 capture from subsequent activation (Fig. 5H), while differential charge-density analysis and optimized intermediate structures further resolved the associated electronic and structural evolution (**Supplementary Figs. S47-S49**). Framework Ti stabilizes the initially coordinated H_2O_2 species, whereas introduction of neighbouring Cu preferentially stabilizes the reorganized Ti–O–O–Cu configuration. The associated charge redistribution shows that Cu modifies the electronic environment of Ti-bound H_2O_2 before formation of the activated coupled state. Ti and Cu therefore perform complementary roles: Ti provides a thermodynamically favourable site for H_2O_2

interception and coordination, while neighbouring Cu reshapes the electronic structure of the coordinated species and favours progression toward the Ti–O–O–Cu configuration.

Together, these results support a confined H₂O₂ activation mechanism based on sequential Ti-mediated capture and Ti–Cu electronic coupling (Fig. 5I). Channelled H₂O₂ is first intercepted by framework Ti through closed-shell coordination. Interaction with a neighbouring Cu centre then induces charge redistribution, O–O polarization and spin delocalization within a Ti–O–O–Cu configuration. This electronically activated state remains associated with the confined catalytic domain and is consistent with the limited contribution of freely diffusing radicals observed experimentally. Ti-mediated interception and Cu-mediated electronic activation therefore constitute distinct but coupled steps that convert channelled H₂O₂ into a locally reactive peroxide-derived state for contaminant oxidation.

Water-Matrix Robustness and Operational Assessment

We next examined whether this reaction pathway remains operative under conditions relevant to water treatment. In the current laboratory-scale ultrasonic system, energy input and reactor throughput remain limiting factors compared to high-throughput centralized oxidation methods.⁴⁶ Nevertheless, these results indicate that coupling interfacial peroxide generation with confined catalytic consumption can reduce reliance on externally supplied oxidants in scenarios where oxidant storage, transport, or continuous dosing introduces additional constraints.

In comparison with deionized water, 2-FP degradation decreased in tap water, secondary effluent and lake water (Fig. 6A), reflecting interference from dissolved ions, natural organic matter and other matrix constituents.³ Nevertheless, measurable oxidation activity was retained in all tested waters, indicating that interfacial H₂O₂ generation and downstream catalytic utilization remain functional in chemically complex aqueous matrices.

To identify the major sources of matrix interference, representative inorganic ions and humic substances were examined individually. Chloride, bicarbonate, carbonate, sulfate, nitrate, phosphate and humic acid (HA) inhibited 2-FP degradation to different extents (Fig. 6C). In radical-dominated AOPs, such effects are commonly attributed to ROS scavenging,⁴⁷ whereas several additional processes may operate here. Ions can alter interfacial charge development and thereby affect CEC-driven H₂O₂ generation, while strongly adsorbing ions or dissolved organic matter can influence H₂O₂ access to internal catalytic domains or compete for reactive peroxide-derived species. Humic substances may additionally consume oxidizing equivalents and partially obstruct pore access. The observed inhibition therefore reflects interference with multiple steps of the H₂O₂ channelling pathway, including interfacial generation, transport and catalytic consumption.

A proof-of-concept flow-through experiment was then used to examine whether H₂O₂ generation and catalytic utilization could be sustained under dynamic operation. PTFE@Cu/TS-1 maintained 2-FP

degradation and TOC removal over increasing treated-water volumes, although both gradually declined during extended operation (Fig. 6B, **Supplementary Fig. S50**). These results show that in situ H_2O_2 generation and downstream oxidation can proceed continuously over the tested operating period without external H_2O_2 addition, while the gradual activity loss identifies catalyst retention, interfacial contact and long-term mass transport as parameters requiring further optimization.

Based on this operating principle, we further considered a flow-through reactor configuration in which PTFE@Cu/TS-1 is retained within an acoustically driven treatment module (Fig. 6D). Such a configuration would combine interfacial H_2O_2 generation and catalytic consumption within the same treatment unit, avoiding separate H_2O_2 storage and continuous oxidant dosing. At the present stage, this reactor scheme should be regarded as a conceptual implementation of H_2O_2 channelling rather than an optimized treatment technology. Its practical relevance will depend on maintaining catalyst retention, sufficient interfacial renewal and efficient energy transfer at increased throughput.

The environmental trade-offs of the present operating mode were assessed using life-cycle assessment (LCA). Relative to the externally dosed Cu/TS-1 + H_2O_2 reference, local H_2O_2 generation reduced contributions associated with H_2O_2 supply and handling, whereas electricity consumption for ultrasonic excitation remained the dominant burden in the laboratory-scale system (Fig. 6E). Sankey and heat-map analyses further show the redistribution of environmental contributions away from oxidant supply and toward electrical energy demand (Fig. 6F, G). The current configuration therefore does not derive its principal environmental advantage from reduced total energy use; instead, it replaces external oxidant supply with electrically driven interfacial generation. Improving the overall environmental performance will require lower-energy excitation, more efficient interfacial contact and higher reactor throughput.

Overall, these results show that H_2O_2 channelling remains operative in complex water matrices and can be sustained under proof-of-concept flow conditions, although both matrix interference and energy demand constrain the present configuration. The broader operational value of this approach lies in controlling H_2O_2 formation and consumption within a connected reaction pathway while reducing dependence on externally supplied peroxide. Further reactor development should therefore focus on preserving this mechanistic advantage while improving energy efficiency, mass transfer and treatment throughput.

Conclusion

In summary, this work establishes reactive-intermediate channelling as a strategy for controlling the post-formation fate and utilization of in situ generated H_2O_2 in heterogeneous AOPs. In PTFE@Cu/TS-1, the PTFE–water interface generates H_2O_2 through contact electrification, while the hierarchical MFI framework directs the newly generated H_2O_2 toward internal catalytic domains before bulk equilibration. Framework Ti sites intercept and coordinate H_2O_2 , and neighbouring Cu centres subsequently regulate its electronic structure through a Ti–O–O–Cu intermediate. The coupled Ti–Cu environment polarizes

the O–O unit and favours coordinated peroxide activation over extensive radical dissociation, enabling localized contaminant oxidation within confined catalytic domains. PTFE@Cu/TS-1 consequently achieves enhanced contaminant degradation and mineralization, while H₂O₂ fate analysis reveals greater pollutant-coupled consumption and a higher apparent utilization index despite lower bulk H₂O₂ accumulation. These results distinguish productive H₂O₂ utilization from simple bulk accumulation and show that oxidation efficiency depends on directing newly generated H₂O₂ into connected transport, capture and activation pathways. More broadly, reactive-intermediate channelling provides a framework for organizing the transfer of in situ generated oxidants between their formation and catalytic consumption in heterogeneous AOPs.

Methods

Chemicals

All reagents were of analytical grade and used as received without further purification. For the synthesis of catalysts, tetraethyl orthosilicate (TEOS), tetrabutyl orthotitanate (TBOT), tetrapropylammonium hydroxide (TPAOH, 25 wt% in water), (3-mercaptopropyl)trimethoxysilane (KH-590), tetrapropylammonium bromide (TPABr) and polytetrafluoroethylene (PTFE) aqueous dispersion (60 wt%) were purchased from Shanghai Macklin Biochemical Co., Ltd. Target pollutants including 2-fluorophenol (2-FP), nitrobenzene (NB), bisphenol A (BPA), tetracycline (TC), and rhodamine B (RhB) were supplied by Aladdin Biochemical Technology Co., Ltd. Reagents for mechanism investigation, including tert-butanol (TBA), p-benzoquinone (p-BQ), L-histidine (L-His), ethylenediaminetetraacetic acid disodium salt (EDTA-Na), and methyl phenyl sulfoxide (PMSO), along with spin trapping agents 5,5-dimethyl-1-pyrroline N-oxide (DMPO) and 2,2,6,6-tetramethylpiperidine (TEMP), were obtained from Sigma-Aldrich. Deuterium oxide (D₂O, 99.9 atom% D) and hydrogen peroxide (H₂O₂, 30 wt%) were purchased from Energy Chemical. Various inorganic salts and humic acid (HA) used for matrix interference experiments were supplied by Sinopharm Chemical Reagent Co., Ltd. Experimental solutions were prepared using ultrapure water (18.2 MΩ·cm) produced by a Millipore Milli-Q system. Real-water samples were collected from the tap water system of the University of Jinan, local municipal sewage, and Jiazi Lake.

Catalyst preparation

Synthesis of Cu/TS-1. A precursor solution was prepared by mixing TEOS (40 g), TBOT (2.64 g), TPAOH (46.72 g, 25 wt%), and deionized water (8.68 g) under ice-bath stirring for 1 h. The mixture was heated at 70°C for 30 min in an open vessel to remove alcohol generated during hydrolysis, followed by replenishment of deionized water equivalent to the evaporated mass. Subsequently, the mixture was further stirred at 70°C for 3 h, after which isopropanol (48 g) was introduced to obtain Solution A. Separately, NaOH (0.1 g), deionized water (2 g), and 3-mercaptopropyltrimethoxysilane (0.2 g) were mixed and hydrolysed for 30 min. The pH was adjusted to ~ 6, followed by addition of Cu(NO₃)₂ solution (1 mol/L, 1 mL). The resulting mixture was stirred for an additional 30 min to obtain Solution B. Solution B was slowly added to Solution A under stirring and aged for 30 min. The resulting gel was transferred

into a Teflon-lined stainless-steel autoclave and crystallized at 170°C for 24 h. The obtained solids were collected by filtration, washed thoroughly with deionized water, dried overnight, and calcined in air to obtain Cu/TS-1.

Deposition of PTFE Overlayer. PTFE dispersion (100 μ L, 60 wt%) was diluted to 1 mL with deionized water and manually homogenized to obtain Solution C. Subsequently, 100 μ L of Solution C was further diluted with 400 μ L deionized water to form Solution D. Calcined Cu/TS-1 (234 mg) was dispersed in Solution D, followed by mild ultrasonication for 5 min to promote PTFE distribution over the external surface and pore entrances. The suspension was dried under vacuum at 60°C for 6 h and subsequently calcined in air at 350°C for 2 h to stabilize the PTFE-containing surface layer, yielding PTFE@Cu/TS-1.

Pore blocking and regeneration of Cu/TS-1. To investigate the role of internal pore accessibility in peroxide transport and catalytic utilization, Cu/TS-1 was subjected to TPABr-assisted pore blocking and subsequent thermal regeneration. Briefly, Cu/TS-1 was treated with an aqueous TPABr solution (0.05 M) at room temperature for 6 h under stirring to allow TPABr molecules to enter and occupy the MFI microporous channels. The TPABr-treated sample was collected by filtration, washed with deionized water, and dried to obtain TPABr@Cu/TS-1. The regenerated catalyst was obtained by calcination of TPABr@Cu/TS-1 in air at 400°C for 4 h to remove confined TPABr molecules and restore pore accessibility. The parent Cu/TS-1, TPABr-blocked Cu/TS-1 and regenerated Cu/TS-1 were used to evaluate the contribution of pore accessibility to peroxide transport and confined oxidation.

Characterization

The crystalline structures of the prepared samples were recorded on a Smart Lab 9 kW X-ray diffractometer (Rigaku, Japan) equipped with Cu K α radiation. Surface morphologies and elemental distributions were characterized using a field-emission scanning electron microscope (FESEM, Gemini 300, Zeiss, Germany). High-resolution transmission electron microscopy (HRTEM) images were acquired on a JEM-2100F microscope operating at 200 kV. To visualize the atomically dispersed Cu species and subnanometric clusters within the zeolitic framework, aberration-corrected high-angle annular dark-field scanning transmission electron microscopy (AC-HAADF-STEM) and integrated differential phase-contrast STEM (iDPC-STEM) imaging were performed on an FEI Titan Themis microscope (300 kV) equipped with an X-FEG electron source and a DCOR spherical aberration corrector. The specific surface areas and pore size distributions were determined by N₂ adsorption-desorption isotherms at 77 K using a Micromeritics ASAP 2460 analyzer. Surface chemical states and electronic structures were analyzed via X-ray photoelectron spectroscopy (XPS, ESCALAB Xi+, Thermo Fisher Scientific, UK) with C 1s (284.8 eV) as the binding energy reference. The local coordination environments of Cu species were characterized using X-ray absorption fine structure (XAFS) spectroscopy at the Shanghai Synchrotron Radiation Facility (SSRF). The macroscopic hydrophobicity and surface charge of the catalysts were evaluated by water contact angle measurements (Krüss DSA100) and Zeta potential measurements (Malvern Zetasizer Nano ZS90). The leaching of metal active sites was monitored by inductively coupled plasma mass spectrometry (ICP-MS, Agilent 7800).

Experimental procedures

Unless otherwise stated, catalytic oxidation experiments were conducted in a 50 mL glass reactor containing 30 mL pollutant solution and a specified amount of PTFE@Cu/TS-1 catalyst. Prior to reaction, the suspension was magnetically stirred in the dark for 30 min to establish adsorption–desorption equilibrium between the catalyst and pollutant molecules.

The reactor was subsequently placed in an ultrasonic cleaner to initiate contact-electrification-driven H_2O_2 generation and confined catalytic oxidation. During ultrasonic treatment, the ultrasonic bath was cooled using an ice-water circulation system to minimize heat accumulation and maintain the reaction temperature close to room temperature.

At predetermined intervals, aliquots were withdrawn and immediately filtered through a 0.22 μm membrane to remove catalyst particles. The filtrates were analyzed by HPLC, LC–MS, TOC analysis, ion chromatography, or H_2O_2 quantification depending on the specific experiment.

All experiments were performed at least in triplicate, and the results are presented as mean values with standard deviations.

Declarations

Data availability

The data supporting the findings of this study are available within the article and its Supplementary Information files. All other relevant raw data can be obtained from the corresponding author upon request. Source data are provided with this paper.

Competing interests

The authors declare no conflict of interest.

Author contributions

Y. W., G. Z. C., and F. R. F. conceived and coordinated this work. R. Y. W. and H. J. Y conducted experiments. H. B. L. and X. H. R. conducted the theoretical studies. C. L. assisted with the DFT calculations. R. Y. W. and W. X. L. analyzed the results and co-wrote the paper. All authors contributed to the discussion of manuscript.

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Figures

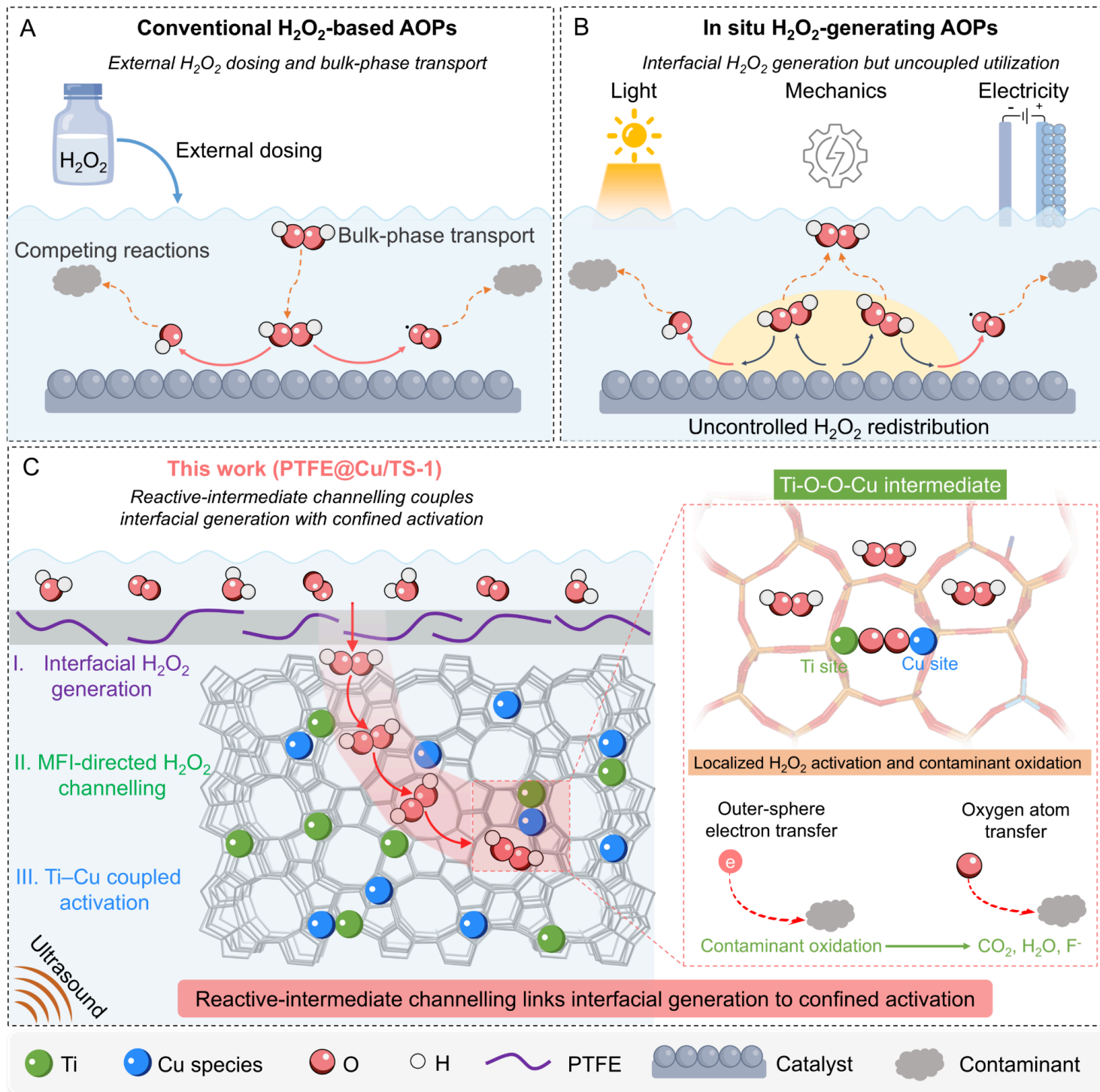


Figure 1

(A) External H_2O_2 dosing with bulk-phase transport to catalytic sites. **(B)** In situ interfacial H_2O_2 generation with uncoupled downstream utilization. **(C)** Reactive-intermediate channelling in PTFE@Cu/TS-1 through MFI-directed transport, Ti-mediated capture and neighbouring Cu-mediated activation.

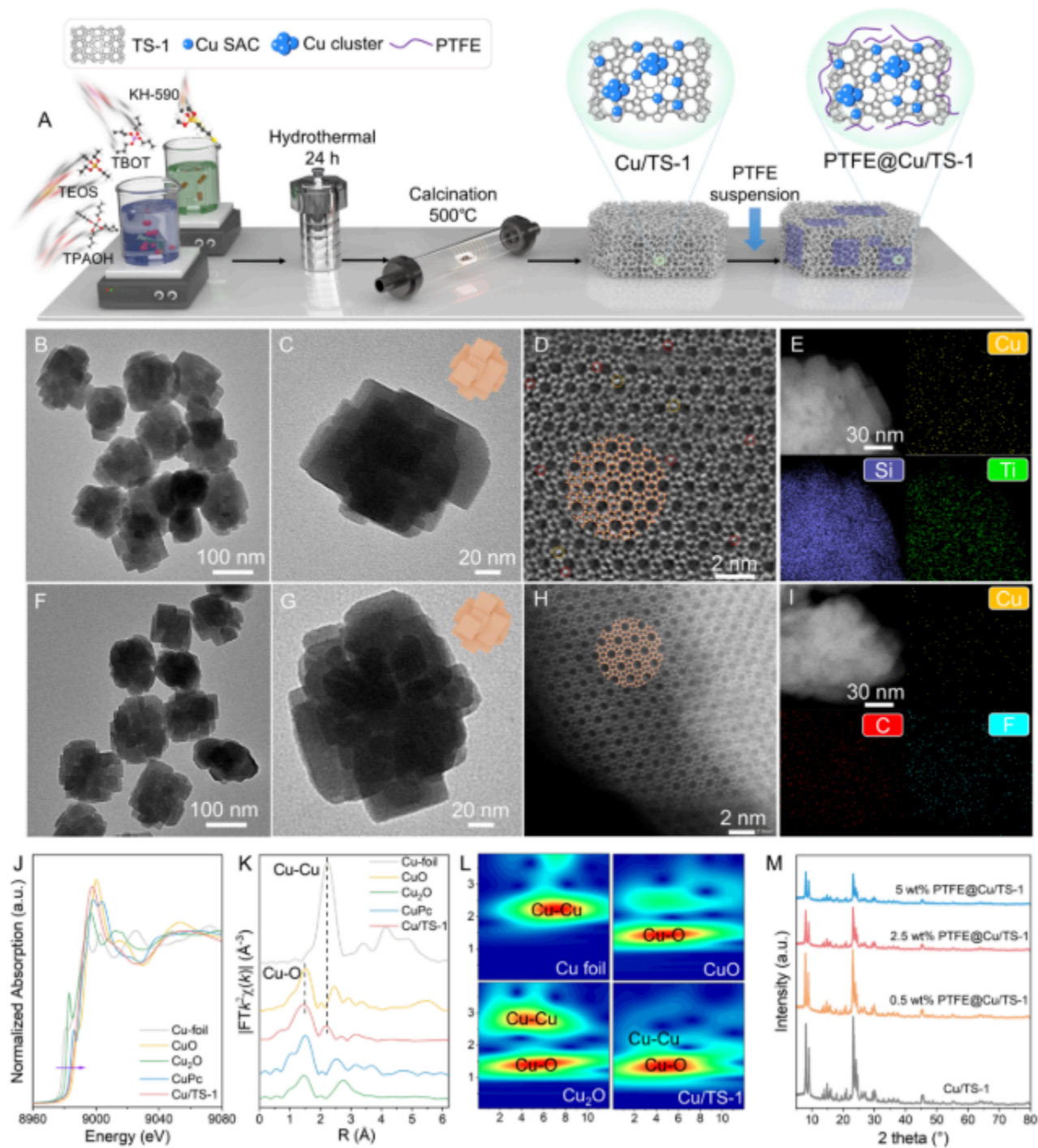


Figure 2

(A) Schematic illustration of the synthesis of PTFE@Cu/TS-1. (B, C) TEM images of Cu/TS-1. (D) iDPC-STEM image of Cu/TS-1 showing confined Cu species within the MFI framework. (E) EDS elemental mapping of Cu/TS-1. (F, G) TEM images of PTFE@Cu/TS-1. (H) Aberration-corrected HAADF-STEM image of PTFE@Cu/TS-1. (I) EDS elemental mapping of PTFE@Cu/TS-1. (J) Cu K-edge XANES spectra of Cu/TS-1 and reference samples. (K) Fourier-transformed Cu K-edge EXAFS spectra. (L) Wavelet-transform EXAFS analysis of Cu/TS-1 and reference samples. (M) XRD patterns of Cu/TS-1 and PTFE@Cu/TS-1 with different PTFE loadings.

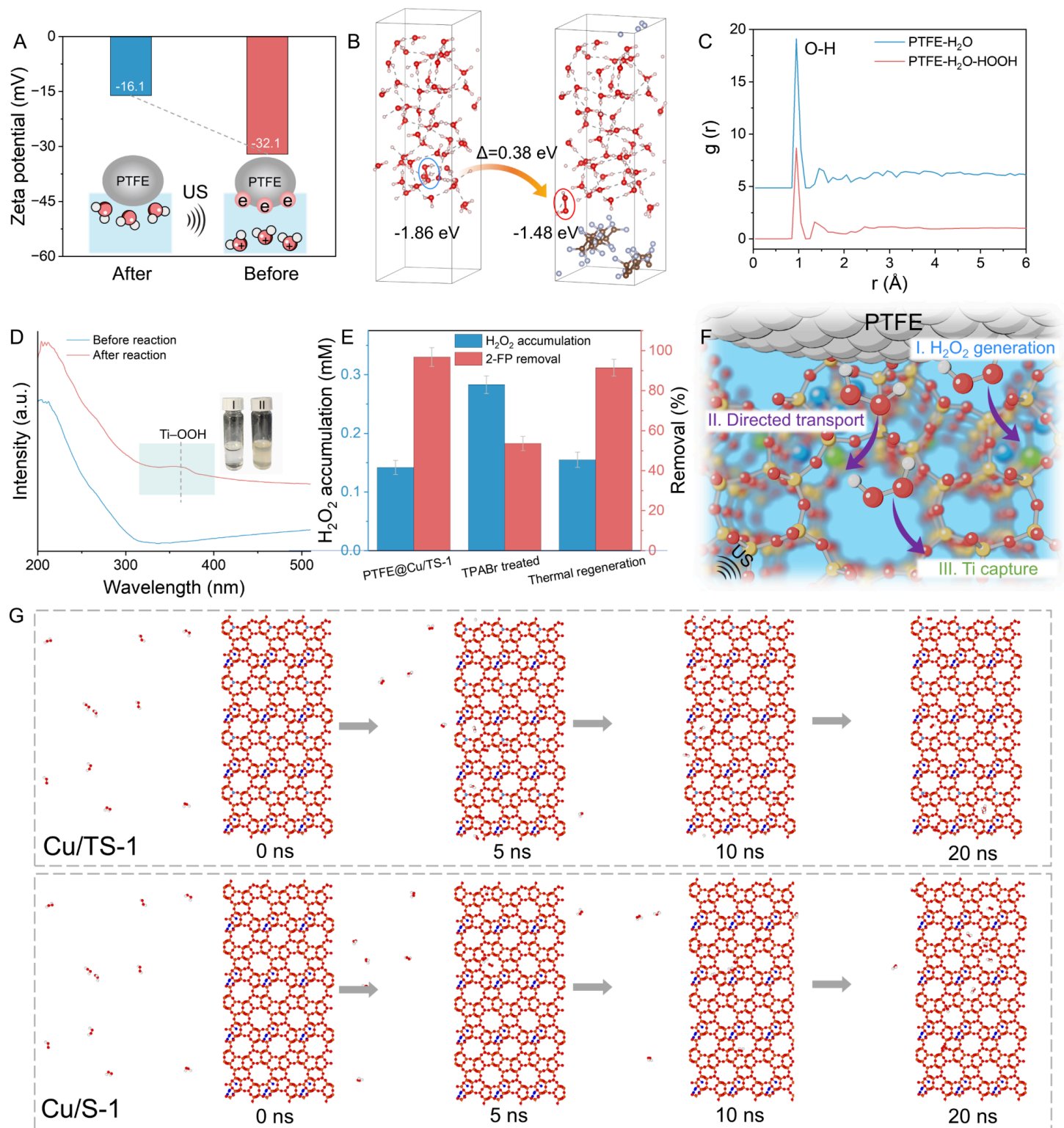


Figure 3

(A) Zeta potential of PTFE before and after ultrasonic excitation. (B) DFT-calculated interaction energies of HOOH at the PTFE interface and in bulk water. (C) Radial distribution functions describing interfacial water structures in PTFE-H₂O and PTFE-H₂O-HOOH systems. (D) UV-vis diffuse reflectance spectra and corresponding colour changes after ultrasonic activation. (E) Bulk H₂O₂ concentration and 2-FP degradation performance of parent PTFE@Cu/TS-1, TPABr-treated and regenerated samples. (F)

Proposed pathway for interfacial H_2O_2 generation, transport and Ti-mediated capture. (G) MD snapshots comparing H_2O_2 migration in Ti-containing Cu/TS-1 and Ti-free Cu/S-1 frameworks.

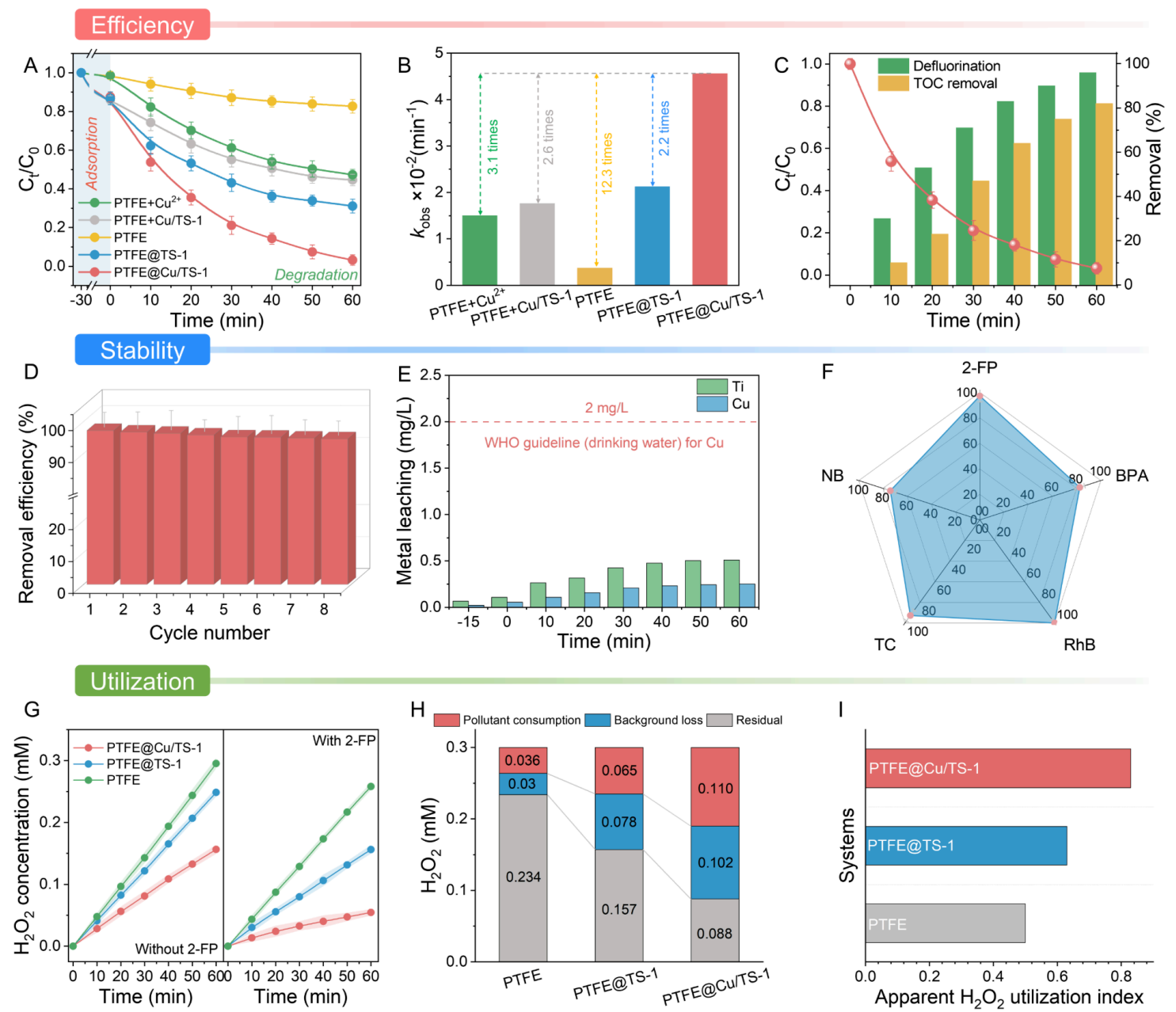


Figure 4

(A) Time-dependent 2-FP removal profiles over different catalytic systems. (B) Apparent pseudo-first-order rate constants. (C) Time-dependent defluorination efficiency, TOC removal and 2-FP concentration decay. (D) Cycling stability of PTFE@Cu/TS-1. (E) Ti and Cu leaching during reaction. (F) Degradation efficiencies toward representative organic contaminants. (G) Bulk H_2O_2 accumulation during CEC operation in the absence and presence of 2-FP. (H) Apparent fate distribution of externally supplied H_2O_2 derived from residual H_2O_2 , background H_2O_2 loss, and pollutant-coupled H_2O_2 consumption. (I)

Apparent H_2O_2 utilization index calculated from 2-FP transformation relative to pollutant-coupled H_2O_2 consumption.

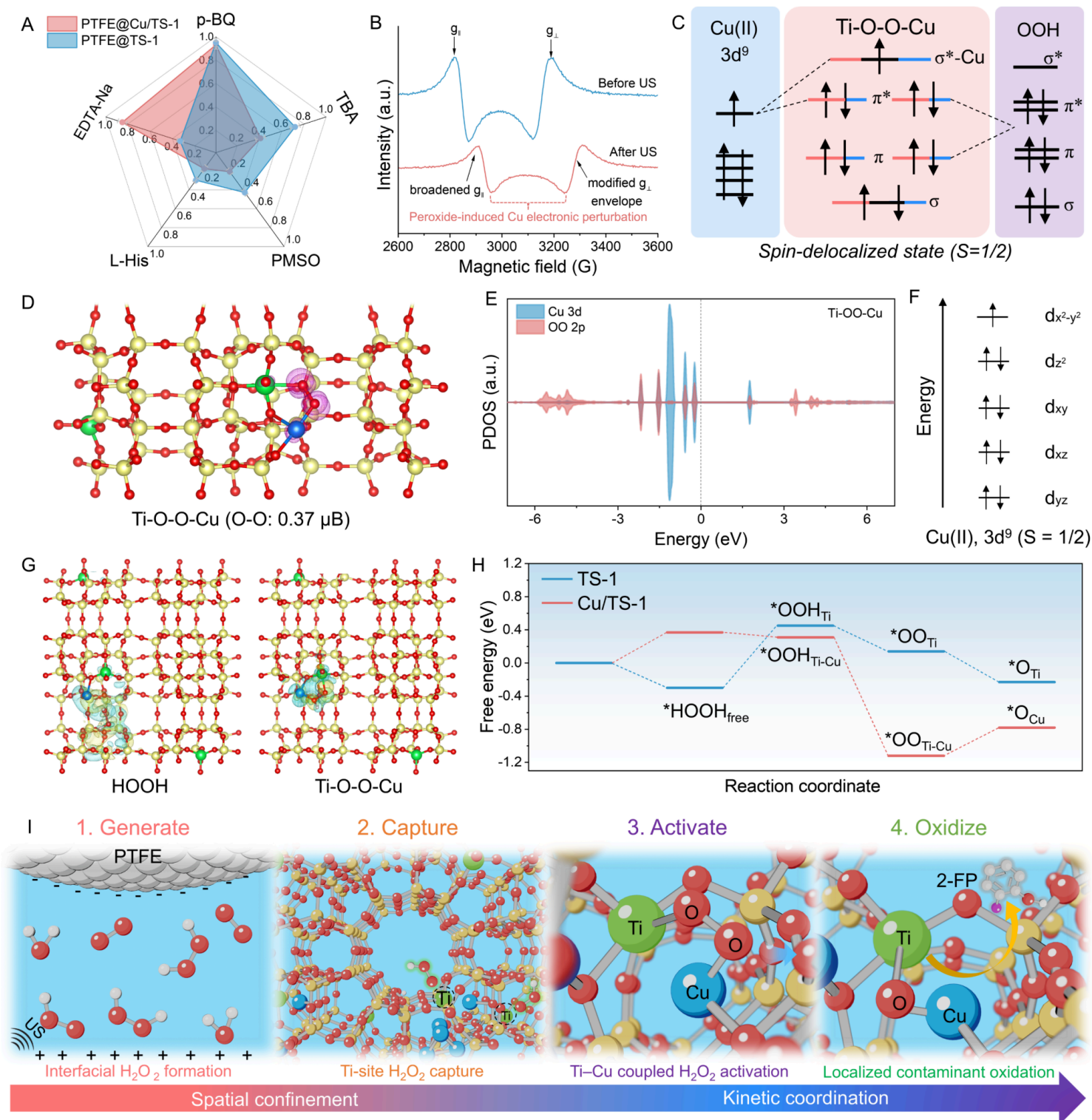


Figure 5

(A) Radical scavenging and selective oxygen-transfer probe experiments over PTFE@Cu/TS-1 and PTFE@TS-1. **(B)** X-band EPR spectra of PTFE@Cu/TS-1 before and after H_2O_2 activation, showing

perturbation of the Cu electronic environment. **(C)** Calculated structural and electronic evolution from free H_2O_2 to Ti-bound H_2O_2 and the Ti–O–O–Cu configuration, together with schematic orbital interactions. **(D)** Calculated spin-density distribution of the Ti–O–O–Cu configuration. **(E)** Projected density of states of the Ti–O–O–Cu configuration. **(F)** Cu 3d orbital states involved in electronic coupling with peroxide-derived O 2p states. **(G)** Differential charge-density distributions of Ti-bound H_2O_2 and the Ti–O–O–Cu configuration. **(H)** Relative energetic evolution of H_2O_2 coordination and activation on TS-1 and Cu/TS-1. **(I)** Proposed sequence of interfacial H_2O_2 generation, Ti-mediated interception, Ti–Cu electronic activation and localized contaminant oxidation.

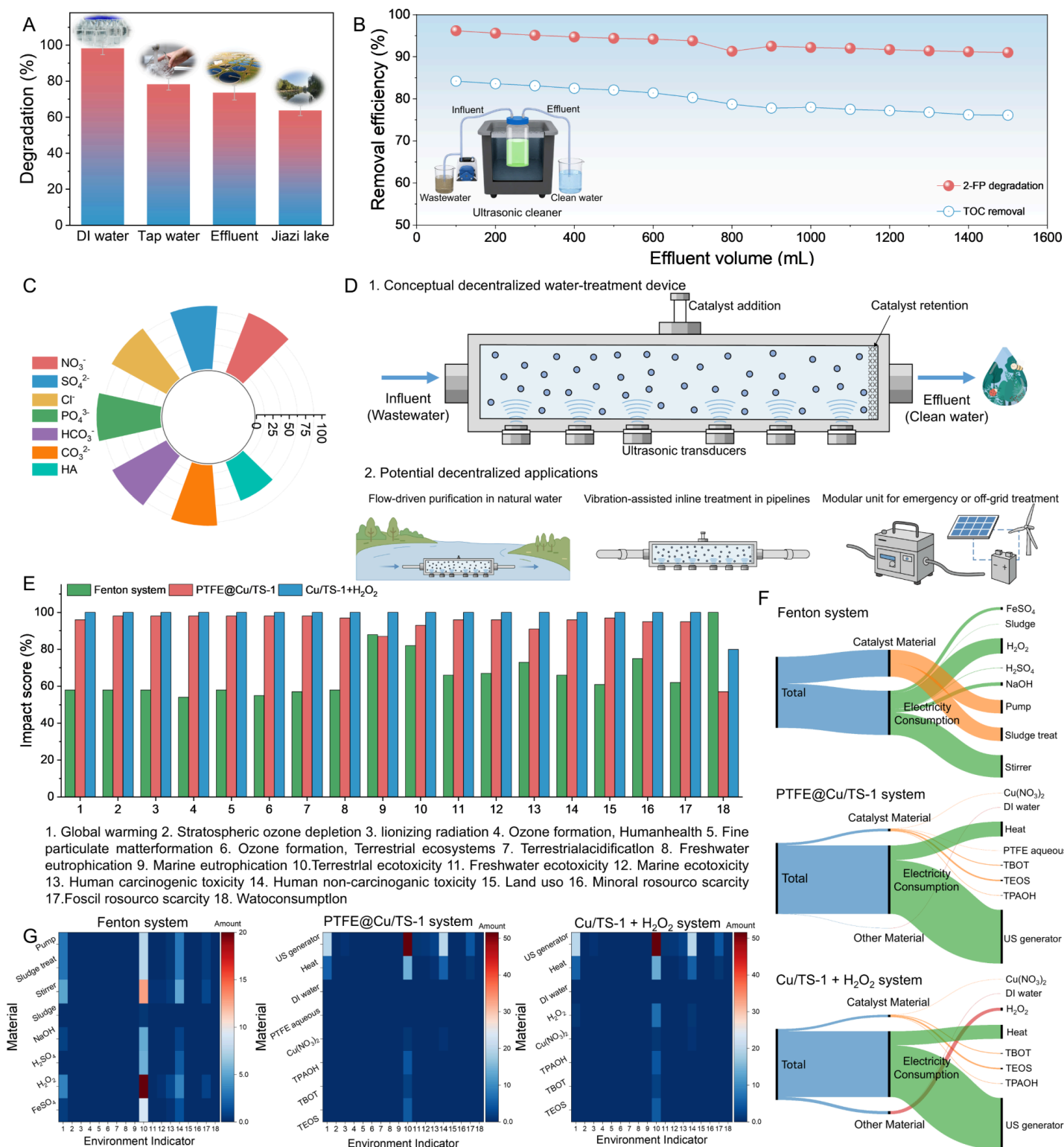


Figure 6

(A) 2-FP degradation in DI water and representative real-water matrices, including tap water, secondary effluent and Jiazi Lake water. (B) Continuous-flow 2-FP degradation and TOC removal performance under increasing effluent volume. Inset show the corresponding flow-through reactor configuration. (C) 2-FP degradation efficiencies in representative anions and natural organic matter. (D) Conceptual illustration of a decentralized continuous-flow reactor. Bottom panels illustrate representative

deployment scenarios. (E) Comparative life-cycle impact assessment of PTFE@Cu/TS-1, Fenton oxidation, and Cu/TS-1+H₂O₂ systems across multiple environmental categories. (F) Sankey-diagram analysis showing the relative contributions of electricity consumption, catalyst materials, and auxiliary chemicals to the overall environmental footprint of different oxidation systems. (G) Heatmap analysis of material-specific environmental impacts associated with representative oxidation technologies.

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