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# Self-healing redox chemistry in Cu–TiO<sub>2</sub> photocatalysts for enhanced hydrogen production

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Hydrogen production from sunlight and abundant feedstock is central to a sustainable energy future, yet most efficient photocatalysts rely on costly noble metals. Here we report a scalable one-pot synthesis of CuO<sub>x</sub>–TiO<sub>2</sub> photocatalysts that achieve a methanol-assisted hydrogen evolution rate of 30.6 mmol g<sup>-1</sup> h<sup>-1</sup>, among the highest reported for Cu-based systems. The optimized 12% CuO<sub>x</sub>–TiO<sub>2</sub> maintains >90% activity retention over 50 h and performs reproducibly at the gram scale, underscoring its industrial potential. Spectroscopic and computational analyses uncover a dynamic CuO ⇌ Cu<sub>2</sub>O ⇌ Cu<sup>0</sup> cycle and a previously unrecognized corrosion–healing redox loop, in which transient Cu(OH)<sub>2</sub> is continuously reduced back to Cu<sub>2</sub>O by methanol-derived intermediates. This self-healing mechanism stabilizes the active Cu<sub>2</sub>O phase, suppresses deactivation, and sustains long-term performance. Density functional theory reveals near-optimal hydrogen adsorption free energy (ΔG<sub>H\*</sub> = -0.06 eV) on Cu–TiO<sub>2</sub>(101), comparable to Pt(111), confirming copper's potential as a low-cost alternative to noble metals. These findings establish redox self-healing catalysis as a powerful design principle for durable, scalable, and earth-abundant photocatalysts for solar hydrogen production.

## 1. Introduction

The transition to clean and renewable energy systems has placed hydrogen (H<sub>2</sub>) at the forefront as a promising energy carrier due to its high energy density and carbon-free combustion.<sup>1–5</sup> However, current hydrogen production is dominated by methanol steam reforming (MSR), which is

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### New concepts

This work introduces a simple one-pot synthesis of CuO<sub>x</sub>–TiO<sub>2</sub> photocatalysts with precise control over Cu<sup>0</sup>, Cu<sup>+</sup>, and Cu<sup>2+</sup> redox states. Beyond achieving a record methanol-assisted hydrogen evolution rate (>30 mmol g<sup>-1</sup> h<sup>-1</sup>) with excellent stability and scalability, we reveal a novel corrosion–healing redox loop at the CuO<sub>x</sub>–TiO<sub>2</sub> interface. In this process, transient Cu(OH)<sub>2</sub> formed under illumination is dynamically reduced back to Cu<sub>2</sub>O by methanol-derived intermediates, sustaining the active Cu<sub>2</sub>O phase and preventing irreversible deactivation. This self-healing cycle, coupled with an S-scheme charge transfer pathway, provides a new mechanistic design principle for robust and scalable photocatalysts, bridging fundamental redox chemistry with real-world hydrogen production technologies.

energy-intensive (for example, 200–350 °C and 20–50 bar), carbon-emitting, and of high cost.<sup>6–8</sup> Photocatalytic reforming of methanol–water mixtures offers an attractive alternative for solar-to-fuel (STF) conversion: methanol contains 12.5 wt% hydrogen and water contains 11.1 wt% hydrogen, and their combination enables hydrogen release under ambient conditions with lower thermodynamic barriers than for water splitting alone.<sup>9–19</sup> However, the deployment of photocatalytic hydrogen evolution remains constrained by the reliance on noble-metal cocatalysts such as Pt, Ru, or Rh, whose scarcity and cost limit scalability. Replacing these with earth-abundant metals requires not only high activity but also a fundamental understanding of how dopant chemistry governs interfacial charge transfer, stability, and durability under operating conditions.<sup>20–31</sup>

Among earth-abundant candidates (Ni, Fe, Zn, and Co), copper-doped TiO<sub>2</sub> (Cu–TiO<sub>2</sub>) is particularly promising due to the multiple accessible oxidation states (Cu<sup>0</sup>, Cu<sup>+</sup>, and Cu<sup>2+</sup>), which can act as electron mediators, hole scavengers, or active sites depending on the local environment.<sup>23,26,32,33</sup> Under illumination, these oxidation states coexist dynamically at CuO<sub>x</sub>–TiO<sub>2</sub> interfaces, generating heterojunctions that promote charge separation and oxygen vacancy (Ov) formation.<sup>8,34–44</sup>



Such a dynamic system leads to an ambiguous relationship among microscopic structure, active sites, and catalytic performance.<sup>18,45,46</sup> Previous approaches, including single-atom Cu doping (CuSAs-TiO<sub>2</sub>), ternary heterostructures (Cu/TiO<sub>2</sub>/SrTiO<sub>3</sub>), and rare-earth co-doping (Pr-CuSA-TiO<sub>2</sub>), have shown performance improvements but suffer from complex synthesis, poor reproducibility, and limited scalability.<sup>36,42,47–57</sup>

Despite considerable research, several key challenges remain unresolved: the upper limit of stable Cu incorporation in TiO<sub>2</sub>, the precise location of Cu species in the lattice *versus* surface, and the role of reversible Cu redox cycling in sustaining long-term activity. Excessive doping often leads to agglomeration of metallic Cu, collapse of mesoporosity, and accelerated recombination, while under-doping fails to exploit the redox flexibility of Cu.<sup>55,58</sup> The mechanistic understanding also remains elusive: while Cu<sub>2</sub>O is frequently suggested as the active hydrogen evolution site, the competing contributions of CuO and Cu<sup>0</sup>, and their interplay with surface hydroxyl groups (OH<sup>-</sup>) and oxygen vacancies (Ov), are not clearly established.<sup>23,38,49,59–64</sup> Consequently, there is a critical need for a synthetic strategy that can precisely tune Cu<sup>0</sup>/Cu<sup>+</sup>/Cu<sup>2+</sup> ratios and simultaneously reveal how their interconversion influences catalytic performance and durability.

Here, we report a scalable one-pot hydrothermal synthesis of CuO<sub>x</sub>-TiO<sub>2</sub> photocatalysts that directly addresses these challenges. By regulating Cu incorporation, we achieve a balanced synergy of Cu redox states at an optimal loading of 12 wt%, yielding a record methanol-assisted hydrogen evolution rate of 30.6 mmol g<sup>-1</sup> h<sup>-1</sup>, nearly an order of magnitude higher than that of pristine TiO<sub>2</sub>.<sup>65</sup> Through *operando* spectroscopic analysis, we uncover a previously unrecognized corrosion-healing redox loop, in which transient Cu(OH)<sub>2</sub> formed during illumination is dynamically reduced back to Cu<sub>2</sub>O by methanol-derived intermediates (Fig. 7).<sup>39</sup> This self-healing cycle stabilizes Cu<sub>2</sub>O active sites, suppresses irreversible deactivation, and underpins the long-term durability of the catalyst.<sup>39</sup> Together with an S-scheme heterojunction charge-transfer pathway, where metallic Cu acts as an electron sink, and DFT

confirmation of near-Pt hydrogen adsorption energetics ( $\Delta G_{\text{H}^*} \approx -0.06$  eV on Cu-TiO<sub>2</sub>(101)), our results establish not only the scalability of Cu-based photocatalysts but also introduce redox self-healing catalysis as a new design principle for durable, earth-abundant hydrogen evolution systems.<sup>38</sup>

## 2. Results and discussion

### 2.1. Scalable one-pot synthesis enables precise control of Cu redox states

Developing Cu-based photocatalysts that are both active and scalable requires synthetic control over the interplay of Cu<sup>0</sup>, Cu<sup>+</sup>, and Cu<sup>2+</sup> species, which govern charge separation and interfacial dynamics. Conventional multi-step or post-treatment strategies often suffer from poor reproducibility, phase segregation, and uncontrolled reduction, leading to inconsistent catalytic performance.<sup>22,66,67</sup> To overcome these limitations, we designed a one-pot hydrothermal route in which Ti(OBu)<sub>4</sub> and Cu(NO<sub>3</sub>)<sub>2</sub> precursors undergo co-condensation in the presence of HF, enabling direct incorporation of Cu species into the TiO<sub>2</sub> lattice (Fig. 1). This method not only preserves the anatase phase up to 14 wt% Cu loading but also stabilizes a balanced mixture of CuO, Cu<sub>2</sub>O, and metallic Cu at the catalyst surface.

The optimized 12% Cu-TiO<sub>2</sub> material exhibits a record HER rate of 30.6 mmol g<sup>-1</sup> h<sup>-1</sup> in methanol photo reforming (MPR), an order of magnitude higher than pristine TiO<sub>2</sub>. Importantly, the synthesis was reproduced at the gram scale (6 g per batch) with a negligible variation in performance, establishing scalability and reproducibility that are rarely demonstrated in Cu-TiO<sub>2</sub> systems. Beyond activity, this material displays exceptional durability, maintaining >90% of its HER performance over 50 h of continuous operation, a stability that correlates with the dynamic restructuring of Cu redox states.<sup>66</sup>

Structural and spectroscopic analyses reveal that this synthetic approach enables a self-regulating CuO  $\leftrightarrow$  Cu<sub>2</sub>O  $\leftrightarrow$  Cu<sup>0</sup> cycle, where excess Cu after the doping limit segregates into surface heterojunctions without collapsing the anatase lattice.

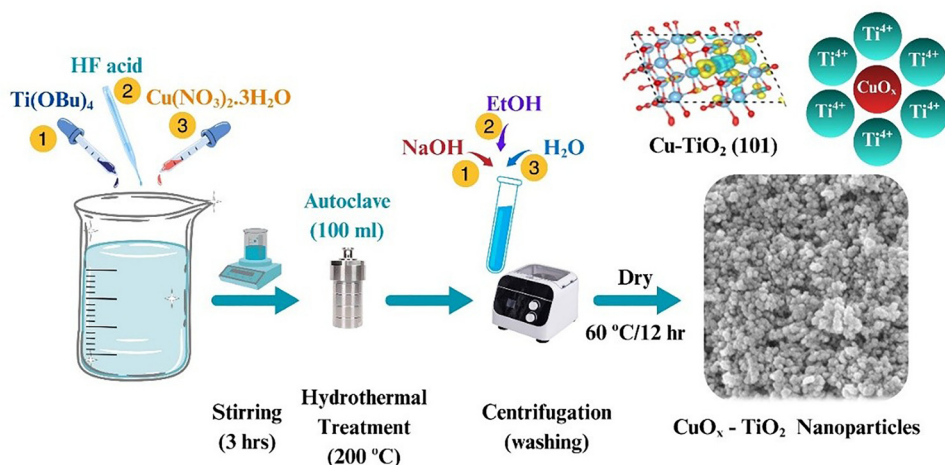


Fig. 1 Schematic illustration of the one-pot hydrothermal synthesis of the CuO<sub>x</sub>-TiO<sub>2</sub> photocatalyst.





reached, reduced  $\text{Cu}_2\text{O}$  and  $\text{Cu}^0$  species begin to deposit, agglomerate, and form clusters at the surface, leading to pore clogging—a trend consistent with XRD results.<sup>80,81</sup> The  $\text{N}_2$  adsorption isotherm follows a Type IV profile with an H3 hysteresis loop, indicating the presence of mesoporous structures.<sup>82</sup> Additionally, the Barrett-Joyner-Halenda (BJH)  $\text{N}_2$  adsorption isotherm confirms the pore size distribution and the catalyst's porous nature (Fig. S4d–f). However, a slight variation in the surface area between 11%, 12%, and 13% Cu– $\text{TiO}_2$  indicates that the surface area alone may not be the primary factor responsible for the enhanced photocatalytic activity.

Furthermore, when the 12% Cu– $\text{TiO}_2$  catalyst is dispersed in water, hydration, protonation, and deprotonation processes lead to surface charging, causing the nanoparticles to behave like zwitterions. This is measured as a zeta potential, which depends on the suspension's isoelectric point (IEP).<sup>83</sup> Compared to the pristine  $\text{TiO}_2$  (+3.4 mV at pH 5.09), 12% Cu– $\text{TiO}_2$  exhibits significantly negative zeta potential  $-28.9$  mV, closely matching that of commercial CuO ( $-26.3$  mV) (Fig. 2f). This supports the presence of a hydroxylated Cu layer (Cu–OH) at the surface, which enhances charge accumulation and transfer, thereby promoting hydrogen production.<sup>84</sup> The higher surface charge also prevents particle aggregation, improving stability in water. This stability is attributed to charge imbalance caused by the substitution of  $\text{Ti}^{4+}$  atoms with  $\text{Cu}^{2+}$  in the  $\text{TiO}_2$  lattice.<sup>71</sup>

The morphology and chemical composition of the best-performing 12% Cu– $\text{TiO}_2$  and pristine  $\text{TiO}_2$  were further analyzed using scanning electron microscopy (SEM) and energy-dispersive X-ray spectrometry (EDS) (Fig. S5–S7). The uniform morphology consists of spherical-shaped particles aggregated into lamellar, cluster-like structures with clear boundaries, with an average size of 41 nm (Fig. 3a). High-angle annular dark-

field scanning transmission electron microscopy (HAADF-EDS) mapping confirms the uniform dispersion of  $\text{CuO}_x$  over  $\text{TiO}_2$  (Fig. S7a–f). High-resolution transmission electron microscopy (HRTEM) analysis reveals lattice spacing values of 0.34 nm and 0.36 nm, corresponding to Cu(220) and anatase  $\text{TiO}_2$ (101), respectively, matching well with the corresponding diffraction results (Fig. 3c).<sup>85–88</sup> Line scan analysis further demonstrates the homogeneous distribution of  $\text{CuO}_x$  within the nanoparticles (Fig. 3b). The coexistence of  $\text{Cu}^{1+}$  with  $\text{Cu}^0$  at  $\text{TiO}_2$  crystal lattice interfaces cannot be ignored, which is consistent with XRD results, confirming the formation of  $\text{CuO}_x$ – $\text{TiO}_2$  heterostructures.

These results indicate that 12%  $\text{CuO}_x$ – $\text{TiO}_2$  doping comprises  $\text{Cu}^{2+}/\text{Cu}^+/\text{Cu}^0$  species, forming multiple heterojunctions that contribute to the high photocatalytic HER rate.<sup>89,90</sup> Therefore, developing a synthetic strategy to control the ratio of  $\text{Cu}^0/\text{Cu}^+/\text{Cu}^{2+}$  redox species by adjusting % Cu doping is crucial for optimizing photocatalytic performance.<sup>21,91</sup>

### 2.3. Optical properties of the $\text{CuO}_x$ – $\text{TiO}_2$ photocatalyst

UV-visible absorption spectroscopy (UV-Vis) reveals a redshift in the light absorption edge of  $\text{CuO}_x$ – $\text{TiO}_2$ , shifting from 447 nm to the visible region at 554 nm. This corresponds to a bandgap reduction from 3.0 eV for anatase  $\text{TiO}_2$  to 2.5 eV for 12% Cu– $\text{TiO}_2$ , as calculated using the Kubelka–Munk function. (Fig. 4a, b, and Table S2). The enhanced absorption in the visible region arises from introduced intermediate energy levels (Cu 3d states) within the band gap, which reduces the effective band gap, allowing absorption of visible light (400–800 nm) (Fig. 4a).<sup>65</sup> Cu doping into  $\text{TiO}_2$  induces crystal lattice distortion and introduces defect states, creating additional energy levels near the conduction band that facilitate charge transfer.<sup>22,92</sup> Photoluminescence (PL) spectra exhibit a significant reduction

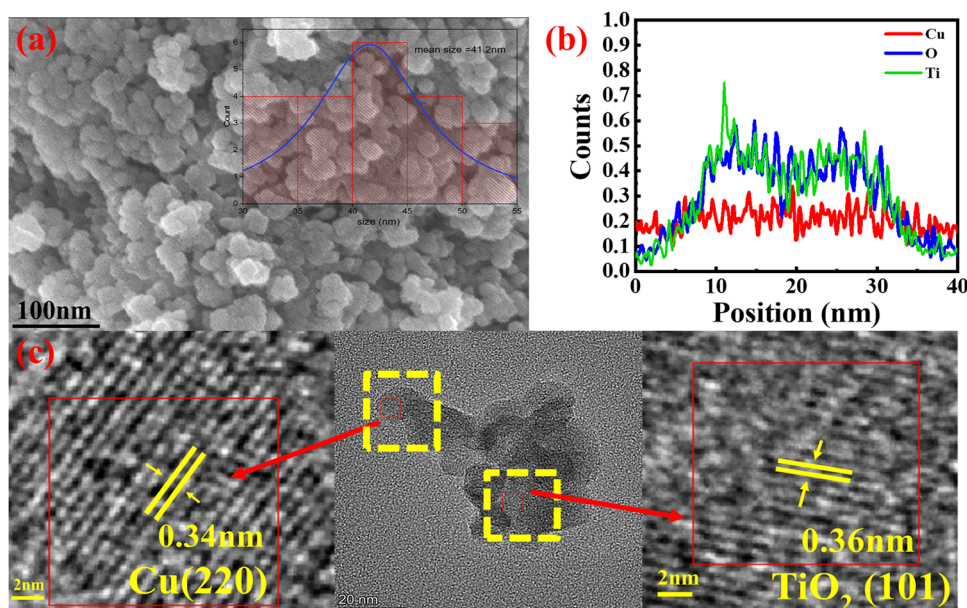


Fig. 3 Characterization images of 12% Cu– $\text{TiO}_2$ . (a) SEM image. (b) EDS line scan of Cu, Ti, and O (c) HRTEM 12% Cu– $\text{TiO}_2$ .



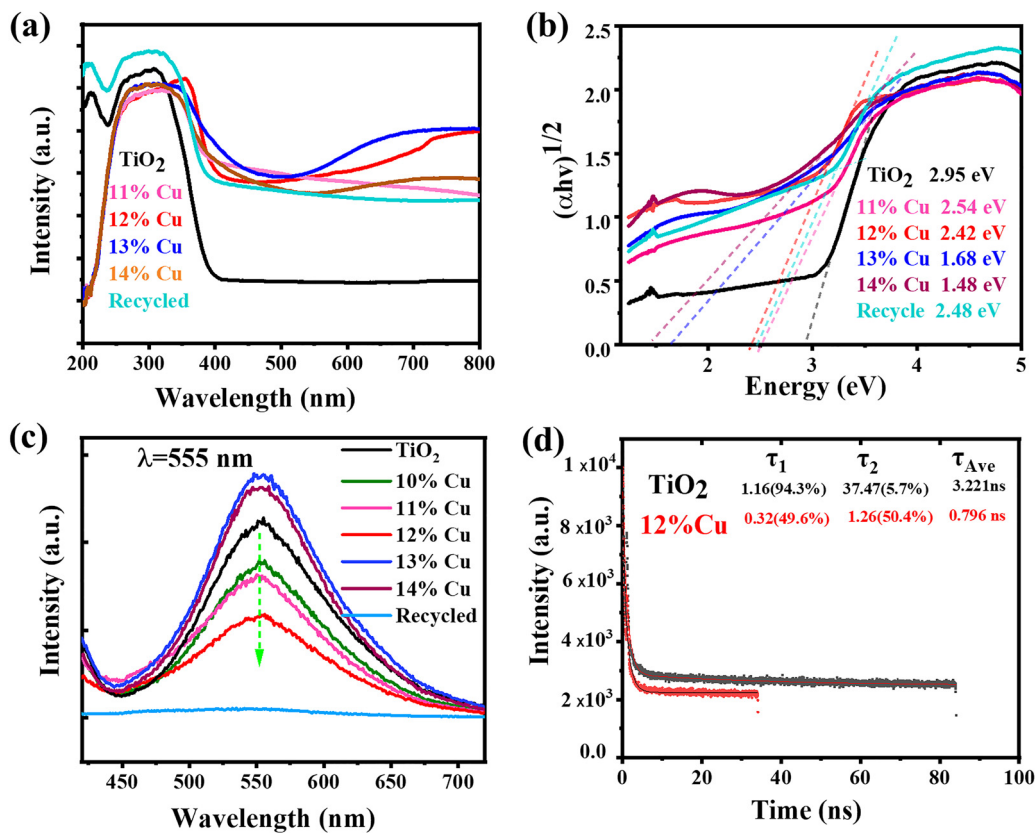


Fig. 4 (a) UV-visible absorption spectra of pristine TiO<sub>2</sub> and Cu-TiO<sub>2</sub> with different doped concentrations. (b) Tauc plot of pristine TiO<sub>2</sub> and Cu-doped TiO<sub>2</sub>. (c) PL-spectroscopy of pristine TiO<sub>2</sub> and CuO<sub>x</sub>-TiO<sub>2</sub>. (d) Low-temperature TRPL spectra of pristine TiO<sub>2</sub> and 12% Cu-TiO<sub>2</sub>.

in PL peak intensity upon Cu doping, with 12% Cu-TiO<sub>2</sub> showing the weakest emission, indicating maximum charge separation (Fig. 4c). Time-resolved photoluminescence (TRPL) further confirms charge transfer at the CuO<sub>x</sub>-TiO<sub>2</sub> heterojunction, as the fluorescence average lifetime of pristine TiO<sub>2</sub> decreases from 3.2 ns to 0.8 ns for 12% Cu-TiO<sub>2</sub> (Fig. 4d and Fig. S8). This suggests that Cu doping enhances electron extraction and electron transfer to Cu sites.<sup>91,93</sup> This charge extraction mechanism is supported by the fact that the reduction potential of Cu<sup>2+</sup>/Cu<sup>+</sup> (0.16 V vs. NHE) is more positive than the conduction band of TiO<sub>2</sub> (-0.1 V vs. NHE), making it possible for CuO to reduce to Cu<sub>2</sub>O, which is consistent with the XRD data.<sup>50,91,94</sup>

To further assess the electronic changes at the Cu-TiO<sub>2</sub> interface, ultraviolet photoelectron spectroscopy (UPS) was used to measure the work function and valence band maximum (VBM), and a secondary cutoff shift for pristine and 12% Cu-TiO<sub>2</sub> (Fig. S9). In comparison, the UPS shifts show a lower work function (6.3 to 5.5 eV), a deeper VBM (3.8 to 4.5 eV), and an altered secondary cutoff (14.89 to 15.6 eV), consistent with the Fermi level upshift, enhanced surface metallicity, and a stronger hole oxidation power. This shift likely arises from the formation of Cu<sup>0</sup>/Cu<sup>+</sup> species and modified surface dipoles, facilitating easier electron transfer for the HER.<sup>55,95</sup> However, HER performance also depends on the oxidation state of

surface Cu species (Cu<sup>0</sup>, Cu<sup>+</sup>, and Cu<sup>2+</sup>). These states affect how electrons and holes are trapped or shuttled. That is why XPS is needed to see how these oxidation states change during MPR operation conditions.

#### 2.4. Dynamic oxidation state in the Cu redox cycle and surface reconstruction

X-ray photoelectron spectroscopy (XPS) was conducted to investigate the evolution of Cu oxidation states as a function of Cu doping and to correlate dynamic changes under irradiation with HER activity. The Cu 2p spectra of 12% Cu-TiO<sub>2</sub> exhibited two dominant sets of spin-orbit peaks with associated satellite features (Fig. S10). The first set, at 934.2 eV (Cu 2p<sub>3/2</sub>) and 954.2 eV (Cu 2p<sub>1/2</sub>), was assigned to Cu<sup>2+</sup>, while the second set, at 932.9 eV (Cu 2p<sub>3/2</sub>) and 952.2 eV (Cu 2p<sub>1/2</sub>), was attributed to reduced Cu<sup>0</sup>/Cu<sup>+</sup> species, consistent with previous reports.<sup>62,96</sup> An additional peak at 936.0 eV was assigned to Cu(OH)<sub>2</sub>.

Systematic variations in both binding energy and the Cu 2p<sub>3/2</sub> intensity ratio of Cu<sup>0</sup>/Cu<sup>+</sup> to Cu<sup>2+</sup> were observed as the Cu content increased from 11% to 13%. Compared with 11% Cu-TiO<sub>2</sub>, where the ratio of Cu<sup>0</sup>/Cu<sup>+</sup> to Cu<sup>2+</sup> was ~1:1, the relative intensity of Cu<sup>0</sup>/Cu<sup>+</sup> increased to ~2:1 at 12% Cu-TiO<sub>2</sub>, indicating the growth of reduced Cu species. This was accompanied by a positive shift of 0.5 eV in the Cu<sup>0</sup>/Cu<sup>+</sup> peak (from 932.4 eV to 932.9 eV) and a negative shift of 0.7 eV for CuO, consistent with the formation of Cu<sub>2</sub>O as also



observed by XRD. At 13% Cu–TiO<sub>2</sub>, a negative shift of 0.6 eV was detected for the Cu<sup>0</sup>/Cu<sup>+</sup> peak, together with the disappearance of satellite features for Cu<sup>2+</sup>, reflecting enhanced metallic character due to further reduction to Cu<sup>0</sup>. The Cu<sup>2+</sup> peak at 934.2 eV (12% Cu) further shifted negatively to 934.0 eV ( $\Delta = 0.2$  eV), confirming progressive surface reduction with an increase in Cu doping. The corresponding satellite peaks at 940.3 and 943.2 eV, characteristic of CuO, were most prominent at 12% loading, supporting the maximum doping threshold before extensive reduction occurs at 13%. Hence, the approximated concentration trend at the surface found to be: CuO > Cu > Cu<sub>2</sub>O (11% Cu–TiO<sub>2</sub>), Cu<sub>2</sub>O > Cu > CuO (12% Cu–TiO<sub>2</sub>), and Cu > Cu<sub>2</sub>O > CuO (13% Cu–TiO<sub>2</sub>), which is consistent with XRD results. These results confirm the coexistence of Cu<sup>0</sup>, Cu<sub>2</sub>O, and CuO in 12% Cu–TiO<sub>2</sub> in well-defined ratios, where Cu<sub>2</sub>O has the highest concentration and corresponding higher HER activity.

The high-resolution O 1s spectra of pristine TiO<sub>2</sub> and 12% Cu–TiO<sub>2</sub> reveal two deconvoluted peaks at 529.29 eV and 531.8 eV corresponding to lattice oxygen vacancies (Ov) and surface O<sub>OH</sub>, respectively (Fig. S10d).<sup>90,91</sup> Compared to pristine TiO<sub>2</sub>, in 12% Cu–TiO<sub>2</sub>, the O<sub>OH</sub> peak intensity increases from ~30% to 44%, confirming an increase in OH adsorption sites, which facilitate accelerating proton–electron transfer during the HER. The binding energy difference ( $\Delta E_{BE}$ ) between Ov and

O<sub>OH</sub> progressively widens from 1.5 eV in pristine TiO<sub>2</sub> to 2.44 eV (11%), 2.56 eV (12%), and 2.55 eV (13%) in CuO<sub>x</sub>–TiO<sub>2</sub>. The  $\Delta E_{BE}$  reaches a maximum of 2.56 eV in 12% Cu–TiO<sub>2</sub> indicating stronger interfacial electronic and dipole interactions between Cu species and the TiO<sub>2</sub> lattice, leading to enhanced stabilization of surface O<sub>OH</sub> intermediates.<sup>97,98</sup> Notably, the correlation between the  $\Delta E_{BE}$  increase and the concurrent reduction of Cu<sup>2+</sup> to Cu<sup>+</sup>/Cu<sup>0</sup> (as observed in the Cu 2p spectra) highlights a synergistic effect, wherein Cu redox dynamics enhance charge redistribution at oxygen sites. These findings suggest that the optimal Cu loading of ~12% not only just optimizes the Cu<sup>0</sup>/Cu<sup>+</sup>/Cu<sup>2+</sup> ratio but also tunes the electronic environment of oxygen species, thereby promoting HER activity.

The Ti 2p spectra exhibit peaks at 458.54 eV (Ti 2p<sub>3/2</sub>) and 464.59 eV (Ti 2p<sub>1/2</sub>), which shift toward lower binding energies upon Cu doping: ~0.4 eV in 11% Cu–TiO<sub>2</sub>, ~0.47 eV in 12% Cu–TiO<sub>2</sub>, and partially reverting to ~0.11 eV in 13% Cu–TiO<sub>2</sub> (Fig. 5b and Fig. S10c). This negative shift is attributed to electron donation from oxygen vacancies, which enhances Ti<sup>3+</sup> character and modifies the electronic structure of the TiO<sub>2</sub> lattice.<sup>48,69</sup> The trend correlates with the Cu-induced reduction of surface species, suggesting a synergistic effect between Cu doping, Ti<sup>3+</sup> character, and oxygen vacancy generation, all of which can influence HER activity.

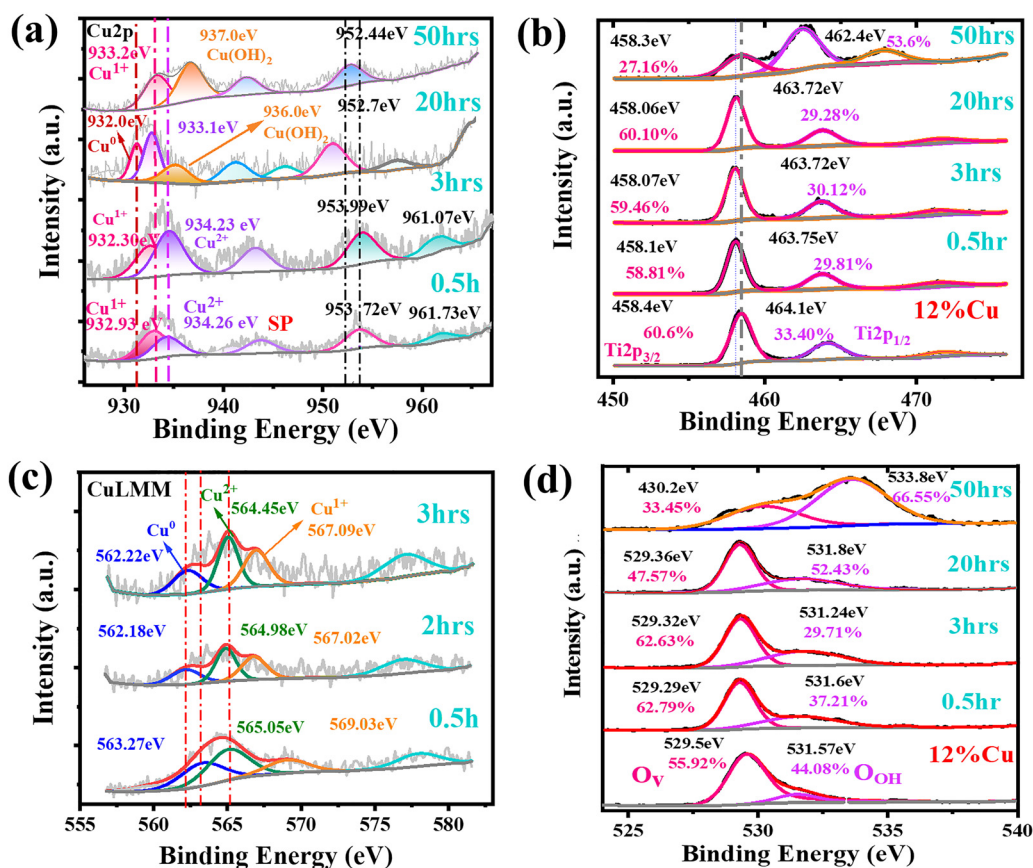


Fig. 5 XPS data analysis for 12% Cu–TiO<sub>2</sub> at different time intervals during photocatalytic HER. (a) Cu 2p<sub>2/3</sub> scan. (b) Ti 2p<sub>2/3</sub> scan. (c) Cu LMM Auger scan. (d) O 1s scan.



Overall, these analyses demonstrate that an optimal Cu loading of  $\sim 12\%$  simultaneously optimizes the  $\text{Cu}^0/\text{Cu}^+/\text{Cu}^{2+}$  content, enhances surface OH adsorption, and tunes  $\text{Ti}^{4+}$  and oxygen vacancy states, thereby creating an electronically favorable environment for the HER. Further doping beyond this level leads to minor electronic changes, consistent with diminishing catalytic activity.

Under light irradiation during MPR, the 12% Cu-TiO<sub>2</sub> catalyst exhibits a significantly higher H<sub>2</sub> generation rate (30.6 mmol g<sup>-1</sup> h<sup>-1</sup>) compared to 11% (8.0 mmol g<sup>-1</sup> h<sup>-1</sup>) and 13% (17.0 mmol g<sup>-1</sup> h<sup>-1</sup>). This enhanced performance correlates with the optimized Cu<sup>0</sup>/Cu<sub>2</sub>O/CuO concentration ratio, increased surface OH availability, and the synergistic interplay among Cu<sup>0</sup>, Cu<sup>+</sup>, Cu<sup>2+</sup>, and Ti<sup>4+</sup> species at the CuO<sub>x</sub>-TiO<sub>2</sub> interface.<sup>67,68</sup> Consistent with XRD observations (Fig. 2c), monitoring of Cu 2p<sub>3/2</sub> peaks over 50 h of irradiation reveals dynamic restructuring and redox behavior, which leads to stabilizing Cu<sub>2</sub>O (933.2 eV) and Cu(OH)<sub>2</sub> (937.0 eV) at the surface (Fig. 5a).<sup>99</sup> The broad Cu 2p<sub>3/2</sub> peak assigned to Cu<sup>+/Cu</sup><sup>0</sup> at 932.9 eV (after 0.5 h) shifted negatively to 932.0 eV (Cu<sup>0</sup>) after 20 h, followed by a reversible positive shift to 933.2 eV (Cu<sup>+</sup>) after 50 h, demonstrating the reversible Cu<sup>+</sup> ⇌ Cu<sup>0</sup> redox process that stabilizes interfacial Cu<sub>2</sub>O. Simultaneously, the Cu 2p<sub>3/2</sub> peak of CuO at 934.2 eV (0.5 h) evolved or overlapped into the concurrent growth of Cu<sup>+</sup> (933.2 eV) and Cu(OH)<sub>2</sub> at 937 eV after 50 h of irradiation, demonstrating the reversible Cu<sup>+</sup> ⇌ Cu<sup>2+</sup> redox process.<sup>39,100,101</sup> Auger Cu LMM analysis further confirmed the negative shifts in binding energies by 1.05 eV (Cu<sup>0</sup>), 1.94 eV (Cu<sup>+</sup>), and 0.6 eV (Cu<sup>2+</sup>) over three hours of irradiation (Fig. 5c).<sup>42,102-104</sup> The negative shifts indicate that photogenerated electrons in TiO<sub>2</sub> are transferred to the Cu dopants, stabilizing Cu<sub>2</sub>O at 567 eV, consistent with Cu 2p<sub>3/2</sub> and XRD results (Fig. 2c). Cu<sup>+</sup> ions are most strongly affected, showing that Cu acts as an electron acceptor under irradiation.

After 50 h of irradiation, the O 1s spectra of 12% Cu-TiO<sub>2</sub> exhibit (in addition to the peaks at 530 eV (O<sub>v</sub>) and 532 eV (O<sub>OH</sub>)), a third dominant peak at 533.8 eV, assigned to a substantial amount of chemisorbed OH<sup>-</sup> (H<sub>2</sub>O) groups on the surfaces, consistent with the growth of Cu(OH)<sub>2</sub> observed in the Cu 2p<sub>3/2</sub> spectra (Fig. 5d).<sup>105-111</sup> The pronounced Cu(OH)<sub>2</sub> signal indicates efficient water dissociation at the Cu sites, a favorable feature for H<sub>2</sub> generation in aqueous media.<sup>98</sup> Furthermore, the ΔE<sub>BE</sub> between O<sub>v</sub> and the predominant chemisorbed O<sub>OH</sub> increased to 3.6 eV after 50 h of irradiation (Fig. 5d), indicating that the O<sub>OH</sub> sites became more electron-poor. This electronic polarization of surface hydroxyls can enhance water adsorption, thereby promoting HER activity.<sup>59,112,113</sup> In the Ti 2p<sub>3/2</sub> spectra, the BE initially decreased by 0.34 eV after 20 h of irradiation and subsequently increased by 0.30 eV after 50 h of irradiation (Fig. 5b), aligned with Cu 2p<sub>3/2</sub> peaks. The initial negative shift is consistent with increased Ti<sup>3+</sup> character, reflecting a more reducing surface environment as methanol scavenges photogenerated holes and promotes electron accumulation. The Ti 2p<sub>3/2</sub> peak broadened and became asymmetrical, which also suggests the formation of non-stoichiometric TiO<sub>2-x</sub> (CuO → Cu<sub>2</sub>O conversion) and/or

partially reduced Ti<sup>3+</sup> species.<sup>114</sup> The Ti 2p<sub>3/2</sub> positive shift may be due to the contribution of surface Ti<sup>3+</sup> in the conversion of Cu<sup>2+</sup> to Cu<sup>+</sup> and reduces its reducing character (Fig. 5b). The positive shift in Ti 2p<sub>3/2</sub> may also be due to the increased presence of Cu(OH)<sub>2</sub> species on the surface, which may introduce a strong dipole moment or local electric field.<sup>33,65,90,115,116</sup> Surprisingly, an abnormal change in 2p<sub>3/2</sub>/2p<sub>1/2</sub> intensity ratio ( $\sim 2:1$ ) was observed as a result of attenuation of the 2p<sub>3/2</sub> signal, which may be due to accumulation of dynamic Cu<sub>2</sub>O, Cu(OH)<sub>2</sub>, and OH<sup>-</sup> at the surface, segregation of Cu species or overlapping of other species at the 2p<sub>1/2</sub> peak position.<sup>114,117</sup>

These trends suggest a zwitterionic electrostatic polarization effect due to an unexpectedly large amount of OH<sup>-</sup> in the Cu-TiO<sub>2</sub> aqueous solution (despite near-neutral pH) that can only be explained by water dissociation.<sup>98</sup> Consequently, Ti-O or Cu-O bonds cooperate to stabilize intermediates where the electron-rich O<sub>v</sub> and polarized OH groups create synergistic active sites that enhance charge separation, improve adsorption of H<sub>2</sub>O and H<sup>+</sup>, and facilitate HER kinetics.<sup>59,112</sup> Contrarily, as a trade-off, while Cu(OH)<sub>2</sub> enrichment enhances surface reactivity, it also leads to the formation of a dense “insulating or diffusion layer” that can block light penetration and impede reactant access to the underlying active TiO<sub>2</sub> sites.<sup>97,98</sup> Additionally, Cu segregation may also reduce the effective participation of TiO<sub>2</sub> in photocatalysis by limiting light absorption and decreasing the generation of photogenerated charge carriers, ultimately impairing the overall efficiency of the photocatalyst.<sup>59, 112</sup> Hence, the abundance of hydroxyl groups (-OH) renders the surface more oxidative, potentially influencing methanol oxidation during the HER.<sup>118</sup> Consequently, these findings highlight the reversible dynamic redox behavior of CuO<sub>x</sub> species (CuO ⇌ Cu<sub>2</sub>O ⇌ Cu) and their role in thermodynamically and kinetically stable Cu(OH)<sub>2</sub> and Cu<sub>2</sub>O towards optimized HER performance.<sup>40,119</sup>

## 2.5. Photocatalytic hydrogen evolution performance

The photocatalytic hydrogen evolution reaction (HER) was systematically evaluated for pristine TiO<sub>2</sub> and 1–14% Cu-doped TiO<sub>2</sub> samples under Xe lamp irradiation, using 20% methanol as a sacrificial hole scavenger (Fig. 6 and Fig. S11–S13). All Cu-doped catalysts outperformed pristine TiO<sub>2</sub> (3.3 mmol g<sup>-1</sup> h<sup>-1</sup>), with the 12% Cu-TiO<sub>2</sub> sample achieving a highest rate of 30.6 ± 2 mmol g<sup>-1</sup> h<sup>-1</sup>—tenfold higher than that of pristine TiO<sub>2</sub> (Fig. 6a). The superior performance of 12% Cu-TiO<sub>2</sub> compared to 11% and 13% loadings arises from a favorable balance of porosity, Cu<sup>0</sup>/Cu<sub>2</sub>O/CuO concentration ratio, charge-transfer efficiency, and oxygen-vacancy defects, as confirmed by BET (Fig. S4), XPS (Fig. 5 and Fig. S10), PL (Fig. 4c), and XRD (Fig. 2a). At 11% doping, the CuO/Cu<sub>2</sub>O ratio is higher relative to the optimal 12% sample (XPS, Fig. S10b), reducing the fraction of catalytically active Cu<sub>2</sub>O. At 13% doping, the Cu<sup>0</sup>/Cu<sup>+</sup> ratio is higher, which leads to Cu<sup>0</sup> aggregation and clustering that clogs mesopores, reduces pore volume, and partially blocks photocatalytic sites. BET analysis confirmed that the pore volume of 12% Cu-TiO<sub>2</sub> (0.31 cm<sup>3</sup> g<sup>-1</sup>) exceeds that of both 11% (0.23 cm<sup>3</sup> g<sup>-1</sup>) and 13%



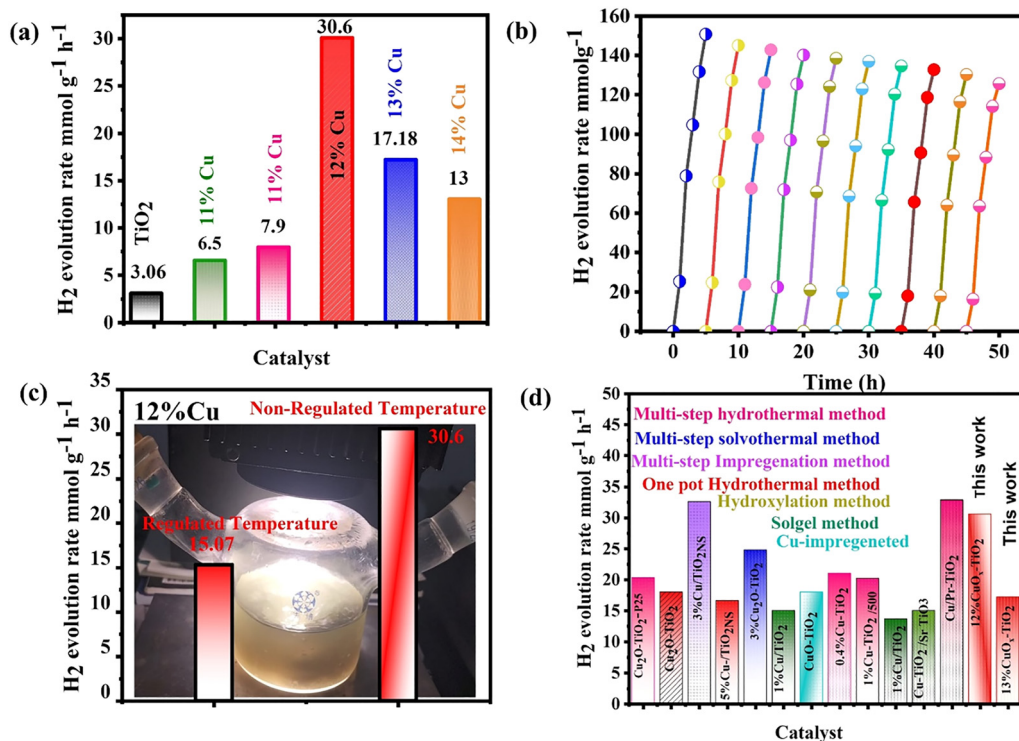


Fig. 6 H<sub>2</sub> evolution rate (HER) of pristine TiO<sub>2</sub> and CuO<sub>x</sub>-TiO<sub>2</sub> in the 20% methanol in water system. (a) HER of pristine TiO<sub>2</sub> and 10–14% Cu-TiO<sub>2</sub>. (b) Stability test in 10 cycles (50 h). (c) HER of 12% Cu-TiO<sub>2</sub> at regulated temperature. (d) High-performing methanol photo reforming HER rate for CuO<sub>x</sub>-TiO<sub>2</sub> and color-coded synthesis methods from Table S2.

(0.21 cm<sup>3</sup> g<sup>-1</sup>), in good agreement with HER activity trends (Table S2).<sup>65,120</sup> This effect is further supported by PL measurements, where 12% Cu-TiO<sub>2</sub> shows the most pronounced quenching of emission intensity, consistent with its higher Cu<sub>2</sub>O fraction and more efficient electron extraction (Fig. 4c).<sup>63,121</sup>

The long-term stability and recyclability of 12% Cu-TiO<sub>2</sub> were assessed over 50 h of continuous irradiation (10 cycles of 5 h), with >90% retention in the hydrogen evolution rate (Fig. 6b and Fig. S11). Control experiments conducted at 20 °C under identical conditions ruled out thermal contributions, giving a reduced HER rate of 15 mmol g<sup>-1</sup> h<sup>-1</sup> (Fig. 6c and Fig. S13). Furthermore, 100% recovery of activity was observed after replenishment of 20% methanol following 15 h of operation (Fig. S13c), confirming methanol's essential role in sustaining performance. Finally, the optimized 12% Cu-TiO<sub>2</sub> exhibited an apparent quantum efficiency (AQE) of 9.7% at 450 nm (Fig. S14), reflecting efficient utilization of monochromatic visible light.

## 2.6. Charge transfer mechanism and the corrosion-healing redox loop cycle

Under photocatalytic conditions, the interfacial dynamics of CuO, Cu<sub>2</sub>O, and metallic Cu in CuO<sub>x</sub>-TiO<sub>2</sub> heterostructures are governed by the heterojunction configuration, band alignment, and charge-transfer pathways. The most plausible mechanism follows an S-scheme model, in which band bending and

internal electric fields direct carrier separation, with metallic Cu acting as an efficient cocatalyst (Fig. 7). This assignment is substantiated by steady-state and time-resolved PL, XRD, XPS, and UPS analyses (Fig. 2c, 4c, d, 5a, c and Fig. S9) and is consistent with prior literature.<sup>122,123</sup> For 12% CuO<sub>x</sub>-TiO<sub>2</sub>, photoluminescence quenching and the reduction of the average TRPL lifetime from 3.2 ns (pristine TiO<sub>2</sub>) to 0.8 ns (Fig. 4d) demonstrate accelerated electron extraction by Cu sites. Concurrently, UPS spectra show a work function decrease from 6.3 to 5.5 eV, indicative of enhanced metallic character (Cu<sup>0</sup>/Cu<sup>+</sup> species) and improved surface electron transfer kinetics for hydrogen evolution. XPS reveals negative shifts in the Cu 2p<sub>3/2</sub> binding energies, corroborating electron transfer into Cu redox states (Cu<sup>2+</sup> → Cu<sup>+</sup> → Cu<sup>0</sup>), while XRD and XPS confirm the light-induced reduction of Cu<sup>2+</sup> to Cu<sub>2</sub>O and metallic Cu (Fig. 2c and 5a).<sup>8</sup>

Within the S-scheme framework, photogenerated e<sup>-</sup> in the TiO<sub>2</sub> CB and h<sup>+</sup> in the Cu<sub>2</sub>O VB undergo interfacial selective recombination of low-energy carriers, while the remaining high-energy carriers (e<sup>-</sup> in the Cu<sub>2</sub>O CB and h<sup>+</sup> in the TiO<sub>2</sub> VB) drive hydrogen evolution and methanol oxidation, respectively.<sup>123–125</sup> This pathway effectively suppresses overoxidation of Cu<sup>+</sup> to Cu<sup>2+</sup>, thereby limiting the formation of CuO/Cu(OH)<sub>2</sub> and stabilizing the Cu<sub>2</sub>O phase. Simultaneously, metallic Cu establishes Schottky junctions with TiO<sub>2</sub> that collect high energy CB electrons and preferably catalyze proton reduction, preventing the over-reduction of Cu<sub>2</sub>O. The dynamic



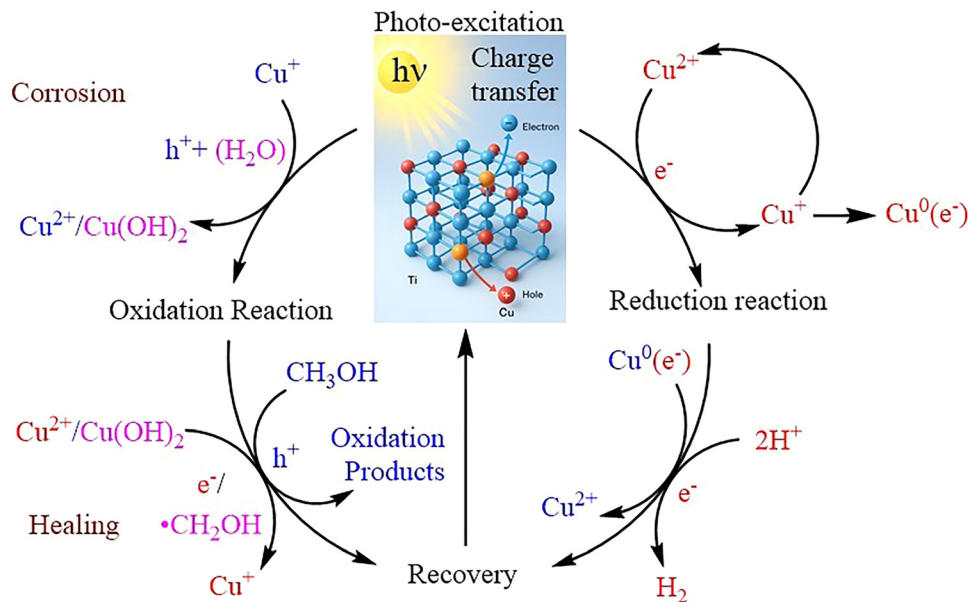


Fig. 7 The proposed photocatalytic hydrogen evolution reaction (HER) mechanism (corrosion–healing redox loop) over 12% Cu<sub>x</sub>–TiO<sub>2</sub> in the presence of methanol and water.<sup>23,39</sup>

Cu<sup>2+</sup>/Cu<sup>+</sup>/Cu<sup>0</sup> redox cycle, confirmed by Cu LMM spectra (Fig. 5c), facilitates efficient charge transport and underpins the enhanced HER activity and long-term durability of the composite catalyst (Fig. 7).<sup>23,122,126</sup>

Under prolonged irradiation in 20% methanol, both Cu<sub>2</sub>O and Cu(OH)<sub>2</sub> continue to grow due to a self-sustaining corrosion–healing redox loop at the Cu<sub>2</sub>O–TiO<sub>2</sub> interface.<sup>39</sup> In this process, holes reaching Cu<sub>2</sub>O oxidize Cu<sup>+</sup> to Cu<sup>2+</sup>, which hydrolyzes to Cu(OH)<sub>2</sub>, while electrons and methanol-derived intermediates (such as •CH<sub>2</sub>OH or formaldehyde) favoring reduction of transient Cu(OH)<sub>2</sub> back to Cu<sub>2</sub>O at other locations. Because these oxidation and reduction events occur at different sites and time, XPS and XRD may show concurrent growth of Cu<sup>+</sup> and Cu<sup>2+</sup> species despite originating from the same redox cycling. However, this loop consumes photogenerated carriers inefficiently, introduces recombination centers, and accumulates insulating Cu(OH)<sub>2</sub> deposits that progressively shift the system toward mimicking type-II-like charge separation with higher recombination probability. The result has diminished hydrogen evolution activity.<sup>127</sup>

Nevertheless, the Cu<sup>+</sup>/Cu<sup>2+</sup> redox couple also functions as a dynamic electron shuttle, mediating charge transfer while buffering the copper oxidation state under continuous photo-irradiation. This redox buffering suppresses irreversible Cu<sub>2</sub>O oxidation, while TiO<sub>2</sub> serves as both a structural matrix and electronic stabilizer, dissipating excess charge and mitigating rapid degradation of the Cu-based species. To maintain efficient H<sub>2</sub> evolution, continuous supply/addition of 20% methanol as a sacrificial agent is required (Fig. S13c). Its oxidation products act as rapid hole scavengers, ensuring reductive equivalents are delivered to transient Cu(OH)<sub>2</sub> sites, limiting their accumulation and restoring Cu<sub>2</sub>O.

In summary, the proposed S-scheme Cu<sub>2</sub>O–TiO<sub>2</sub>(101) heterojunction, synergistically coupled with metallic Cu as an electron sink, provides the most consistent mechanistic framework with the experimental observations. This model explains the stabilization of Cu<sub>2</sub>O(111) and the controlled presence of Cu(OH)<sub>2</sub> under prolonged irradiation, while simultaneously accounting for enhanced charge separation, efficient methanol oxidation, and sustained hydrogen evolution activity.<sup>123</sup>

## 2.7. Density functional theory (DFT) insights into hydrogen adsorption and stability

To rationalize the experimentally observed enhancement in the HER activity of Cu–TiO<sub>2</sub> systems, we performed density functional theory (DFT) calculations to probe structural, electronic, and catalytic properties. Anatase TiO<sub>2</sub>(101) and (001) facets were considered, followed by construction of Cu-doped, CuO–TiO<sub>2</sub>(101), and Cu<sub>2</sub>O–TiO<sub>2</sub>(101) models (Fig. 8a, 9a and Fig. S15–S19). Projected density of states (PDOS) analysis revealed strong hybridization between Cu-3d and Ti-3d/O-2p orbitals, with the d-band centers ( $\epsilon_d$ ) of Cu–TiO<sub>2</sub>(101) lying closer to the Fermi level (0.81 eV) compared to Cu–TiO<sub>2</sub>(001) (1.91 eV) (Fig. 8b). This shift indicates stronger hydrogen adsorption at the (101) surface, in line with its superior HER activity. Charge density difference (CDD) maps further confirmed greater electron accumulation around Cu on (101), with Bader analysis showing higher charge transfer (1.41 e) relative to the (001) surface (0.71 e) (Fig. 8c).

The calculated Gibbs free energy ( $\Delta G_{H^*}$ ) profiles provide a direct comparison with HER benchmarks. Cu–TiO<sub>2</sub>(101) exhibits a nearly thermoneutral hydrogen adsorption energy ( $\Delta G_{H^*} = -0.06$  eV), closely matching Pt(111) ( $-0.09$  eV), whereas Cu–TiO<sub>2</sub>(001) shows stronger binding ( $\Delta G_{H^*} = -0.65$  eV), which



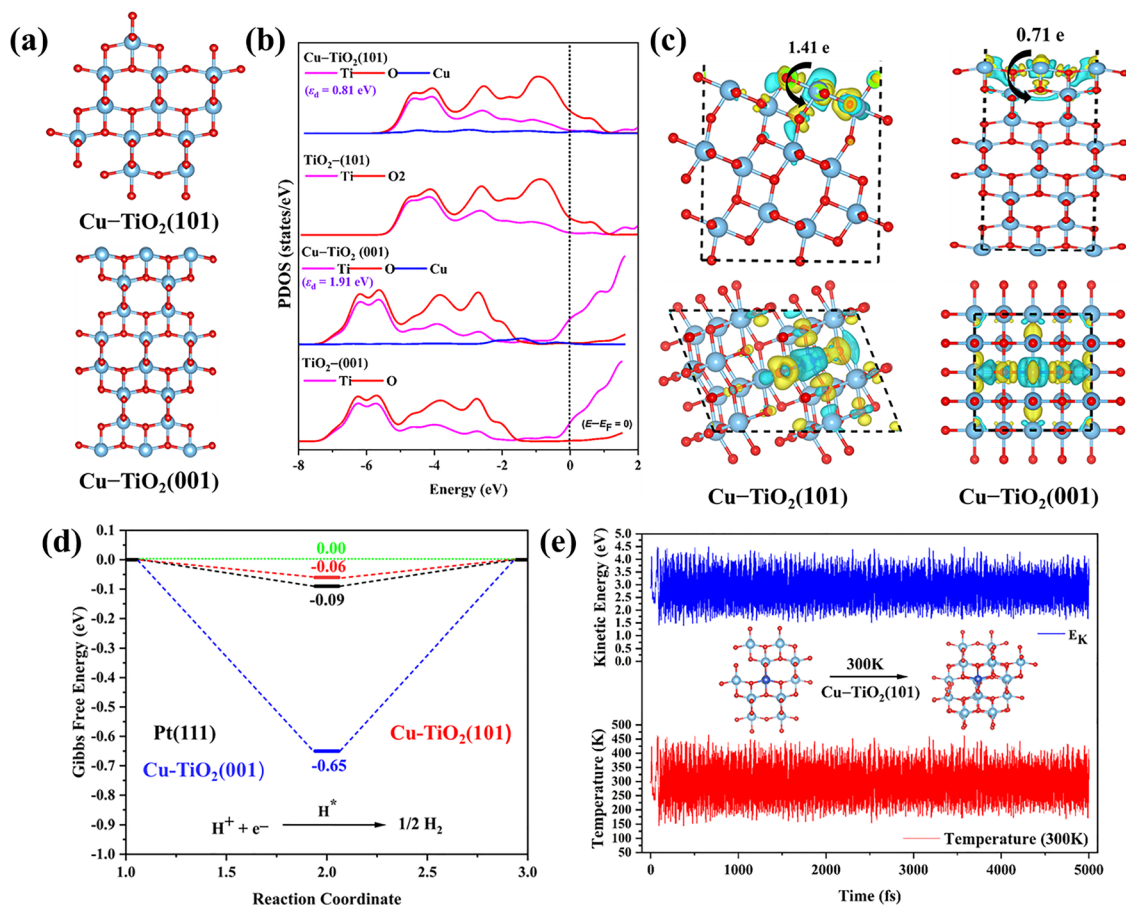


Fig. 8 (a) Cu-TiO<sub>2</sub> surface at two phases at 101 and 001, (b) the PDOS plots of pristine and newly adopted models, (c) charge density differences (CDDs) of investigated surfaces, (d)  $\Delta G_{H^+}$  of Cu-TiO<sub>2</sub> at (101) and (001) phase comparison with experimental Pt(111), and (e) AIMD simulations showing the thermal stability of the Cu-TiO<sub>2</sub>(101) phase.

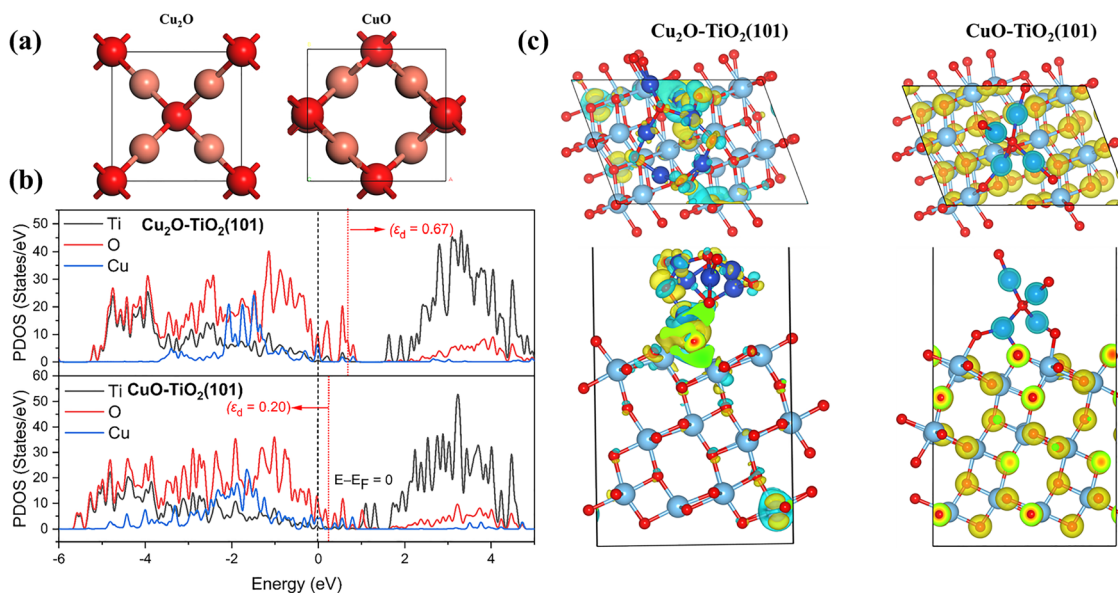


Fig. 9 (a) Structural configuration of CuO and Cu<sub>2</sub>O, (b) the PDOS plots of CuO-TiO<sub>2</sub>(101), and Cu<sub>2</sub>O-TiO<sub>2</sub>(101), and (c) charge density differences of CuO-TiO<sub>2</sub>(101) and Cu<sub>2</sub>O-TiO<sub>2</sub>(101).



hinders H<sub>2</sub> desorption (Fig. 8d). *Ab initio* molecular dynamics (AIMD) simulations confirmed the thermal stability of Cu-TiO<sub>2</sub>(101) at 300 K (Fig. 8e). These theoretical findings support the experimental observation that Cu-TiO<sub>2</sub>(101) serves as the most active HER interface.

To further assess the role of Cu oxidation states, CuO-TiO<sub>2</sub>(101) and Cu<sub>2</sub>O-TiO<sub>2</sub>(101) models were constructed (Fig. 9a). PDOS and CDD analyses (Fig. 9b and c) show distinct charge redistribution, with Bader charges of 0.73 e and 0.84 e, respectively, compared to 1.41 e for metallic Cu. Correspondingly,  $\Delta G_{H^+}$  values follow the order: Cu-TiO<sub>2</sub>(101) (-0.06 eV) > Cu<sub>2</sub>O-TiO<sub>2</sub>(101) (-1.37 eV) > CuO-TiO<sub>2</sub>(101) (+1.20 eV), indicating that metallic Cu provides the most favourable H adsorption-desorption balance (Fig. S19). This agrees with experimental evidence where metallic Cu functions as an electron sink, Cu<sup>+</sup>/Cu<sup>2+</sup> acts as a redox mediator, and TiO<sub>2</sub> stabilizes the composite against irreversible oxidation.

Overall, the DFT results corroborate the proposed charge transfer mechanism by demonstrating that (i) Cu doping lowers the work function and enhances electron transfer, (ii) Cu-TiO<sub>2</sub>(101) offers the most optimal hydrogen binding energy among all tested models, and (iii) the oxidation state of Cu critically tunes HER activity, with metallic Cu enabling efficient electron transfer and HER kinetics.

### 3. Conclusion

This study presents a one-pot scalable strategy for CuO<sub>x</sub>-TiO<sub>2</sub> photocatalysts, achieving a record HER rate of 30.6 mmol g<sup>-1</sup> h<sup>-1</sup> with excellent durability and scalability. Beyond the dynamic CuO  $\rightleftharpoons$  Cu<sub>2</sub>O  $\rightleftharpoons$  Cu<sup>0</sup> redox cycle, we identify for the first time a corrosion-healing redox loop, wherein Cu<sub>2</sub>O is continually regenerated *via* reversible oxidation to CuO/Cu(OH)<sub>2</sub> and reduction by methanol-derived intermediates. This self-healing process stabilizes active sites, suppresses irreversible deactivation, and underpins the long-term photocatalytic stability. An S-scheme heterojunction charge transfer pathway combined with DFT validation of near-Pt-like hydrogen binding energetics on Cu-TiO<sub>2</sub>(101) position Cu-based systems as strong contenders to replace noble metals for photocatalytic hydrogen production. The demonstrated structural robustness, scalability, and redox self-healing open a new avenue for designing durable and economically viable solar-to-hydrogen catalysts.

### Conflicts of interest

The authors declare no conflicts of interest.

### Data availability

The data supporting this article have been included as part of the supplementary information (SI). Supplementary information: XRD, SEM, XPS, BET, and DFT measurements data. See DOI: <https://doi.org/10.1039/d5mh01679g>.

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