

# Plastron-mediated direct H<sub>2</sub>O<sub>2</sub> synthesis

Received: 29 December 2025

Accepted: 20 July 2026

Published online: 04 August 2026



Kang Wang<sup>1</sup>, Vivekananda Sinha<sup>1</sup>, Anthony J. Hayes<sup>2</sup>, Alexandre Boucher<sup>1</sup>, Alberto Roldan<sup>1</sup>, David J. Morgan<sup>3</sup>, Richard J. Lewis<sup>3</sup>, Graham J. Hutchings<sup>3</sup> & Marc Pera-Titus<sup>1</sup> ✉

Gas-liquid-solid catalytic reactions are ubiquitous in the chemical industry and environmental chemistry. The efficacy of these reactions is constrained by the inherently low solubility of gases in liquids and poor mass transfer of reactants/products to/from the catalyst surface. We show that a gas layer trapped on a hydrophobic catalyst (plastron) substantially enriches local gas concentration, alleviating mass-transfer limitations and accelerating reaction rates. Using gold-palladium catalyst for direct hydrogen peroxide synthesis as a model, hydrogen/air plastrons on hydrophobic organosilica yield up to a 20-fold rate enhancement without sub-ambient temperatures, high pressures, or alcohol co-solvents. Combined with selective adsorption of butanethiol on gold-palladium nanoparticles, plastrons further inhibit undesirable decomposition pathways of hydrogen peroxide by repelling water from the catalytic center, eliminating the need for acid and halide promoters. This strategy serves as a new class of heterogeneous catalysts for gas-liquid-solid reactions, offering a route to chemical processes with reduced cost and carbon footprint.

Direct hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) synthesis can present a sustainable alternative to the current commercial process comprising the sequential hydrogenation and oxidation of an alkylanthraquinone precursor dissolved in a mixture of organic solvents<sup>1,2</sup>. This indirect route is highly capital-intensive, requires significant energy input [198.58 kWh / ton<sub>H<sub>2</sub>O<sub>2</sub></sub> (27.5%)], and leads to considerable CO<sub>2</sub> emissions (~3 kg CO<sub>2eq</sub> / kg<sub>H<sub>2</sub>O<sub>2</sub></sub>)<sup>1,2</sup>. Furthermore, transportation, storage, and handling of bulk H<sub>2</sub>O<sub>2</sub> represent a major safety risk and contribute further to the CO<sub>2</sub> footprint of the commercially sourced oxidant<sup>3</sup>. Despite the progress in catalyst design at the laboratory scale<sup>4–6</sup>, translation to industrially viable direct H<sub>2</sub>O<sub>2</sub> synthesis processes has remained elusive. Insufficient H<sub>2</sub>O<sub>2</sub> concentrations and the operational need for H<sub>2</sub>-lean gas mixtures—typically diluted with inert gases (e.g., N<sub>2</sub>, CO<sub>2</sub>) to suppress flammability risks—both compromise productivity and increase process costs<sup>7</sup>.

The rate of direct H<sub>2</sub>O<sub>2</sub> synthesis in aqueous or alcoholic media is strongly governed by the dissolved gas concentrations, with  $r_{\text{H}_2\text{O}_2} \propto [\text{H}_2]^{0.1} [\text{O}_2]^{0.1}$ <sup>8,9</sup>. The solvent plays a non-innocent mechanistic role: H<sub>2</sub>O<sub>2</sub> formation is promoted by proton-mediated electron transfer resulting from heterolytic H<sub>2</sub> activation and subsequent reaction with

surface-bound intermediates<sup>7,10</sup>. Given the inherently low solubility of gases in water, elevated pressures (> 30 bar) are typically required to achieve meaningful reaction rates, thereby raising processing costs<sup>11</sup>.

Hydrophobic interfaces have been exploited in electrochemical systems to improve gas accessibility. Gas-diffusion electrodes can sustain thin gas layers—or plastrons—that facilitate mass transport under imposed potentials and continuous gas feed<sup>12,13</sup>. However, plastrons arise under nonequilibrium conditions specific to electrochemical operation, and their existence or functional relevance in thermocatalytic, liquid-phase H<sub>2</sub>/O<sub>2</sub> reaction environments is unknown. Whether analogous interfacial H<sub>2</sub> + O<sub>2</sub> reservoirs can form spontaneously on hydrophobically modified particulate catalysts, and whether such structures could enhance direct H<sub>2</sub>O<sub>2</sub> synthesis at near-ambient pressure, remains unexplored.

Inspired by these observations, we hypothesize that the local enrichment of H<sub>2</sub> and O<sub>2</sub> at a hydrophobic catalyst surface—beyond concentrations predicted by Henry's Law—via the formation of an interfacial H<sub>2</sub> + O<sub>2</sub> plastron can enhance the rate of H<sub>2</sub>O<sub>2</sub> production in pure water at near-ambient pressure. To test this hypothesis, we prepared a series of hydrophobic catalysts consisting of AuPd nanoalloys

<sup>1</sup>Cardiff Catalysis Institute, School of Chemistry, Cardiff University; Translational Research Hub, Cardiff, UK. <sup>2</sup>Cardiff School of Biosciences, Cardiff University, Cardiff, UK. <sup>3</sup>Max Planck-Cardiff Centre on the Fundamentals of Heterogeneous Catalysis FUNCAT, Cardiff Catalysis Institute, School of Chemistry, Cardiff University; Translational Research Hub, Cardiff, UK. ✉e-mail: [peratitum@cardiff.ac.uk](mailto:peratitum@cardiff.ac.uk)

supported on an organosilica support<sup>5,14</sup>. We systematically investigated plastron formation and regeneration on the catalysts, and evaluated its influence on both  $\text{H}_2\text{O}_2$  formation and decomposition. Our results demonstrate that gas plastrons enable efficient direct  $\text{H}_2\text{O}_2$  synthesis in water without the sub-ambient temperatures, elevated pressures, or alcohol co-solvents typically required for high activity and selectivity.

## Results and discussion

### Preparation of hydrophobic catalysts

In brief, an AuPd/SiO<sub>2</sub> catalyst (0.25 wt.% metal loading, Au: Pd = 1:1 by weight, Supplementary Table 1) was prepared by the sol-immobilization method<sup>15</sup>, and grafted with 1H,1H,2H,2H-perfluorooctyltriethoxysilane (PFOTES) and octyltriethoxysilane (OTES) to impart hydrophobicity. Next, self-assembled butanethiol monolayers (SAMs) were deposited using a one-pot immersion protocol (Supplementary Fig. 1a–c)<sup>16–18</sup>. The metal loading and average size of AuPd nanoparticles (4.6 nm) remained unchanged after surface modification relative to the parent AuPd/SiO<sub>2</sub> catalyst (Fig. 1a–c & Supplementary Fig. 2a–c). Energy-Dispersive X-ray Spectroscopy (EDS) analysis of the catalysts confirmed the formation of a AuPd nanoalloy and the grafting of PFOTES on SH-AuPd/SiO<sub>2</sub>-F-60  $\mu\text{L}$ <sup>19</sup>. Metal immobilization and PFOTES grafting had minimal impact on the specific surface area of the different catalysts ( $\sim 200 \text{ m}^2/\text{g}$ , Supplementary Table 1).

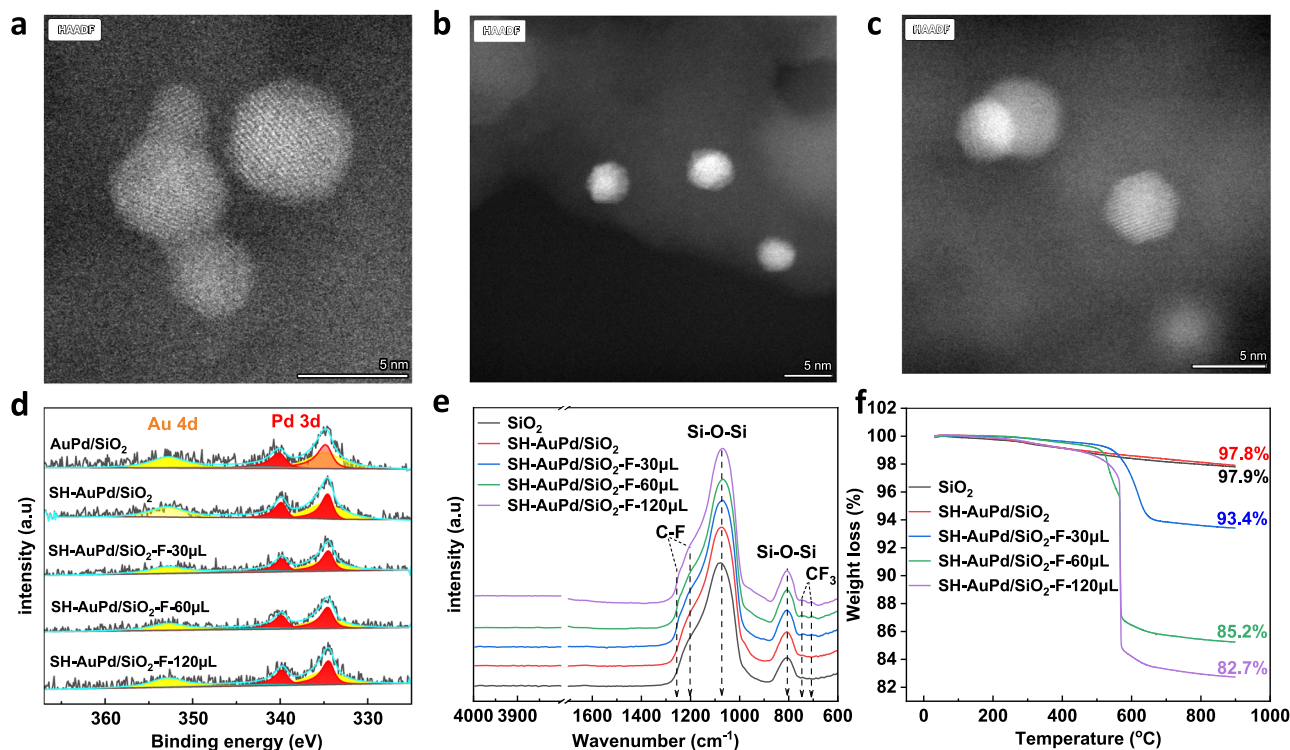
### Characterization of hydrophobic catalysts

X-ray photoelectron spectroscopy (XPS) confirmed the presence of metallic Pd and Au species on AuPd/SiO<sub>2</sub>, SH-AuPd/SiO<sub>2</sub>, and SH-AuPd/SiO<sub>2</sub>-F-60  $\mu\text{L}$  formulations (Fig. 1d)<sup>20</sup>. Thiol functionalization did not induce any detectable changes in the chemical state of either metal. Sulfur, fluorine, and carbon species demonstrated successful functionalization (Supplementary Fig. 3a–d). Fourier Transform Infrared (FT-IR) spectra evidenced the effective surface grafting of PFOTES with

characteristic bands at  $1170 \text{ cm}^{-1}$  and  $1245 \text{ cm}^{-1}$ , indicative of C-F bond vibrations<sup>21,22</sup>, with additional bands also visible at  $745 \text{ cm}^{-1}$  and  $707 \text{ cm}^{-1}$  that are consistent with symmetric stretching vibrations of CF<sub>3</sub> moieties (Fig. 1e)<sup>23,24</sup>. The surface density of PFOTES chains was 0.374, 1.03, and 1.26 groups/nm<sup>2</sup>, respectively, measured from thermogravimetric (TG) analysis between 400 and 800 °C (Fig. 1f)<sup>25</sup>. The contact angles for SH-AuPd/SiO<sub>2</sub>-F-30  $\mu\text{L}$ , SH-AuPd/SiO<sub>2</sub>-F-60  $\mu\text{L}$ , and SH-AuPd/SiO<sub>2</sub>-F-120  $\mu\text{L}$  in water (110°, 125°, 137°) were substantially higher than that of control SH-AuPd/SiO<sub>2</sub> catalyst ( $\sim 16^\circ$ ) (Supplementary Fig. 4a–d & Supplementary Table 1). These results evidence the effective surface modification and increasing hydrophobicity of the catalysts with higher PFOTES loading.

Analysis by diffuse reflectance infrared Fourier transform spectroscopy, using CO as a probe molecule, was used to assess surface accessibility of metal sites. CO-DRIFTS analysis of AuPd/SiO<sub>2</sub> and AuPd/SiO<sub>2</sub>-F-60  $\mu\text{L}$  catalysts reveals typical CO adsorption bands on Pd at  $\sim 2050\text{--}2100 \text{ cm}^{-1}$  (linear mode) and  $\sim 1800\text{--}2000 \text{ cm}^{-1}$  (bridged mode), indicating the presence of accessible metallic sites for CO binding (Supplementary Fig. 3e)<sup>26</sup>. In contrast, the thiol-functionalized samples, SH-AuPd/SiO<sub>2</sub> and SH-AuPd/SiO<sub>2</sub>-F-60  $\mu\text{L}$ , show no detectable CO adsorption features, which is attributed to strong coordination between Pd(0) centers and thiolate ligands, effectively blocking CO access to the active Pd sites<sup>27,28</sup>.

Density functional theory (DFT) calculations further substantiate this interpretation. The results show that butanethiol preferentially adsorbs on Pd sites of the AuPd(111) alloy surface, binding at bridge positions with Pd–S bond distances of  $\sim 2.31 \text{ \AA}$  and a strong adsorption energy of  $\sim 1.57 \text{ eV}$  (Supplementary Fig. 5). This selective chemisorption leads to effective occupation of Pd surface ensembles. The calculated binding configuration therefore provides molecular-level evidence that thiol ligands directly coordinate to Pd atoms, rationalizing the disappearance of CO adsorption bands observed experimentally upon thiol functionalization.



**Fig. 1 | Characterization of catalysts.** AC-STEM micrographs of AuPd nanoparticles in (a), AuPd/SiO<sub>2</sub>, (b) SH-AuPd/SiO<sub>2</sub>, (c) SH-AuPd/SiO<sub>2</sub>-F-60  $\mu\text{L}$  particles. (d) XPS spectra of Au 4d and Pd 3d core levels for AuPd/SiO<sub>2</sub>, SH-AuPd/SiO<sub>2</sub>, SH-AuPd/SiO<sub>2</sub>-F-30  $\mu\text{L}$ , SH-AuPd/SiO<sub>2</sub>-F-60  $\mu\text{L}$ , and SH-AuPd/SiO<sub>2</sub>-F-120  $\mu\text{L}$ . (e) FT-IR spectra of

pristine SiO<sub>2</sub>, SH-AuPd/SiO<sub>2</sub>, SH-AuPd/SiO<sub>2</sub>-F-30  $\mu\text{L}$ , SH-AuPd/SiO<sub>2</sub>-F-60  $\mu\text{L}$ , and SH-AuPd/SiO<sub>2</sub>-F-120  $\mu\text{L}$ . (f) Thermal profiles of pristine SiO<sub>2</sub>, SH-AuPd/SiO<sub>2</sub>, SH-AuPd/SiO<sub>2</sub>-F-30  $\mu\text{L}$ , SH-AuPd/SiO<sub>2</sub>-F-60  $\mu\text{L}$ , and SH-AuPd/SiO<sub>2</sub>-F-120  $\mu\text{L}$ .

To further support this assignment, vibrational spectra were calculated for both gas-phase butanethiol and adsorbed butanethiol@AuPd(111) (Supplementary Fig. 5). Upon adsorption, the S–H stretching mode present in the gas phase disappears and is replaced by new vibrational features associated with Pd–S interactions, consistent with dissociative chemisorption of the thiol on the metal surface. In addition, the S–C vibrational mode shifts from approximately 900 cm<sup>−1</sup> in the gas phase to around 1200 cm<sup>−1</sup> after adsorption. This shift is accompanied by elongation of the S–C bond from 1.845 Å to 1.863 Å, indicating modification of the sulfur electronic environment upon coordination to Pd.

### Computational investigation of the active sites for H<sub>2</sub>O<sub>2</sub> synthesis

To further clarify the nature of the active sites involved in direct H<sub>2</sub>O<sub>2</sub> synthesis, density functional theory (DFT) calculations were performed on the AuPd(111) surface to investigate the adsorption behavior of H<sub>2</sub>O<sub>2</sub>, O<sub>2</sub>, H<sub>2</sub>O, and butanethiol (S-but). The calculations reveal that H<sub>2</sub>O<sub>2</sub> adsorbs most favorably on top of Pd atoms with an adsorption energy of −1.03 eV and a Pd–O distance of 2.412 Å (Supplementary Fig. 6). Upon adsorption, the O–O bond length increases slightly from 1.483 Å in the gas phase to 1.488 Å at the AuPd surface, accompanied by the appearance of new vibrational modes at 500 and 3500 cm<sup>−1</sup>, indicating direct interaction between H<sub>2</sub>O<sub>2</sub> and Pd surface atoms.

We next investigated the co-adsorption of butanethiol and H<sub>2</sub>O<sub>2</sub> on AuPd(111). The calculations show that butanethiol preferentially adsorbs at a Pd–Pd bridge configuration, while H<sub>2</sub>O<sub>2</sub> remains adsorbed on top of a Pd atom, resulting in a total adsorption energy of −2.58 eV (Supplementary Fig. 7). The adsorbed thiolate forms two Pd–S interactions with bond distances of 2.308 and 2.317 Å. Interestingly, the Pd–O distance for H<sub>2</sub>O<sub>2</sub> decreases from 2.412 Å in the isolated adsorption state to 2.400 Å in the co-adsorbed configuration, suggesting a strengthened metal–adsorbate interaction through synergistic effects between the two adsorbates.

To further probe the active sites involved in the reaction pathway, we compared the co-adsorption of butanethiol with O<sub>2</sub> and H<sub>2</sub>O on AuPd(111). O<sub>2</sub> adsorbs preferentially on Pd-rich regions, forming a bridge configuration between neighboring Pd atoms with an adsorption energy of −3.34 eV (Supplementary Fig. 8). The Pd–O bond distances are approximately 2.080 Å, while the O–O bond elongates from 1.240 Å in the gas phase to 1.327 Å upon adsorption, demonstrating efficient activation of molecular oxygen at Pd ensembles. In contrast, H<sub>2</sub>O adsorption is considerably weaker (−1.57 eV), with the molecule adsorbing on top of a Pd atom at a distance of 2.643 Å.

The calculated adsorption energies follow the order:  $E_{\text{ads}}(\text{S-but}) > E_{\text{ads}}(\text{S-but}/\text{H}_2\text{O}_2) > E_{\text{ads}}(\text{S-but}/\text{H}_2\text{O})$ . These results provide strong evidence that Pd surface atoms constitute the primary active sites for both O<sub>2</sub> activation and H<sub>2</sub>O<sub>2</sub> adsorption during direct synthesis. Importantly, the calculations further demonstrate that thiol functionalization does not block the ability of Pd ensembles to activate the O–O bond. Instead, butanethiol modifies the local adsorption environment by preferentially destabilizing water adsorption relative to O<sub>2</sub> and H<sub>2</sub>O<sub>2</sub>. This effect suppresses the formation of surface hydroxyl species that are known to promote H<sub>2</sub>O<sub>2</sub> decomposition<sup>29</sup>, while simultaneously favoring H<sub>2</sub>O<sub>2</sub> stabilization at the catalyst interface. Collectively, these findings support the conclusion that direct H<sub>2</sub>O<sub>2</sub> synthesis predominantly occurs on Pd-rich surface ensembles of the AuPd nanoalloy, whereas the thiol layer acts as a local interfacial modifier that enhances selectivity and suppresses H<sub>2</sub>O<sub>2</sub> degradation.

### Experimental validation and quantification of plastron formation

To investigate plastron formation, different hydrophobic catalyst dispersions were prepared in pure water by ultrasonication using a

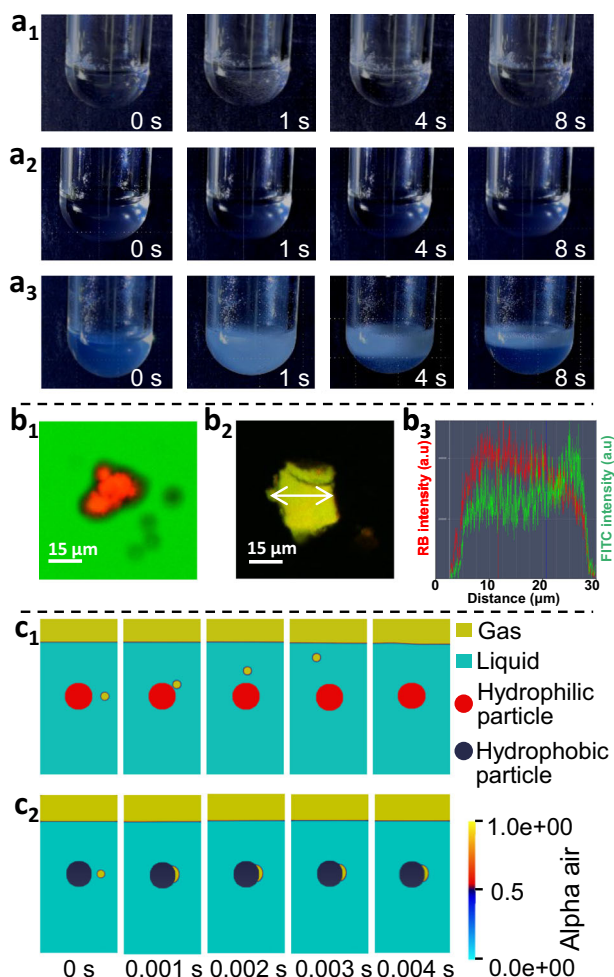
pressure-resistant tube (Supplementary Fig. 1d & Supplementary Movie 1). The sealed tube was saturated with a 4% H<sub>2</sub>/air mixture at 3 bar, followed by depressurization. Only a few bubbles were generated in a control experiment without the catalyst and when using the hydrophilic SH-AuPd/SiO<sub>2</sub> catalyst (Fig. 2a1, a2). In contrast, a dispersion containing hydrophobic SH-AuPd/SiO<sub>2</sub>-F-60 μL particles shows a dramatic increase in bubble generation immediately after depressurization (Fig. 2a3). This behavior is attributed to the release of gas trapped in plastrons (gas layers, Supplementary Fig. 1e) formed on the surface of SH-AuPd/SiO<sub>2</sub>-F-60 μL, which expand and detach as visible bubbles upon pressure release.

Beyond qualitative visualization, the plastron thickness was quantitatively estimated using a buoyancy-gravity equilibrium model (Supplementary Section S1.5). Based on the measured flotation behavior of the particles and the density difference between gas and liquid phases, the average plastron thickness surrounding the 200 nm silica particles was calculated to be approximately 30 nm. This thickness is consistent with a stable nanoscale gas layer capable of locally enriching dissolved reactant gases at the catalyst interface.

The temporal evolution and stability of the plastron were further quantified by monitoring the light transmittance (turbidity) of catalyst suspensions over time (Supplementary Fig. 9d). The SH-AuPd/SiO<sub>2</sub>-F-60 μL particles maintain nearly constant turbidity over at least 30 min, demonstrating persistent suspension stability associated with stable plastron retention. In contrast, the hydrophilic SH-AuPd/SiO<sub>2</sub> particles progressively sediment within 30 min due to the absence of a stabilizing gas layer. Plastron stability was quantified as the ratio between the absorbance after 30 min and the initial absorbance, showing a clear positive correlation with particle hydrophobicity (Supplementary Fig. 9g, h). Zeta potential measurements revealed lower negative surface charge for SH-AuPd/SiO<sub>2</sub> than SH-AuPd/SiO<sub>2</sub>-F-60 μL (−36 mV *vs* −24 mV) (Supplementary Fig. 9e). This finding indicates that plastron formation, rather than electrostatic repulsion, plays a dominant role in maintaining dispersion stability in aqueous media. To investigate the relationship between hydrophobicity and plastron stability, two additional catalysts were synthesized, designated as SH-AuPd/SiO<sub>2</sub>-F-15 μL and SH-AuPd/SiO<sub>2</sub>-F-45 μL. The corresponding contact angle images are provided in Supplementary Fig. 4b, d. The correlation between hydrophobicity and plastron stability is illustrated in Supplementary Fig. 9f.

SH-AuPd/SiO<sub>2</sub>-F-30 μL generate fewer bubbles than SH-AuPd/SiO<sub>2</sub>-F-60 μL, which dissipate within 8 s, consistent with its lower hydrophobicity and reduced plastron stability. The SH-AuPd/SiO<sub>2</sub>-F-120 μL formulation, despite exhibiting the highest contact angle, also shows less bubble release, because the particles float at the air–water interface suppressing effective plastron formation around suspended particles (Supplementary Fig. 9a–c).

Confocal microscopy was additionally used to directly visualize plastron formation on catalyst surfaces<sup>30</sup>. Hydrophilic and hydrophobic silica particles – modified with Rhodamine B (red fluorescence) to yield SiO<sub>2</sub>-RB and SiO<sub>2</sub>-F-RB, respectively – were dispersed into an aqueous solution of fluorescein isothiocyanate (FITC, green fluorescence). A distinct black halo devoid of fluorescence was observed surrounding the SiO<sub>2</sub>-F-RB particles (Fig. 2b1), indicating the presence of an interfacial air layer between the red fluorescent particle (hydrophobic) and surrounding aqueous phase (green FITC solution). In contrast, SiO<sub>2</sub>-RB particles (hydrophilic) display yellow fluorescence resulting from the overlap of red (Rhodamine B) and green (FITC) emissions against a non-luminous background (Fig. 2b2), confirming direct contact between the particle surface and the surrounding aqueous solution with no plastron formation. The intensity profile across the scan line (Fig. 2b3) shows maximum red intensity at the particle center and a gradual decrease toward the edges, inversely correlated with green intensity.



**Fig. 2 | Characterization of plastrons on hydrophobic particles.** **a** Optical images showing gas release from **a1**, pure water, **a2**, SH-AuPd/SiO<sub>2</sub> and **a3**, SH-AuPd/SiO<sub>2</sub>-F-60 μL particles dispersed in water. Experimental conditions: 2 mg particles dispersed in 2 mL pure water, 4% H<sub>2</sub>/air, 3 bar, gas saturation for 20 min at 22 °C followed by depressurization. **b** Confocal micrographs showing **b1**, SiO<sub>2</sub>-F-RB and **b2**, SiO<sub>2</sub>-RB particles immersed in aqueous FITC solution, and **b3**, fluorescent intensity across the particle (white line in b2). The dark area, devoid of fluorescence, delineates the boundary between red hydrophobic particle and green FITC solution in (b1). **c** Simulated gas bubble migration dynamics in water with **c1**, hydrophilic particle (red, contact angle 16°) and **c2**, hydrophobic particle (purple, contact angle 125°).

While advanced operando methods such as in-situ AFM could in principle provide additional interfacial information, their implementation under the present reaction conditions remains experimentally challenging because freely diffusing nanoparticles suspended in bulk liquid cannot currently be tracked with sufficient spatial and temporal resolution under reactive gas-liquid-solid conditions. Therefore, the combined use of buoyancy-based thickness estimation, time-resolved turbidity measurements, bubble-release analysis, and confocal microscopy provides a robust and experimentally accessible characterization of plastron formation, stability, and temporal evolution in the present catalytic system.

### Simulation of plastron formation

To support these findings, we conducted 2D numerical simulations on plastron formation in an air-water system using the volume of fluid (VOF) method<sup>31</sup>. Two types of particles were modeled: hydrophilic (contact angle 16°, representative of SH-AuPd/SiO<sub>2</sub>) and hydrophobic (contact angle 125°, representative of SH-AuPd/SiO<sub>2</sub>-F-60 μL). For the

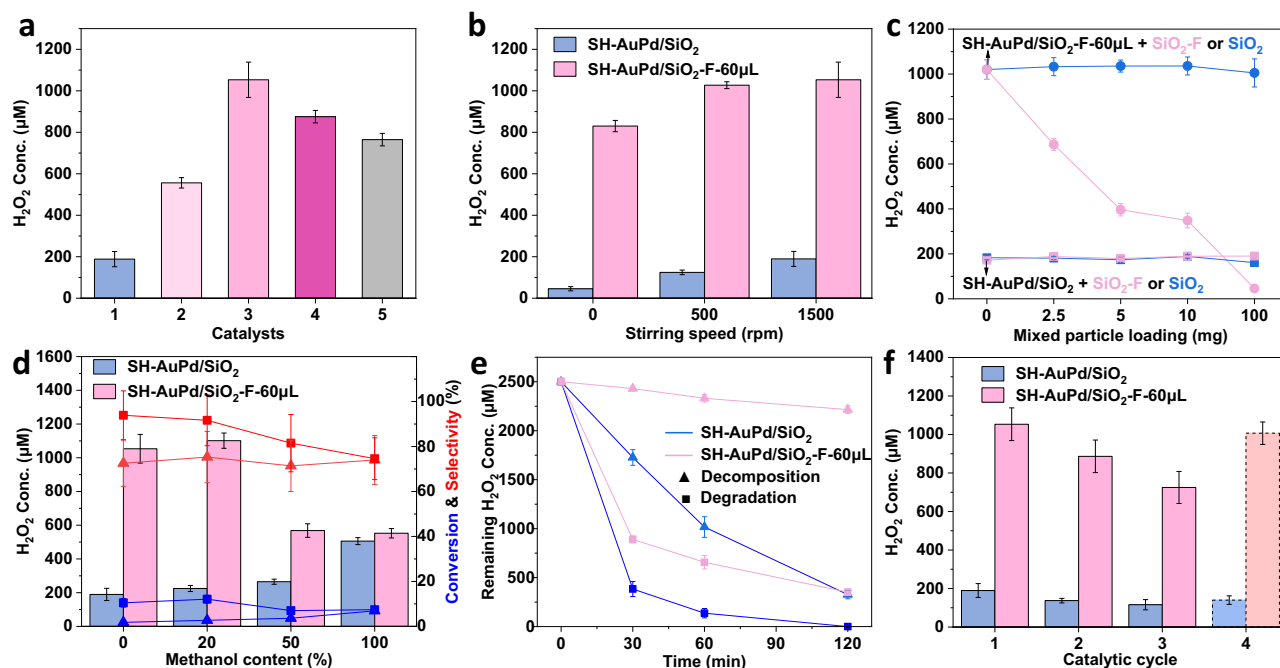
hydrophilic particle, a bubble approaching the surface at 0.001 s slides past it and merges with the air-water interface by 0.004 s (Fig. 2c1). This behavior is driven by capillary forces pushing the bubble toward the surface in the microchannel. However, due to the low contact angle, the reduction in total surface energy upon bubble attachment is minimal. In this case, viscous resistance between the bubble and the particle dominates over capillary pinning, preventing formation of a stable contact line and hence no plastron is formed. In stark contrast, the hydrophobic particle immediately anchors the bubble within 0.001 s, resulting in the formation of a stable gas film (Fig. 2c2; meshing details in Supplementary Fig. 10a, b). Here, the higher contact angle leads to a substantial reduction in surface energy upon bubble attachment, while the capillary pinning force exceeds viscous resistance, stabilizing the bubble-solid interface and facilitating plastron formation. The gas film remains stable up to at least 0.035 s (Supplementary Fig. 10c). Analysis of velocity streamlines at 0.035 s reveals two almost symmetric major recirculation zones flanking the attached bubble (Supplementary Fig. 10d), alongside two weaker secondary vortices at the bubble flanks. These patterns reflect transitions between clockwise and counterclockwise flows, which help stabilize the plastron. Notably, the upper recirculation zone is larger than the lower one, suggesting that buoyancy forces accelerate the flow near the bubble's upper contact point. However, due to strong capillary anchoring enabled by the high contact angle, the bubbles remain attached to the surface, preserving a stable plastron.

### Catalytic performance under plastron formation

We subsequently evaluated the performance of the catalysts for direct H<sub>2</sub>O<sub>2</sub> synthesis in water at ambient temperature and 3 bar using a 4% H<sub>2</sub>/air mixture – conditions that lie safely outside the explosive region (13–59%) (Fig. 3a)<sup>32</sup>. The H<sub>2</sub>O<sub>2</sub> concentration increased monotonically with the catalyst hydrophobicity, from 190 μM for non-hydrophobic SH-AuPd/SiO<sub>2</sub> catalyst to 560 μM and 1050 μM for SH-AuPd/SiO<sub>2</sub>-F-30 μL and SH-AuPd/SiO<sub>2</sub>-F-60 μL, respectively (Fig. 3a1–a3). However, the most hydrophobic catalyst, SH-AuPd/SiO<sub>2</sub>-F-120 μL, produced a lower concentration (870 μM), attributed to its flotation on water (Fig. 3a4). For comparison, SH-AuPd/SiO<sub>2</sub>-C grafted with OTES chains with a contact angle of 120° (Supplementary Fig. 4e) – yielded lower H<sub>2</sub>O<sub>2</sub> concentration compared to SH-AuPd/SiO<sub>2</sub>-F-60 μL (760 μM) with a slightly higher contact angle (125°) (Fig. 3a5). Two additional particles, SH-AuPd/SiO<sub>2</sub>-F-15 μL and SH-AuPd/SiO<sub>2</sub>-F-45 μL, with different degrees of hydrophobicity, exhibit catalytic activities of 290 μM and 750 μM, respectively, in agreement with the observed trend (Supplementary Fig. 9f). The H<sub>2</sub>O<sub>2</sub> concentration for SH-AuPd/SiO<sub>2</sub>-F-60 μL displayed a bell-shaped curve with catalyst loading, which is attributed to competitive H<sub>2</sub>O<sub>2</sub> degradation activity (Supplementary Fig. 11a).

The SH-AuPd/SiO<sub>2</sub> catalyst exhibits minimal activity towards H<sub>2</sub>O<sub>2</sub> synthesis under static conditions due to prominent mass transfer limitations (Fig. 3b). Even upon stirring at 500 rpm, H<sub>2</sub>O<sub>2</sub> concentration remains low at 125 μM, increasing only slightly to 190 μM at 1500 rpm. In contrast, SH-AuPd/SiO<sub>2</sub>-F-60 μL achieves 830 μM without stirring. Upon stirring, the H<sub>2</sub>O<sub>2</sub> concentration increases modestly to 1020 μM at 500 rpm and remains nearly constant at 1050 μM even at 1500 rpm, highlighting the dominant role of plastron-mediated mass transport over mechanical agitation.

To further elucidate the role of gas plastrons in direct H<sub>2</sub>O<sub>2</sub> synthesis and exclude any possible promotion effects from F-containing PFOTES grafted species<sup>33,34</sup>, we performed reactions using mixtures of SH-AuPd/SiO<sub>2</sub> with either SiO<sub>2</sub>-F or SiO<sub>2</sub> particles (Fig. 3c). No significant change in H<sub>2</sub>O<sub>2</sub> concentration (~180 μM) was observed for SiO<sub>2</sub>-F or SiO<sub>2</sub> at variable loadings, indicating that both particles do not hinder gas accessibility to SH-AuPd/SiO<sub>2</sub>, even if gas plastrons form on the SiO<sub>2</sub>-F surface. Additional control experiments revealed no activity toward H<sub>2</sub>O<sub>2</sub> formation or degradation for both SiO<sub>2</sub>-F and SiO<sub>2</sub> (Supplementary Fig. 11b).



**Fig. 3 | Catalytic results with/without plastron. a**  $\text{H}_2\text{O}_2$  concentration for: **a1**, SH-AuPd/SiO<sub>2</sub>, **a2**, SH-AuPd/SiO<sub>2</sub>-F-30  $\mu\text{L}$ , **a3**, SH-AuPd/SiO<sub>2</sub>-F-60  $\mu\text{L}$ , **a4**, SH-AuPd/SiO<sub>2</sub>-F-120  $\mu\text{L}$ , and **a5**, SH-AuPd/SiO<sub>2</sub>-C. Reaction conditions:  $\text{H}_2$ :Air = 4%, 3 bar, 22 °C, 30 min, 2.5 mg catalyst, 5 mL of deionized water, 1500 rpm. **b**  $\text{H}_2\text{O}_2$  concentration for SH-AuPd/SiO<sub>2</sub> and SH-AuPd/SiO<sub>2</sub>-F-60  $\mu\text{L}$  at variable stirring rates. Reaction conditions:  $\text{H}_2$ :Air = 4%, 3 bar, 22 °C, 30 min, 2.5 mg catalyst, 5 mL of deionized water, variable stirring rates. **c**  $\text{H}_2\text{O}_2$  concentration for SH-AuPd/SiO<sub>2</sub> and SH-AuPd/SiO<sub>2</sub>-F-60  $\mu\text{L}$  particles combined with noncatalytic particles. Reaction conditions:  $\text{H}_2$ :Air = 4%, 3 bar, 22 °C, 30 min, using either 2.5 mg of SH-AuPd/SiO<sub>2</sub> or 2.5 mg of SH-AuPd/SiO<sub>2</sub>-F-60  $\mu\text{L}$  combined with various amounts (2.5, 5, 10, 100 mg) of noncatalytic SiO<sub>2</sub>-F or SiO<sub>2</sub> particles. **d**  $\text{H}_2\text{O}_2$  concentration,  $\text{H}_2$

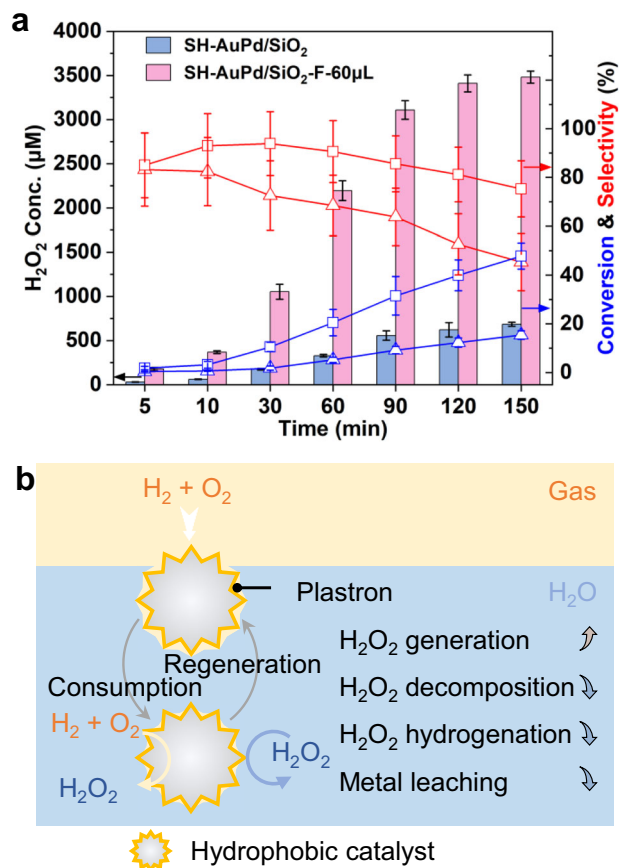
conversion, and  $\text{H}_2\text{O}_2$  selectivity in methanol/water mixtures with schematic illustration of plastron behavior at variable particle wettability. Reaction conditions:  $\text{H}_2$ :Air = 4%, 3 bar, 22 °C, 30 min, 5 mL of methanol/water mixture. **e** Time-evolution of  $\text{H}_2\text{O}_2$  decomposition and degradation (Triangles, decomposition; Squares, degradation). Reaction conditions: 2.5 mg of catalyst, 5 mL of deionized water with 2500  $\mu\text{M}$   $\text{H}_2\text{O}_2$ , 3 bar air (decomposition) or 3 bar  $\text{H}_2$ : $\text{N}_2$  = 4% (degradation), 22 °C, 1500 rpm, 30, 60, and 120 min. **f** Recyclability and reuse of SH-AuPd/SiO<sub>2</sub> and SH-AuPd/SiO<sub>2</sub>-F-60  $\mu\text{L}$  particles. Reaction conditions:  $\text{H}_2$ :Air = 4%, 3 bar, 22 °C, 30 min, 2.5 mg catalyst, 5 mL of deionized water, 1500 rpm. run 4 was carried out after redoping the spent catalyst from run 3 with the same concentration of butanethiol as fresh catalyst. Error bars represent standard deviation.

Collectively, these findings confirm that the observed promotive effect on SH-AuPd/SiO<sub>2</sub>-F-60  $\mu\text{L}$  does not result from halide-induced promotion of AuPd surfaces. Further addition of 10 mg of SiO<sub>2</sub>-F to a dispersion of SH-AuPd/SiO<sub>2</sub>-F-60  $\mu\text{L}$  led to a sharp decrease in  $\text{H}_2\text{O}_2$  concentration from 1050  $\mu\text{M}$  to 350  $\mu\text{M}$ . Increasing the SiO<sub>2</sub>-F amount to 100 mg resulted in a further drop to 44  $\mu\text{M}$ . This decline is attributed to competition for plastron formation between the inert SiO<sub>2</sub>-F particles and the active SH-AuPd/SiO<sub>2</sub>-F-60  $\mu\text{L}$  catalysts, which reduced the availability of gases for the reaction, with an observed decrease in  $\text{H}_2$  conversion consistent with this observation (Supplementary Fig. 11c). Conversely, the catalytic activity remained unaffected when SH-AuPd/SiO<sub>2</sub>-F-60  $\mu\text{L}$  was combined with hydrophilic SiO<sub>2</sub> particles, consistent with the fact that unmodified SiO<sub>2</sub> particles cannot induce plastron formation.

Plastron formation on SH-AuPd/SiO<sub>2</sub>-F-60  $\mu\text{L}$  was discouraged by introducing methanol as a low-surface tension co-solvent (22.5 mN/m) to decrease the contact angle (Fig. 3d & Supplementary Fig. 4f–i). Introducing 20% methanol slightly increased the  $\text{H}_2\text{O}_2$  concentration from 1053  $\mu\text{M}$  to 1100  $\mu\text{M}$ . However, a sharp decline to 550  $\mu\text{M}$  occurred when pure methanol was used. This was attributed to the disruption of plastron formation (Fig. 3d) preventing stable gas layer retention on the particle surface<sup>35</sup>. Interestingly, dropping methanol into a SH-AuPd/SiO<sub>2</sub>-F-60  $\mu\text{L}$  aqueous dispersion led to gas plastron release (Supplementary Fig. 5c2 & Supplementary Movie 2). This was not observed for SH-AuPd/SiO<sub>2</sub> catalyst aqueous dispersion (Supplementary Fig. 5c4). For this catalyst,  $\text{H}_2\text{O}_2$  production increased from 190 to 505  $\mu\text{M}$  as methanol content increased owing to the higher gas solubility and no plastron formation<sup>36</sup>. For comparison, isopropanol with also low surface tension (22.9 mN/m) and lower contact angles

(Supplementary Fig. 4j–m) was also used to check the generality. A similar trend was also observed, as shown in Supplementary Fig. 11d.

We monitored the kinetic profiles of  $\text{H}_2\text{O}_2$  formation over the SH-AuPd/SiO<sub>2</sub> and SH-AuPd/SiO<sub>2</sub>-F-60  $\mu\text{L}$  catalysts (Fig. 4a). The  $\text{H}_2\text{O}_2$  concentration increased almost linearly within 90 min for SH-AuPd/SiO<sub>2</sub>-F-60  $\mu\text{L}$ , indicating sustained catalyst activity and stability throughout the reaction that coincides with plastron formation exhibiting a protective role reducing metal leaching, observed to be four times lower compared to SH-AuPd/SiO<sub>2</sub> without plastron protection (Supplementary Table 2). Correspondingly, the  $\text{H}_2\text{O}_2$  productivity reached 1900  $\text{mol}_{\text{H}_2\text{O}_2} \text{kg}_{\text{metal}}^{-1} \text{h}^{-1}$  for SH-AuPd/SiO<sub>2</sub>-F-60  $\mu\text{L}$ , substantially higher than 300  $\text{mol}_{\text{H}_2\text{O}_2} \text{kg}_{\text{metal}}^{-1} \text{h}^{-1}$  for SH-AuPd/SiO<sub>2</sub>. The gradual decrease in selectivity after 30 min is mainly attributed to the progressive degradation of the generated  $\text{H}_2\text{O}_2$ . This pronounced activity is attributed to gas plastrons on SH-AuPd/SiO<sub>2</sub>-F-60  $\mu\text{L}$ , facilitating  $\text{H}_2$  and  $\text{O}_2$  transfer from the reactor headspace to the catalyst surface, thereby maintaining high local concentration of reactant gases. In addition, at a fixed  $\text{H}_2$  conversion of ~10%, SH-AuPd/SiO<sub>2</sub>-F-60  $\mu\text{L}$  shows a higher selectivity of 94% compared with SH-AuPd/SiO<sub>2</sub> (64%). The presence of the plastron layer limits the direct interaction between  $\text{H}_2\text{O}_2$  and the catalytic active sites, suppressing its subsequent degradation. We also evaluated the extent of  $\text{H}_2\text{O}_2$  (2500  $\mu\text{M}$ ) decomposition and degradation over both catalysts (Fig. 3e). SH-AuPd/SiO<sub>2</sub>-F-60  $\mu\text{L}$  exhibits lower decomposition activity compared to the SH-AuPd/SiO<sub>2</sub> analog. Similarly,  $\text{H}_2\text{O}_2$  degradation rates for SH-AuPd/SiO<sub>2</sub>-F-60  $\mu\text{L}$  were found to be lower than for SH-AuPd/SiO<sub>2</sub>. Collectively, these findings highlight the critical role of gas plastrons in shielding catalytic sites from direct interaction with  $\text{H}_2\text{O}_2$  in solution, thereby suppressing  $\text{H}_2\text{O}$  formation and enhancing catalyst durability and performance<sup>12</sup>.



**Fig. 4 | Kinetic profiles for H<sub>2</sub>O<sub>2</sub> synthesis and proposed reaction process with plastron on hydrophobic catalysts. a** Kinetic profiles for H<sub>2</sub>O<sub>2</sub> direct synthesis for SH-AuPd/SiO<sub>2</sub> and SH-AuPd/SiO<sub>2</sub>-F-60μL particles. Conversion and selectivity (triangle, SH-AuPd/SiO<sub>2</sub>; squares, SH-AuPd/SiO<sub>2</sub>-F-60μL). Reaction conditions: 2.5 mg of catalyst, 5 mL of deionized water, 3 bar H<sub>2</sub>/Air = 4%, 22 °C, 1500 rpm, variable times (5, 10, 30, 60, 90, 120, 150 min). **b** The advantages of the plastron catalysis in the direct synthesis of H<sub>2</sub>O<sub>2</sub>. Error bars represent standard deviation.

The apparent activation energies were obtained from Arrhenius plots based on the initial H<sub>2</sub>O<sub>2</sub> formation rates measured at different temperatures. For the SH-AuPd/SiO<sub>2</sub>-F-60 μL catalyzed plastron system, the H<sub>2</sub>O<sub>2</sub> production rate increased at higher temperatures (Supplementary Fig. 11e) indicating kinetically controlled behavior. In contrast, for SH-AuPd/SiO<sub>2</sub> without plastron, the H<sub>2</sub>O<sub>2</sub> production rate remained nearly constant over the investigated temperature range (Supplementary Fig. 11f), suggesting that the reaction is controlled by gas-liquid mass transfer rather than intrinsic surface kinetics. The corresponding apparent activation energies are presented in Supplementary Fig. 11g. The distinct difference in the activation energies between both systems demonstrates that the plastron configuration effectively reduces gas-liquid mass transfer resistances, thereby enabling intrinsic kinetic control.

The SH-AuPd/SiO<sub>2</sub>-F-60μL formulation was recycled twice. The net H<sub>2</sub>O<sub>2</sub> concentration declined from 1050 μM to 880 μM and further to 700 μM. A similar deactivation trend was observed for the SH-AuPd/SiO<sub>2</sub> catalyst, albeit with significantly lower absolute concentrations of 190, 140, and 120 μM, respectively. This deactivation can be attributed to moderate leaching of bonded thiol groups during washing and drying<sup>37</sup>. This interpretation is supported by an increase in the H<sub>2</sub> conversion for the spent catalysts owing to enhanced gas-metal interactions as a result of reduced thiol group coverage; similarly, the H<sub>2</sub>O<sub>2</sub> selectivity declined, which can be interpreted by the direct interaction between the metal and H<sub>2</sub>O<sub>2</sub> (Supplementary Fig. 11h). This

interpretation is supported by CO-DRIFTS analysis of the spent catalysts pointing out increased CO adsorption after use (Supplementary Fig. 3f). AC-STEM imaging and XPS analysis of the once-used spent catalyst revealed negligible variation in metal nanoparticle size and the chemical state (Supplementary Fig. 2d & Supplementary Fig. 3g, h). Importantly, re-doping the thrice-used SH-AuPd/SiO<sub>2</sub>-F-60 μL catalyst with butanethiol restored the catalytic activity, supporting this explanation (Fig. 3f). The recycled catalyst exhibits no significant differences in surface hydrophobicity, surface zeta potential, or particle size, as shown in Supplementary Figs. 4h, 5e and i.

We benchmarked the catalytic performance of SH-AuPd/SiO<sub>2</sub>-F-60μL against conventional catalysts for direct H<sub>2</sub>O<sub>2</sub> synthesis at mild reaction conditions (**Entries 2-5**; Supplementary Table 3)<sup>38-40</sup>. The H<sub>2</sub>O<sub>2</sub> productivity of SH-AuPd/SiO<sub>2</sub>-F-60μL is 1.5- to 30-fold higher than that of benchmark catalysts after normalizing by the metal content (1900 mol<sub>H<sub>2</sub>O<sub>2</sub></sub> kg<sub>metal</sub><sup>-1</sup> h<sup>-1</sup> vs 66-1300 mol<sub>H<sub>2</sub>O<sub>2</sub></sub> kg<sub>metal</sub><sup>-1</sup> h<sup>-1</sup>). This catalyst also exceeds the performance of catalysts operated under conditions widely utilized for H<sub>2</sub>O<sub>2</sub> direct synthesis (alcohol co-solvent, sub-ambient temperatures and elevated pressures) (**Entries 6-10**; Supplementary Table 3). Notably, under identical conditions, our previously reported AuPd/TiO<sub>2</sub> catalyst produced no detectable H<sub>2</sub>O<sub>2</sub> (Supplementary Fig. 11i)<sup>37</sup>.

Forming a gas layer between a hydrophobic catalyst and water combined with a butanethiol promoter not only significantly enhances gas accessibility but also effectively suppresses metal leaching, a primary cause of catalyst deactivation. Additionally, preferential extraction of water from the catalytic center enhances H<sub>2</sub>O<sub>2</sub> stability against decomposition (Fig. 4b), providing a promising strategy to mitigate over-oxidation in a broad range of reactions. Beyond H<sub>2</sub>O<sub>2</sub> synthesis, we consider that this plastron-enabled platform offers broad applicability to a range of gas-solubility-limited processes including those used in electrochemical and thermally-driven reactions. Overall, this work opens a new avenue for designing robust and selective catalytic systems through interface engineering.

## Methods

### Preparation of hydrophobic particles

Loading of AuPd alloy nanoparticles over SiO<sub>2</sub>: 0.403 mL of HAuCl<sub>4</sub> ([Au] = 12.4 mg/mL), 0.5 mL of PdCl<sub>2</sub> ([Pd] = 10 mg/mL), and 1 mL of PVA (10 mg/mL, 1:1 w/w (Au+Pd): PVA) aqueous solutions were added to 140 mL of water. After stirring for 10 min, a 0.1 mM aqueous solution of NaBH<sub>4</sub> (Au+Pd)/NaBH<sub>4</sub> = 1:10 mol/mol was added to the yellow solution under vigorous magnetic stirring. A black AuPd alloy sol was immediately formed. The colloidal suspension was stirred for 30 min. Then, 4 g of Aerosil® 200 was added to the suspension, and the pH was decreased to 2 by adding concentrated sulfuric acid. After aging for 2 h, the suspension was filtered and washed with 1.5 L of deionized water, and the catalyst was dried at 110 °C (16 h) and calcined at 400 °C under air flow [100 mL(STP)/min] for 3 h at a heating rate of 10 °C/min. The calcined catalyst was subsequently reduced at 400 °C under 5% H<sub>2</sub>/Ar with a flow rate of 100 mL(STP)/min atmosphere for 3 h at a rate of 10 °C/min. The prepared catalyst was denoted as AuPd/SiO<sub>2</sub> (Supplementary Fig. 1a).

Surface modification of AuPd/SiO<sub>2</sub> particles: 0.5 g AuPd/SiO<sub>2</sub> was dispersed into 30 mL of toluene in a 100-mL round-bottom flask, and 15, 30, 45, 60, or 120 μL of PFOTES were added. 2 mg PTSA was added as the catalyst. The mixture was heated to 112 °C in an oil bath for 1.5 h. After the reaction, the dispersion was filtered and washed with ethanol, and the filter cake was dried at 110 °C overnight. The modified catalyst was denoted as AuPd/SiO<sub>2</sub>-F-XμL, where X = 15, 30, 45, 60, or 120. The same protocol was used to graft (non-fluorinated) alkyl chains on AuPd/SiO<sub>2</sub> using 60 μL of OTES instead of PFOTES. The modified catalyst was denoted as AuPd/SiO<sub>2</sub>-C (Supplementary Fig. 1b).

Self-assembled butanethiol monolayers of AuPd/SiO<sub>2</sub> and AuPd/SiO<sub>2</sub>-F-XμL particles: 0.4 g of the as-prepared AuPd/SiO<sub>2</sub> and AuPd/SiO<sub>2</sub>-F-XμL catalysts were dispersed into 20 mL of ethanol and 10 μL of

butanethiol were added. This dispersion was stirred at 22 °C for 4 hours. After the reaction, the dispersion was filtered, washed with ethanol, and the filter cake was dried at 22 °C under vacuum. Both catalysts were denoted as SH-AuPd/SiO<sub>2</sub> and SH-AuPd/SiO<sub>2</sub>-F-X $\mu$ L, respectively (Supplementary Fig. 1c)<sup>41</sup>.

Preparation of SiO<sub>2</sub>-RB and SiO<sub>2</sub>-F-RB particles: A mixture consisting of 0.3 g of SiO<sub>2</sub>, 2  $\mu$ L of APTES, 2 mg of PTSA, and 4 mg of RBITC was dispersed in 20 mL of toluene in a 50-mL round-bottom flask. The reaction was carried out at 112 °C for 1.5 h. After the reaction, the dispersion was filtered, and the resulting solid was washed with ethanol. The collected filter cake was subsequently dried at 110 °C overnight, yielding a pink solid denoted as SiO<sub>2</sub>-RB<sup>42</sup>. The same protocol was adapted to prepare RB-containing particles functionalized with fluorinated chains by including 36  $\mu$ L of PFOTES in the initial dispersion. The sample was denoted as SiO<sub>2</sub>-F-RB.

### Plastron release tests

To investigate plastron formation, catalyst dispersions were prepared in pure water by ultrasonication using a 15-mL pressure-tolerance tube, 2 mg prepared catalysts were dispersed in 2 mL of water using a Sonics VCX-750 ultrasonic processor equipped with a tapered probe operating at 40% amplitude in pulsed mode (1 s on / 1 s off) for 5 s. The dispersion was purged with 4% H<sub>2</sub>/air (3 bar) for 20 min to saturate the aqueous phase, followed by rapid pressure release. The release of plastron was also demonstrated by dropping methanol into the particle aqueous dispersion. The catalyst dispersions were prepared by the aforementioned method. 100  $\mu$ L of methanol was dropped into the catalyst dispersions at ambient pressure. The observation was shown in Supplementary Fig. 5c.

### Plastron stability tests

The light absorbance of particle dispersions was employed as a quantitative descriptor of plastron stability. Specifically, 2.5 mg of each particle sample was dispersed in 5 mL of water, and 3 mL of the resulting suspension was transferred to a UV-Vis cuvette for absorbance measurement at 600 nm. The corresponding absorbance values are presented in Supplementary Fig. 9g, h. Plastron stability was defined as the ratio of the absorbance at 30 min to that at 0 min, expressed as a percentage. The correlation between hydrophobicity and plastron stability is shown in Supplementary Fig. 9f.

### Catalytic tests

H<sub>2</sub> and air were mixed in a cylinder with different ratios. Deionized water and different amounts of the given catalyst were added into a 15 mL pressure-tolerance tube with a magnetic stirrer. Prior to the reaction, the catalyst was dispersed in DI water using a Sonics VCX-750 ultrasonic processor equipped with a tapered probe at 40% amplitude in pulsed mode (1 s on / 1 s off) for 5 s. The tube was purged 3 times before the reaction. The reaction started when the tube was charged with the mixed gas at a given pressure. After the reaction, the catalyst was filtered with a syringe filter. The H<sub>2</sub>O<sub>2</sub> concentration in the recovered liquid samples was analyzed using titanium oxalate method. Briefly, 1.5 mL of a potassium titanyl oxalate sulfuric acid solution was mixed with an equal volume filtrate<sup>43</sup>. Formation of a yellow peroxotitanic acid complex was measured spectrophotometrically at 400 nm to calculate the H<sub>2</sub>O<sub>2</sub> concentration using an external calibration method<sup>44</sup>. Besides, the catalytic activity results with error bars are reported as mean  $\pm$  standard deviation from triplicate experiments.

The catalytic activity of the catalyst is evaluated from the H<sub>2</sub>O<sub>2</sub> concentration after the reaction. The catalytic productivity was calculated as follows

$$P = \frac{n_{\text{H}_2\text{O}_2}}{m_{\text{cat}} \cdot w \cdot t} \quad (1)$$

where P is the H<sub>2</sub>O<sub>2</sub> productivity, n denotes the amount of H<sub>2</sub>O<sub>2</sub> produced (in moles), m is the mass of the catalyst, w represents the metal loading (by weight) in the catalyst, and t is the reaction time.

The H<sub>2</sub> conversion and H<sub>2</sub>O<sub>2</sub> selectivity were determined using gas chromatography (GC). Upon completion of the reaction, the unreacted gases were collected using a syringe and subsequently analyzed by GC using a Varian gas chromatograph (GC) equipped with a CPSIL5CB column (50 m  $\times$  0.33 mm i.d.) and a flame ionization detector (FID).

H<sub>2</sub> conversion (Eq. (2)), H<sub>2</sub>O<sub>2</sub> selectivity (Eq. (3)) and H<sub>2</sub>O<sub>2</sub> production rate (Eq. (4)) were defined as follows:

$$\text{H}_2\text{Conversion} = \frac{\text{mmol}_{\text{H}_2(t_0)} - \text{mmol}_{\text{H}_2(t_1)}}{\text{mmol}_{\text{H}_2(t_0)}} \times 100\% \quad (2)$$

$$\text{H}_2\text{O}_2\text{Selectivity}(\%) = \frac{\text{H}_2\text{O}_2\text{detected}(\text{mmol})}{\text{H}_2\text{consumed}(\text{mmol})} \times 100\% \quad (3)$$

### Apparent activation energy measurements

A total of 2.5 mg of SH-AuPd/SiO<sub>2</sub> or SH-AuPd/SiO<sub>2</sub>-F-60  $\mu$ L particles was dispersed in 5 mL of water via sonication. The reaction conditions were identical to those employed for the direct synthesis of H<sub>2</sub>O<sub>2</sub>. The reaction was conducted at four different temperatures: 273, 293, 313, and 333 K. The concentration of H<sub>2</sub>O<sub>2</sub> was determined at reaction times of 10, 20, and 30 min. The apparent activation energy was derived from Arrhenius plots based on the initial H<sub>2</sub>O<sub>2</sub> formation rates, as presented in Supplementary Fig. 11e–j.

### Characterization of hydrophobic particles

Rhodamine B-modified silica particles were visualized in a confocal microscope using glass well slides. Particles were carefully immobilized onto the concave surface of the wells and 10  $\mu$ L of an aqueous FITC solution (100 ppm) was added. The preparation was cover slipped, and the edges were sealed using clear nail varnish to prevent any possible leakage or evaporation.

The Fourier-transformed infrared spectra (FT-IR) of the different particles were measured from 500 to 4000 cm<sup>−1</sup> on a Bruker Tensor 27 spectrometer equipped with a HgCdTe (MCT) detector and operated with OPUS software. The spectra were measured after 256 scans.

The metal loading in the catalysts was measured by microwave plasma atomic emission spectroscopy (MP-AES) using an Agilent Technologies 4200 instrument using a three-point calibration. Before the analyses, 10 mg of the given catalyst was digested in 1 mL of concentrated *aqua regia* for 16 h in a 10 mL volumetric flask. After digestion, the solution was diluted to 10 mL and filtered using a hydrophilic syringe filter.

The total metal leaching from supported catalysts was quantified through the analysis of post-reaction solutions using an Agilent 7900 ICP-MS equipped with an I-AS auto-sampler using 5-point calibration using certified reference materials from Perkin Elmer and certified internal standards from Agilent. All calibrants were matrix matched.

The morphology and particle size distribution of the catalysts were inspected by high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) and energy-dispersive X-ray spectroscopy (EDXS) analysis in an aberration-corrected ThermoFisher Spectra 200 scanning transmission electron microscope. Samples were prepared using a dry deposition method. Briefly, the powdered catalyst was evenly dispersed onto a carbon-coated copper grid. Prior to loading into the microscope, the grids were plasma-cleaned for 5 min to eliminate surface contaminants and improve sample adhesion. ImageJ software was used to statistically analyze the particle size. For each sample, at least 100 particles were measured.

The surface composition of the catalysts was analyzed by X-ray photoelectron spectroscopy (XPS) on a Kratos Axis Ultra DLD

spectrometer using monochromatic Al K $\alpha$  radiation ( $h\nu = 1486.6$  eV). Samples were mounted using double-sided adhesive tape, and binding energies were referenced to the C(1s) binding energy of adventitious carbon contamination taken at 284.8 eV. The spectra were recorded using a pass energy of 160 eV for survey scans, while 40 eV was employed for detailed regional scans. CasaXPS v2.3.27 using a Shirley background and modified Wagner elemental sensitivity factors as supplied by the instrument manufacturer.

CO-DRIFTS was tested on Bruker Tensor 27 spectrometer and operated with OPUS software. The samples were loaded in a DRIFT Tensor 27 spectrometer and flushed with N<sub>2</sub> for 30 min to record a baseline. The sample was then exposed to 10% CO/N<sub>2</sub> until complete saturation of the Pd sites was achieved. The system was then flushed with pure N<sub>2</sub> until there was no presence of atmospheric CO and then the spectra were recorded.

The thermal profiles of the different particles were measured by thermogravimetric analysis (TGA). The particles (~10 mg in a 100- $\mu$ L alumina crucible) were treated from 30 °C to 900 °C using a heating rate of 10 °C/min under airflow [30 mL(STP)/min].

The contact angle of the particles was measured by the Sessile drop method using a Dataphysics OCA 35 instrument by depositing a small drop (repeated three times per sample) of 5  $\mu$ L of water on pellets formed from powder. The pellets were prepared using at least 200 mg of particle powder and then subjected to compression under a load of 3 tons using a press for 5 min. The shape of the drops was observed and used to measure the contact angle.

The zeta potential of particle dispersions in water was measured using a Malvern Zetasizer Nano ZS zeta potential analyzer at 25 °C. Around 800  $\mu$ L of well-dispersed particle dispersions were transferred into a Malvern Folded Capillary Cell DTS1070. Each measurement was then passed in 100 runs. The repeatability for each dispersion was confirmed after 3 measurements.

RB-modified particles were visualized and scanned on a Zeiss LSM880 Airyscan Fast upright confocal microscope (Zeiss, Jena, Germany) using a 63x/1.4 plan-apochromat oil immersion objective. Appropriate excitation and detection parameters were used for sequential acquisition of red fluorescent signal from RB-modified silica particles (excitation maximum [ex max]: 546 nm; emission maximum [em max]: 567 nm) and green, fluorescent signal from aqueous FITC solution (ex max: 495 nm; em max: 519 nm). Confocal optical sections were taken through individual particles and their surrounding aqueous milieu to visually assess the spatial relationship between the red and green fluorescent signals. Images (16 bit) were presented as 2D or 3D red/green overlays. A line profile tool was used to generate a histogram of red/green, fluorescent intensity values across individual fluorescent particles in selected image fields. The histograms depict the total number of pixels at each fluorescent intensity value across the arbitrarily positioned line (i.e., distance in  $\mu$ m along horizontal axis and pixel intensity value along vertical axis).

The UV-Vis light absorption spectra of particle dispersion in water were measured on an Agilent Technologies Cary 60 UV-Vis monochromator spectrophotometer. The scanning wavelength range of UV-Vis light was set between 200 and 800 nm, whereas the scanning speed was set at medium speed. The baseline was measured by testing deionized water as reference solution.

### Density functional theory (DFT) calculations

The Vienna Ab-initio Simulation Package (VASP) version 6.4 software was employed throughout this work<sup>45,46</sup>. The revised PBE functional from Perdew, Burke, and Ernzerhof by Hammer and Hansen (RPBE) was used to calculate the exchange–correlation energy<sup>47</sup>. Projected-augmented wave (PAW) pseudopotentials were employed to describe the core electrons<sup>48,49</sup>. Dispersion corrections were included through Grimme's dispersion correction scheme, DFT-D3<sup>50</sup>. The plane-wave

kinetic cutoff was set to 550 eV, the electronic energy convergence threshold set to  $1 \times 10^{-6}$  eV, and the ionic convergence to 0.02 eV/Å. Electronic smearing around the Fermi level was described using the order-2 Methfessel-Paxton method in metal bulk and slabs, with a smearing parameter of 0.2 eV and a k-spacing of 0.2 pts.Å<sup>-151</sup>. Metal slabs were separated by 15 vacuum layers along the c-axis, preventing interaction between periodic images (the vacuum layer was appropriately adjusted to accommodate the adsorbent at the surface). Molecules in the gas phase were described by a single gamma-centered k-point in a  $15 \times 15 \times 15$  Å vacuum box, using Gaussian smearing around the Fermi level with a smearing parameter of 0.05 eV. Frequencies were calculated via the finite-difference method implemented in VASP, with electronic energy convergence set to  $1 \times 10^{-9}$  eV and ionic convergence to  $1 \times 10^{-8}$  eV.

The models used to construct the training set for AuPd-alloy global optimization were built from a face-centered-cubic (fcc) (4x4x4) AuPd supercell with a fixed composition of Au<sub>32</sub>Pd<sub>32</sub>. A total of 49 initial cells were created with a lattice parameter calculated by below equation

$$a = \frac{a_{Pd}^{expt} + a_{Au}^{expt}}{2} \times U(\min = 0.95, \max = 1.05) \quad (4)$$

where  $a_{Pd}^{expt} = 3.890$  Å,  $a_{Au}^{expt} = 4.078$  Å represents the experimental lattice constant of each metal<sup>52,53</sup>, and  $U(\min = 0.95, \max = 1.05)$  induces a  $\pm 5\%$  perturbation on the lattice. The resulting cells were relaxed by optimising atomic positions and cell parameters. In addition, a set of optimised structures was selected, and Gaussian noise was injected in atomic positions before undergoing another round of ionic relaxation. The final dataset contained 950 DFT single points.

The atomic environment was described by combining atom-centered symmetry functions (ACSF-G2-2 bodies) with smooth overlap of atomic positions (SOAP, many-bodies) descriptors<sup>54–56</sup>. The hyperparameters for ACSF-G2 were identical for both metal species:  $\eta \in \{0.00, 0.01, 0.07, 0.10, 0.50\}$  [Å<sup>-2</sup>],  $R_s \in \{0.00, 1.50, 3.00, 4.50\}$  [Å], while for SOAP descriptors, the radial degree was set to  $n \in \{1, 2, 3\}$  [∅], and the angular moment of the spherical harmonics used for angular description was set to  $l \in \{1, 2, 3, 4\}$ . Let  $k$  represent the number of elements present in the dataset ( $k = 2$ ), and  $\text{card}(x)$  represent the number of elements in the set  $x$ , the dimension of the fingerprint describing each atom in the system is given by below equation

$$\dim(\mathcal{F}_i) = k \times \text{card}(\eta) \times \text{card}(R_s) + \frac{k(k+1)}{2} \times \frac{\text{card}(n)(\text{card}(n)+1)}{2} \times \text{card}(l) \quad (5)$$

which gives  $\dim(\mathcal{F}_i) = 112$ .

The Behler-Parinello high-dimensional neural network (HDNN) trained had a structure of (112-25-20-1)<sup>54</sup>, i.e., two hidden layers containing 25 and 20 neurons, respectively. The hyperbolic-tangent activation function was used, and the input data was normalized prior to the training via below equation

$$\mathcal{F}_i^{(j)'} = \frac{\mathcal{F}_i^{(j)} - \langle \mathcal{F}^{(j)} \rangle}{\text{std}(\mathcal{F}^{(j)})} \quad (6)$$

setting the mean value of the j-th element of the fingerprint to zero across the whole dataset, and its standard deviation to 1.0. The model was trained for 300 epochs with an exponential learning rate decay starting at  $5e^{-4}$ , decaying by a factor of 0.99 every 5 epochs. The trained model achieves root-mean-squared errors (RMSEs) of 3 meV/atom and 0.094 eV/Å on the test set.

Global optimization of the fcc-AuPd alloy was carried out at constant volume and composition (Au<sub>32</sub>Pd<sub>32</sub>) using a Monte Carlo

**Table 1 | Hyperparameters of the global optimization operators used in the present work**

| Operator (probability) | Hyperparameters                     | Hyperparameter sampling                                                   |
|------------------------|-------------------------------------|---------------------------------------------------------------------------|
| Pair-mutation (40%)    | None                                | None                                                                      |
| Cluster-shuffle (25%)  | Cut-off radius ( $R_{\text{cut}}$ ) | $R_{\text{cut}} = 3.00\text{\AA}$                                         |
| Block-shuffle (25%)    | Cell fraction ( $x$ )               | $x = \max(3, \text{int}(\alpha N))$ , $\alpha \sim \mathcal{U}(0.0, 0.2)$ |
| Full shuffle (10%)     | None                                | None                                                                      |

N represents the number of atoms present in the supercell

selection algorithm. An initial pool of structures is generated by constructing a set of  $\text{Au}_{32}\text{Pd}_{32}$  structures at constant volume obtained during the construction of the training set. At each iteration, a worker selects a structure from its own pool using a Monte Carlo trial. The energy of the candidate,  $E_i$ , is compared to that of the current most stable structure in the pool,  $E_0$ , via Eq. 7

$$p = e^{\frac{-\Delta E}{k_B T}}, \Delta E = E_i - E_0 \quad (7)$$

where the simulation temperature,  $T$  is set to 300 K and  $k_B$  represent Boltzmann's constant ( $8.6173 \times 10^{-5} \text{ eV.K}^{-1}$ ). After determining  $p$ , a value  $\sigma \sim \mathcal{U}(\min=0.0, \max=1.0)$  is sampled. If  $\sigma \leq p$ , the structure is accepted and undergoes a global optimisation (GO) step. Otherwise, a new structure is picked and evaluated until the condition  $\sigma \leq p$  is met. This procedure ensures the algorithm is biased toward selecting low-laying structures. Upon selection, one of the four GO operators is applied to the candidate:

- (1) *Pair-mutation*; two atoms are selected, subject to the constraint that they must have two different chemical elements associated and are swapped,
- (2) *Cluster-shuffle*; An atom is randomly selected in the structure, and all atoms within a given cut-off radius around this atom are shuffled,
- (3) *Block-shuffle*; A fraction of the supercell is randomly selected, and all chemical elements of selected atoms are randomly shuffled,
- (4) *Full shuffle*; Completely reshuffle the supercell.

The different hyperparameters associated with each operator and the values selected in the present work are described in Table 1. Upon application of the selected GO operator, the candidate undergoes local optimization using the trained MLFF, and the resulting energy is compared to the highest energy in the pool. If  $E_i < E_{\text{max}}$ , the structure of highest energy is deleted from the pool and replaced by the new candidate. Otherwise, the candidate is discarded.

### Computer fluid dynamics (CFD) simulations

2D numerical simulation of plastron formation in an air-water system (density ratio:  $1/1000 \text{ kg/m}^3$ ; kinematic viscosity:  $1.148 \times 10^{-5} \text{ m}^2/\text{s}$  for air and  $1 \times 10^{-6} \text{ m}^2/\text{s}$  for water; interfacial tension:  $0.072 \text{ N/m}$ ) was performed using the Volume of Fluid (VOF) method in the open-source CFD software OpenFOAM-v1906. The solver used was *interFoam*, which is designed to track the interface between two incompressible, immiscible fluids without considering heat transfer.

In *interFoam*, the simulation begins by solving a scalar transport equation for the volume fraction of the continuous phase, based on the initial and boundary conditions. From the resulting volume fraction field, the interface curvature was computed and used to evaluate the surface tension force according to Brackbill's Continuum Surface Force (CSF) model<sup>57</sup>. The surface tension force was then included in the momentum equation. Finally, the momentum equation was solved to obtain the velocity and pressure fields. To accurately represent the multiphase nature of the flow, an additional compression term

involving the relative velocity between the phases was added to the volume fraction transport equation.

**Governing equations.** The following equations were solved in this study to simulate gas plastron formation. The mass and momentum conservation equations (Eqs. (8)–(9)) were solved along with the scalar transport equation for the volume fraction as given in Eq. 10

$$\nabla \cdot \mathbf{U} = 0 \quad (8)$$

$$\frac{\partial \rho \mathbf{U}}{\partial t} + \nabla \cdot (\rho \mathbf{U} \mathbf{U}) = -\nabla p^* + \nabla \cdot \boldsymbol{\tau} + \mathbf{f}_b \quad (9)$$

$$\frac{\partial \alpha_{\text{cont}}}{\partial t} + \nabla \cdot (\alpha_{\text{cont}} \mathbf{U}) + \nabla \cdot (\alpha_{\text{cont}}^* (1 - \alpha_{\text{cont}}) \mathbf{U}_r) = 0 \quad (10)$$

In Eq. (5),  $\rho$  is the density of the effective phase,  $\mathbf{U}$  is the velocity vector,  $\boldsymbol{\tau}$  is the shear stress tensor,  $\alpha_{\text{cont}}$  is the volume fraction of the continuous phase,  $\mathbf{U}_r$  is the relative velocity vector, and  $\mathbf{f}_b$  is the body force per unit mass which includes gravity and surface tension forces as given in Eq. 11

$$\mathbf{f}_b = \mathbf{g} \cdot \mathbf{x} \nabla \rho + \mathbf{f} \quad (11)$$

where  $\nabla p^*$  is the modified pressure obtained by subtracting the hydrostatic pressure ( $\rho \mathbf{g} \cdot \mathbf{x}$ ) from the total pressure,  $\mathbf{g}$  is the gravitational acceleration vector and  $\mathbf{x}$  is the position vector, and  $\mathbf{f}$  is the volumetric surface tension force that was computed from the continuum surface force model as given in Eq. 12

$$\mathbf{f} = \sigma \kappa \nabla \alpha_{\text{cont}} \quad (12)$$

where  $\sigma$  is the surface tension and  $\kappa$  is the surface curvature that was calculated by Eq. 13

$$\kappa = -\nabla \cdot \hat{\mathbf{n}} \quad (13)$$

The unit normal vector  $\hat{\mathbf{n}}$  was defined as

$$\hat{\mathbf{n}} = \frac{\nabla \alpha_{\text{cont}}}{|\nabla \alpha_{\text{cont}}|} \quad (14)$$

Near the particle surface,  $\nabla \alpha$  is asymmetric and hence should be modified as given in Eq. 15

$$\hat{\mathbf{n}} = \cos \theta \cdot \hat{\mathbf{n}}_{\text{wall}} + \sin \theta \cdot \mathbf{t} \quad (15)$$

where  $\mathbf{t}$  is the tangential interface direction calculated from the neighboring cell volume fraction values.

The final expression of the curvature ( $\kappa$ ) becomes

$$\kappa = -\nabla \cdot (\cos \theta \cdot \hat{\mathbf{n}}_{\text{wall}} + \sin \theta \cdot \mathbf{t}) \quad (16)$$

where  $\theta$  is the contact angle between the particle surface and the effective phase in the domain, and  $\hat{\mathbf{n}}_{\text{wall}}$  is the unit normal vector at the particle surface.

In Eq. (6), the relative velocity,  $\mathbf{U}_r$  was calculated as given in Eq. 17

$$\mathbf{U}_r = \frac{C_a * |\mathbf{U}| * \nabla \alpha_{\text{cont}}}{|\nabla \alpha_{\text{cont}}|} \quad (17)$$

where  $C_a$  is the artificial compression term supplied by the user.

The density and viscosity of the effective phase was calculated as the summation of individual densities and viscosities of the phases weighted by their respective volume fractions as given in Eqs. 18 and 19

$$\rho = \rho_{\text{cont}} * \alpha_{\text{cont}} + \rho_{\text{disp}} * (1 - \alpha_{\text{cont}}) \quad (18)$$

$$\mu = \mu_{\text{cont}} * \alpha_{\text{cont}} + \mu_{\text{disp}} * (1 - \alpha_{\text{cont}}) \quad (19)$$

The multidimensional universal limiter for explicit solution (MULES) algorithm was used to keep the  $\alpha$  values between 0 and 1. The velocity and pressure fields were obtained by employing the PIMPLE algorithm which is the combination of the PISO (pressure implicit with splitting of operators) and SIMPLE (semi-implicit method for pressure linked equations) to ensure a flexible time stepping along with the improved convergence and stability for multiphase simulations. More details can be found in a previous publication<sup>58</sup>.

**Computational domain and boundary conditions.** The computational domain consisted of a rectangular microchannel (300 \* 600 \* 10  $\mu\text{m}$ ) with approximately 43,000 cells resulting in a hexahedral grid size of 2  $\mu\text{m}$ . A 100- $\mu\text{m}$  cylindrical hole was created at 300  $\mu\text{m}$  height beside which a bubble of 30  $\mu\text{m}$  diameter was placed. The computational domain with the boundaries and the mesh is given in Supplementary Fig. 6a, b. The boundary condition for the volume fraction field was set to zeroGradient at the channel walls, inletOutlet at the top and constant AlphaContactAngle at the particle surface. For the velocity field, noSlip boundary condition was set at the channel walls and the particle surface and pressureInletOutletVelocity boundary condition was set at the top. For the pressure field, a fixedFluxPressure boundary condition was set at the channel walls and particle surface, and a totalPressure boundary condition was set for the top. More details about these boundary conditions can be found in a previous study<sup>45</sup>.

The Courant number (Co) was used as descriptor to reach stable solution. It is defined as the ratio of the fluid velocity to the numerical speed with which the fluid crosses one cell in one time step as follows:

$$\text{Co} = \frac{|\mathbf{U}| \Delta t}{\Delta x} \quad (20)$$

where  $\Delta x$  and  $\Delta t$  are the time and position step, respectively.

An adjustable time stepping method was adopted to automatically modify the time step for faster convergence. Due to the small grid size, a time stepping of  $10^{-8}$  s was chosen (Courant number  $\sim 0.2$ ) to reach a stable solution.

## Data availability

All data are available in the main text and supplementary materials. Source data are provided with this paper and in Figshare with <https://figshare.com/s/306b9b511baac75502f>. Data are available from the corresponding authors upon request. Source data are provided with this paper.

## References

- Campos-Martin, J. M., Blanco-Brieva, G. & Fierro, J. L. Hydrogen peroxide synthesis: an outlook beyond the anthraquinone process. *Angew. Chem. Int. Ed.* **45**, 6962–6984 (2006).
- Centi G., Perathoner S., Abate S. Direct synthesis of hydrogen peroxide: Recent advances. *Modern Heterogeneous Oxidation Catalysis: Design, Reactions and Characterization*, 253–287 (2009).
- Goyal, R., Singh, O., Agrawal, A., Samanta, C. & Sarkar, B. Advantages and limitations of catalytic oxidation with hydrogen peroxide: From bulk chemicals to lab scale process. *Catal. Rev.* **64**, 229–285 (2022).
- Yu, S. et al. High activity and selectivity of single palladium atom for oxygen hydrogenation to  $\text{H}_2\text{O}_2$ . *Nat. Commun.* **13**, 4737 (2022).
- Freakley, S. J. et al. Palladium-tin catalysts for the direct synthesis of  $\text{H}_2\text{O}_2$  with high selectivity. *Science* **351**, 965–968 (2016).
- Wilson, N. M. et al. Direct synthesis of  $\text{H}_2\text{O}_2$  on AgPt octahedra: The importance of Ag–Pt coordination for high  $\text{H}_2\text{O}_2$  selectivity. *ACS Catal.* **8**, 2880–2889 (2018).
- Moreno, T., García-Serna, J. & Cocero, M. J. Direct synthesis of hydrogen peroxide in methanol and water using  $\text{scCO}_2$  and  $\text{N}_2$  as diluents. *Green. Chem.* **12**, 282–289 (2010).
- Seo, M.-G., Kim, H. J., Han, S. S. & Lee, K.-Y. Direct synthesis of hydrogen peroxide from hydrogen and oxygen using tailored Pd nanocatalysts: A review of recent findings. *Catal. Surv. Asia* **21**, 1–12 (2017).
- Flaherty D. W. Direct synthesis of  $\text{H}_2\text{O}_2$  from  $\text{H}_2$  and  $\text{O}_2$  on Pd catalysts: current understanding, outstanding questions, and research needs). ACS Publications (2018).
- Wilson, N. M. & Flaherty, D. W. Mechanism for the direct synthesis of  $\text{H}_2\text{O}_2$  on Pd clusters: heterolytic reaction pathways at the liquid–solid interface. *J. Am. Chem. Soc.* **138**, 574–586 (2016).
- Schröder, V. & Holtappels, K. Explosion characteristics of hydrogen-air and hydrogen-oxygen mixtures at elevated pressures. In *Proc. 1st International Conference on Hydrogen Safety, Pisa, Italy* (2005).
- Yi, K. et al. High  $\text{H}_2\text{O}_2$  production in membrane-free electrolyzer via anodic bubble shielding towards robust rural disinfection. *Nat. Commun.* **16**, 1893 (2025).
- Khan, S., Hwang, J., Horn, Y.-S. & Varanasi, K. K. Catalyst-proximal plastrons enhance activity and selectivity of carbon dioxide electroreduction. *Cell Rep. Phys. Sci.* **2**, 100318–100332 (2021).
- Edwards, J. K. et al. Switching off hydrogen peroxide hydrogenation in the direct synthesis process. *Science* **323**, 1037–1041 (2009).
- Williams, C. et al. Selective oxidation of methane to methanol using supported AuPd catalysts prepared by stabilizer-free sol-immobilization. *ACS Catal.* **8**, 2567–2576 (2018).
- Vericat, C., Vela, M., Benitez, G., Carro, P. & Salvarezza, R. Self-assembled monolayers of thiols and dithiols on gold: New challenges for a well-known system. *Chem. Soc. Rev.* **39**, 1805–1834 (2010).
- Schoenbaum, C. A., Schwartz, D. K. & Medlin, J. W. Controlling the surface environment of heterogeneous catalysts using self-assembled monolayers. *Acc. Chem. Res.* **47**, 1438–1445 (2014).
- F. de L. e Freitas, L. et al. Tunable catalytic performance of palladium nanoparticles for  $\text{H}_2\text{O}_2$  direct synthesis via surface-bound ligands. *ACS Catal.* **10**, 5202–5207 (2020).
- Azcárate, J. C., Fonticelli, M. H. & Zelaya, E. Radiation damage mechanisms of monolayer-protected nanoparticles via TEM analysis. *J. Phys. Chem. C* **121**, 26108–26116 (2017).
- Pawelec, B. et al. AuPd alloy formation in Au-Pd/ $\text{Al}_2\text{O}_3$  catalysts and its role on aromatics hydrogenation. *Appl. Surf. Sci.* **242**, 380–391 (2005).
- Shahabadi, S. M. S., Rabiee, H., Seyedi, S. M., Mokhtare, A. & Brant, J. A. Superhydrophobic dual layer functionalized titanium dioxide/polyvinylidene fluoride-co-hexafluoropropylene ( $\text{TiO}_2/\text{PH}$ ) nanofibrous membrane for high flux membrane distillation. *J. Membr. Sci.* **537**, 140–150 (2017).
- Wang, K. et al. Amphiphilic Janus particles for aerobic alcohol oxidation in oil foams. *ACS Catal.* **14**, 11545–11553 (2024).
- Vilcnik, A. et al. Structural properties and antibacterial effects of hydrophobic and oleophobic sol–gel coatings for cotton fabrics. *Langmuir* **25**, 5869–5880 (2009).

24. Ding, S.-J. et al. XPS characterization of the interface between low dielectric constant amorphous fluoropolymer film and evaporation-deposited aluminum. *Appl. Surf. Sci.* **178**, 140–148 (2001).
25. Qiao, B., Wang, T.-J., Gao, H. & Jin, Y. High density silanization of nano-silica particles using  $\gamma$ -aminopropyltriethoxysilane (APTES). *Appl. Surf. Sci.* **351**, 646–654 (2015).
26. Carter, J. H. et al. Synergy and anti-synergy between palladium and gold in nanoparticles dispersed on a reducible support. *ACS Catal.* **6**, 6623–6633 (2016).
27. Gong, X. et al. Enhanced catalyst selectivity in the direct synthesis of  $\text{H}_2\text{O}_2$  through Pt incorporation into  $\text{TiO}_2$  supported AuPd catalysts. *Catal. Sci. Technol.* **10**, 4635–4644 (2020).
28. Barnes, A., Lewis, R. J., Morgan, D. J., Davies, T. E. & Hutchings, G. J. Enhancing catalytic performance of AuPd catalysts towards the direct synthesis of  $\text{H}_2\text{O}_2$  through incorporation of base metals. *Catal. Sci. Technol.* **12**, 1986–1995 (2022).
29. Plauck, A., Strangland, E. E., Dumesic, J. A. & Mavrikakis, M. Active sites and mechanisms for  $\text{H}_2\text{O}_2$  decomposition over Pd catalysts. *Proc. Natl. Acad. Sci. USA* **113**, E1973–E1982 (2016).
30. Hayes, A. J., Gibson, M. A., Shu, C. & Melrose, J. Confocal microscopy demonstrates association of LTBP-2 in fibrillin-1 microfibrils and colocalisation with perlecan in the disc cell pericellular matrix. *Tissue Cell* **46**, 185–197 (2014).
31. Hirt, C. W. & Nichols, B. D. Volume of fluid (VOF) method for the dynamics of free boundaries. *J. Comput. Phys.* **39**, 201–225 (1981).
32. Xiao, H., Duan, Q. & Sun, J. Premixed flame propagation in hydrogen explosions. *Renew. Sustain. Energy Rev.* **81**, 1988–2001 (2018).
33. Pospelova, T. & Kobozev, N. Palladium catalyzed synthesis of hydrogen peroxide from the elements. 2. The active centers of palladium in the synthesis of  $\text{H}_2\text{O}_2$ . *Zh.Fizicheskoi Khimii* **35**, 535–542 (1961).
34. Pospelova, T. & Kobozev, N. Catalytic synthesis of hydrogen peroxide from the elements on palladium. 3. The active centers of hydrogen peroxide decomposition on palladium. *Zh. Fizicheskoi Khimii* **35**, 1192–1197 (1961).
35. Vazquez, G., Alvarez, E. & Navaza, J. M. Surface tension of alcohol water+ water from 20 to 50. degree. C. *J. Chem. Eng. Data* **40**, 611–614 (1995).
36. Lawrence Clever, H., Battino, R., Miyamoto, H., Yampolski, Y. & Young, C. L. IUPAC-NIST solubility data series. 103. Oxygen and ozone in water, aqueous solutions, and organic liquids (supplement to solubility data series volume 7). *J. Phys. Chem. Refer. Data* **43**, (2014).
37. Marshall, S. T. et al. Controlled selectivity for palladium catalysts using self-assembled monolayers. *Nat. Mater.* **9**, 853–858 (2010).
38. Santos, A. et al. Direct synthesis of hydrogen peroxide over Au–Pd supported nanoparticles under ambient conditions. *Ind. Eng. Chem. Res.* **58**, 12623–12631 (2019).
39. Crole, D. A., Freakley, S. J., Edwards, J. K. & Hutchings, G. J. Direct synthesis of hydrogen peroxide in water at ambient temperature. *Proc. R. Soc. A: Math., Phys. Eng. Sci.* **472**, 20160156 (2016).
40. Sandri, F. et al. The role of acetonitrile in the direct synthesis of hydrogen peroxide over palladium supported by ion-exchange resins. *Catal. Commun.* **174**, 106585 (2023).
41. Love, J. C., Estroff, L. A., Kriebel, J. K., Nuzzo, R. G. & Whitesides, G. M. Self-assembled monolayers of thiolates on metals as a form of nanotechnology. *Chem. Rev.* **105**, 1103–1170 (2005).
42. Nedelčev, T., Račko, D. & Krupa, I. Preparation and characterization of a new derivative of rhodamine B with an alkoxy silane moiety. *Dyes Pigments* **76**, 550–556 (2008).
43. Sandri, F., Danieli, M., Zecca, M. & Centomo, P. Comparing catalysts of the direct synthesis of hydrogen peroxide in organic solvent: is the measure of the product an issue? *ChemCatChem* **13**, 2653–2663 (2021).
44. Falke, S. & Betzel, C. Dynamic Light Scattering (DLS) Principles, perspectives, applications to biological samples. *Radiation in Bioanalysis: Spectroscopic Techniques and Theoretical Methods*, 173–193 (2019).
45. Kresse, G. & Hafner, J. Ab initio molecular dynamics for liquid metals. *Phys. Rev. B* **47**, 558–561 (1993).
46. Kresse, G. & Furthmüller, J. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Phys. Rev. B* **54**, 11169–11186 (1996).
47. Hammer, B., Hansen, L. B. & Nørskov, J. K. Improved adsorption energetics within density-functional theory using revised Perdew–Burke–Ernzerhof functionals. *Phys. Rev. B* **59**, 7413–7421 (1999).
48. Kresse, G. & Joubert, D. From ultrasoft pseudopotentials to the projector augmented-wave method. *Phys. Rev. B* **59**, 1758–1775 (1999).
49. Blöchl, P. E. Projector augmented-wave method. *Phys. Rev. B* **50**, 17953–17979 (1994).
50. Grimme, S., Antony, J., Ehrlich, S. & Krieg, H. A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H–Pu. *J. Chem. Phys.* **132**, 154104–154123 (2010).
51. Methfessel, M. & Paxton, A. T. High-precision sampling for Brillouin-zone integration in metals. *Phys. Rev. B* **40**, 3616–3621 (1989).
52. Pati, S., Avtar Jat, R., Mukerjee, S. K. & Parida, S. C. X-ray diffraction study of thermal parameters of Pd, Pd–Ag and Pd–Ag–Cu alloys as hydrogen purification membrane materials. *Phys. B* **484**, 42–47 (2016).
53. Graf, M., Ngô, B.-N. D., Weissmüller, J. & Markmann, J. X-ray studies of nanoporous gold: Powder diffraction by large crystals with small holes. *Phys. Rev. Mat.* **1**, 076003–076016 (2017).
54. Behler, J. & Parrinello, M. Generalized neural-network representation of high-dimensional potential-energy surfaces. *Phys. Rev. Lett.* **98**, 146401–146405 (2007).
55. Bartók, A. P., Kondor, R. & Csányi, G. On representing chemical environments. *Phys. Rev. B* **87**, 184115–184131 (2013).
56. Behler, J. Atom-centered symmetry functions for constructing high-dimensional neural network potentials. *J. Chem. Phys.* **134**, 074106–074119 (2001).
57. Brackbill, J. U., Kothe, D. B. & Zemach, C. A continuum method for modeling surface tension. *J. Comput. Phys.* **100**, 335–354 (1992).
58. Sinha, V., Vincent, T. & Pera-Titus, M. Modeling dispersed phase holdup and conditions of flooding in a pulsed disc and doughnut solvent extraction column. *Chem. Eng. J.* **505**, 159440 (2025).

## Acknowledgements

R.J.L. and G.J.H. gratefully acknowledge Cardiff University and the Max Planck Centre on the Fundamentals of Heterogeneous Catalysis (FUN-CAT) for financial support. The authors would like to thank the CCI-Electron Microscopy Facility which has been funded in part by the European Regional Development Fund through the Welsh Government, and The Wolfson Foundation. The authors acknowledge the staff of the Cardiff Catalysis Institute for their technical support and assistance with AC-STEM measurements.

## Author contributions

K.W., M.P.T. conceived the study; K.W. performed the experiments, data analysis, and figure drawing; VS conducted the 2-D numerical simulations; A.J.H. ran the confocal microscopy tests; A.B. and A.R. performed the density functional theory calculations; D.J.M. conducted X-ray photoelectron spectroscopy experiments; R.J.L. and G.J.H. provided experimental advice, commented on and amended the manuscript, and M.P.T. conceived the project. All the authors contributed to writing and revising the manuscript.

## Funding

K.W., V.S., and M.P.T. disclose support for the research of this work from ERC grants Michelangelo (contract number #771586) and Nemesys (contract number # 101138920). This work was granted access to the HPC resources of ARCCA. DJM discloses support for publication of this work from EPSRC National Facility for XPS ("HarwellXPS" EP/Y023587/1, EP/Y023609/1, EP/Y023536/1, EP/Y023552/1 and EP/Y023544/1).

## Competing interests

The authors declare no competing interests.

## Additional information

**Supplementary information** The online version contains supplementary material available at <https://doi.org/10.1038/s41467-026-76198-9>.

**Correspondence** and requests for materials should be addressed to Marc Pera-Titus.

**Peer review information** *Nature Communications* thanks Shun Mao and the other, anonymous, reviewer(s) for their contribution to the peer review of this work. A peer review file is available.

**Reprints and permissions information** is available at <http://www.nature.com/reprints>

**Publisher's note** Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

**Open Access** This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons licence, and indicate if changes were made. The images or other third party material in this article are included in the article's Creative Commons licence, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons licence and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this licence, visit <http://creativecommons.org/licenses/by/4.0/>.

© The Author(s) 2026