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Abnormal Copper Coordination obtained by TiO₂ overlayer as a key for enhanced photocatalytic hydrogen generation

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Strong metal-support interaction (SMSI) is a pivotal strategy in thermal catalysis, while its application in photocatalysis leaves ample area for further development. A method inducing the SMSI between earth-abundant metals, such as copper and TiO₂, at room temperature, hindering the agglomeration of copper species remains rarely reported. In this work, we achieve SMSI construction of TiO₂ overlayer on Cu nanoparticles via a straightforward soft-chemistry method. The SMSI coverage is even stable after high-temperature treatment in the air (500°C), as demonstrated by chemical mapping and surface analysis. The method is more accurate than thermal reduction since it produces a metastable, highly active anatase phase. Interestingly, the TiO₂ overlayer induces the formation of six-coordinated copper (II) species surrounded by oxygen atoms, resulting in coexisting CuO₂ planes monitored by high-resolution transmission electron microscopy and electron paramagnetic resonance spectroscopy. The stronger interfacial interaction by forming Ti-O-Cu bonding promotes charge carrier separation, producing twice as much H₂ than the low interfacial interaction within a conventional photoactive system wherein copper was decorated onto TiO₂. Our approach offers a rational design for SMSI materials in photocatalysis, extendable to other catalytic reactions.

Introduction

Solar fuel production presents a promising method for converting sunlight into a renewable, sustainable, and environmentally friendly energy source. Hydrogen, a clean fuel generated through solar water splitting, has emerged as a promising solution for climate challenges. H₂ can be produced through three distinct approaches: photocatalytic (PC), photoelectrochemical (PEC), and photovoltaic–electrolysis (PV–EC) routes.^{1–3} Although PEC and PV–EC are recognized as advanced solar-to-hydrogen chemical fuel technologies, their scalability requires significant investment, leading to high-cost implications. On the other hand, the photocatalytic process has demonstrated low-cost investment and a promising conversion of solar energy to green hydrogen at the 100 m² scale.⁴ Since the discovery of the light-induced water splitting reaction over a titanium dioxide (TiO₂) electrode in the 1970s,⁵ efforts have been devoted to enhancing its efficiency. While the development of novel nanostructures,^{6–8} construction of heterojunctions,⁹ induction of oxygen vacancies,¹⁰ or coupling TiO₂ with the promising 2D graphdiyne carbon allotrope,¹¹ have shown effective improvement in photocatalysis, the most widely adopted strategy involves the surface coupling with metallic nanoparticles. Noble metals, such as Pt, Pd, and Au,¹² generally exhibit the highest photoactivity due to their intrinsic

properties. Recent developments have focused on downsizing these cocatalysts from nanoparticles to single atoms, aiming to modify their electronic properties, although this approach has encountered certain bottlenecks. From this perspective, the design and control of the metal-support interface have emerged as novel factors to enhance activity in catalytic reactions, leading to the development of the so-called strong metal-support interaction (SMSI) concept.^{15,16} While the SMSI construction is a pivotal strategy in thermal catalysis, its application in photocatalysis leaves ample room for further studies.^{17,18} The exploration of the aforementioned MSI phenomena should be extended, as it can lead to a rearrangement of electrons within both materials,¹⁹ favorable separation of photogenerated charge carriers, and modification of the adsorption of H₂O or CO₂.^{6,20} Various methods have been proposed to construct a strong metal-support interface, especially at a mild condition, including the mechano-chemistry, soft-chemistry, photoinduced reduction of the support, etc.^{21,22} instead of the conventional reductive high temperature conditions (500–700°C). However, most reported studies have demonstrated that the SMSI concept works for VIII B group metals, and more recently for IB group metal Au,^{23,24} with a few studies dedicated to earth-abundant copper metal nanoparticles.^{25–27}

In this study, we regulated the interaction between TiO₂ and CuO₂ for photocatalytic hydrogen generation. Copper, and its oxidized forms in general, have become one of the most promising alternatives to noble metals for proton photoreduction. Copper exists in various oxidation states, including Cu⁰, Cu^I, Cu^{II}, and Cu^{III}, can exist not only in an exclusive state but also in mixed states involving both zero-valent metals and oxides.²⁸ Cu⁰, Cu^(I)O, and Cu^(II)O are typically the most common copper species reported in TiO₂-based photocatalysis.^{29,30} Although less explored in photocatalytic

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reactions, especially with TiO₂-based photocatalysts, CuO₂ has been reported for fast charge transport, showing great potential in cuprate superconductor engineering, solid-state physics, and cancer treatment.^{31–33} Herein, we identify CuO₂ as a highly effective candidate for photocatalytic hydrogen generation. Additionally, tuning the interfacial interaction by constructing a metal oxide-support interface facilitates the transport and prolongs the lifetime of charge carriers that play a pivotal role in photon-to-hydrogen conversion.

Results and discussion

Microstructure and morphology characterization

The interaction between titania and cuprate oxide was regulated using a soft-chemistry method.⁶ We impregnated the surface of silica spheres (used as inert support) either with CuCl₂ or titania precursor to construct nanostructures: SiO₂@TiO₂@Cu (TiO₂/Cu) and SiO₂@Cu@TiO₂ (MSI-Cu/TiO₂). The details of the synthesis and the aspect of the samples are shown in Fig. S1. The microstructure and morphology of the as-synthesized photocatalysts were observed using transmission electron microscopy (TEM) and high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) (Fig. 1A, Fig. S2A, and Fig. S3A). The images showed the spherical shape of nanostructures scaffolded using a SiO₂ core. The diameter of the spheres was estimated to be around 200 nm. The SiO₂ microspheres behave as convex nano-lenses, which optimize electromagnetic field enhancement or even lead to an illumination focus point at the front surface of the nanostructure, resulting in optimal light harvesting.³⁴ High-resolution transmission electron microscopy (HRTEM) shows a

TiO₂ anatase phase-structured shell with a thickness of less than 10 nm for SiO₂@TiO₂ (Fig. S2B). The thin TiO₂ overlayer was observed to cover copper nanoparticles with a size of 7–10 nm for MSI-Cu/TiO₂ (Fig. 1B). The crystal of copper oxide species was assigned to orthorhombic CuO₂ and the indexed Fast Fourier Transform (FFT) patterns of the metallic species clearly showed the presence of the {111} and {110} family planes, noting that the observed structure was oriented along its [110] zone axis. For TiO₂/Cu, we could observe a homogeneous dispersion of copper species and TiO₂ forming a continuous shell around the silica spheres. The HRTEM images in Fig. S3-B, C and their corresponding indexed FFT showed that the studied nanoparticle crystallized in the CuO₂ orthorhombic structure with a preferential orientation along the [001] zone axis. From the results, we suspect that the cuprate CuO₂ does not exist separately in such crystalline form. In fact, its coexistence as superconducting CuO₂ planes is evidenced by the abnormal coordination of copper electronic state.³⁵ This will be clarified by EPR and XPS later.

The crystalline structure was further analyzed using X-ray powder diffraction (XRD), as shown in Fig. 1F. Diffractograms exhibited broad peaks at 22°, which correspond to an amorphous SiO₂ core. In addition, characteristic peaks at 25.3° were recorded in the diffraction patterns of samples that identify the lattice plane (101) of TiO₂ anatase phase. Other characteristic peaks of TiO₂ anatase showed up in the patterns, pointing out the presence of their corresponding lattice planes, including (004), (020), (200), (105), and (204). The patterns displayed no trace of cuprate species due to the small size of the nanoparticles and their low quantity as well.

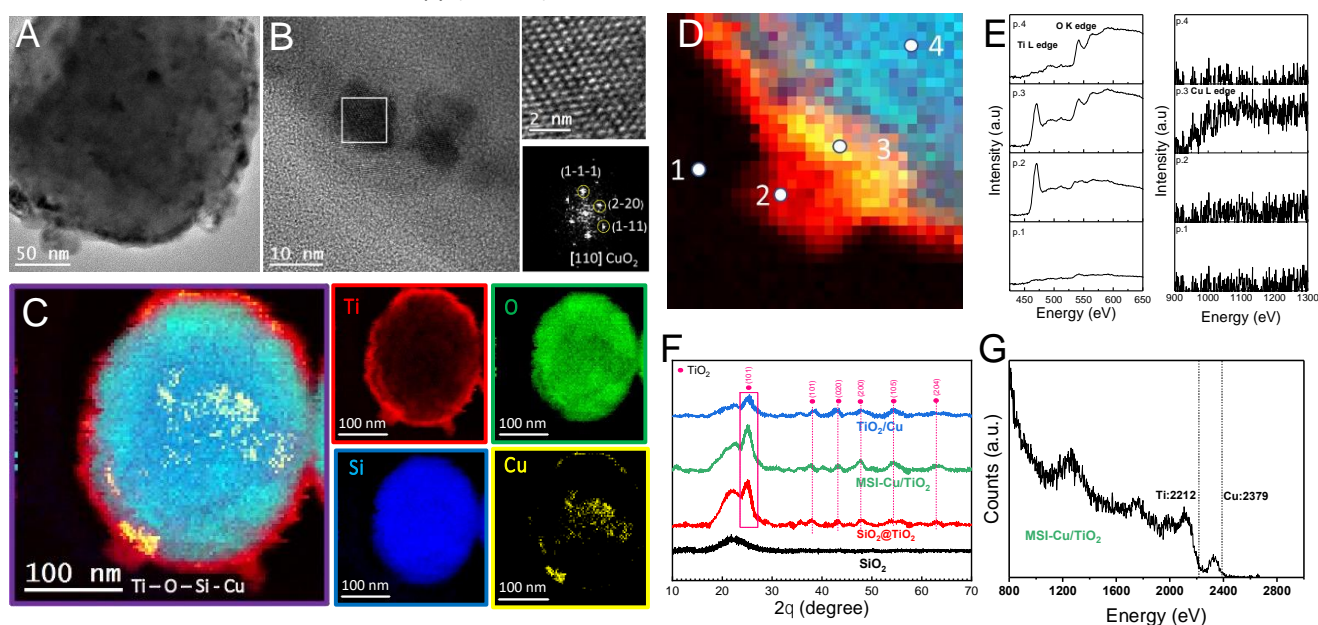


Fig. 1 | Microstructure and morphology of photocatalyst. (A) TEM image of MSI-Cu/TiO₂. (B) High magnification HRTEM image emphasizing encapsulated cuprate nanoparticle and its index power spectrum. (C) EELS-STEM chemical mapping of MSI-Cu/TiO₂ and chemical composition: Ti L edge at 456 eV (scarlet red), O K edge at 532 eV (kelly green), Cu L edge at 931 eV (lemon yellow) and Si K edge at 1839 eV (ultramarine blue). (D) Magnified image of EELS-STEM mapping. (E) Extrapolated EELS spectra at different regions on the MSI-Cu/TiO₂ surface. (F) Powder XRD patterns noted with Miller indices of SiO₂, SiO₂@TiO₂, MSI-Cu/TiO₂, and TiO₂/Cu. (G) LEIS spectra measured at iso-dose of 1x10¹⁵ He⁺ ions.cm⁻² for MSI-Cu/TiO₂.



The scanning transmission electron microscopy coupled with electron energy loss spectroscopy (STEM-EELS) provided chemical mapping of different elements (Ti, O, Si, and Cu), hence visualizing their spatial distribution within the nanostructures. **Fig. 1C, S2D, and S3-E,F** show that the core of the sphere, mainly consisting of Si and O, was surrounded by a homogeneous TiO₂ overlayer. The EELS obtained within the marked regions in **Fig. 1D** evidence the presence of both Ti L edges (456 eV) and O K edges (532 eV) EELS signals at the shell (regions 2 and 3) and the core surface (region 4). Remarkably, the Ti signal appears in region 3, where the Cu EELS signal was also observed (**Fig. 1E**), demonstrating coverage of the Cu by a TiO₂ overlayer. To further investigate the TiO₂ overlayer and confirm the nature of the CuO₂ coverage, we performed low-energy ion scattering (LEIS) depth profiling spectroscopy. The LEIS reveals information about the composition in the depth of a surface (1-5 nm) by bombarding a sample with noble gas ions of well-defined and low energy at 4.1×10^{15} He⁺ ions.cm⁻² (**Fig. 1G**). As the surface is progressively etched by the ion beam, gradients of concentrations from the uppermost layers to the layers below can be inspected. The first recorded signals, at a very low ion dose, were moderate, reflecting the removal of contamination (carbon, hydrogen, etc.) by the ion beam; these species were discarded for analysis. Given the lack of standardization for measurements on nanoparticles distributed over a porous support and the initial presence of contamination layers, translation of the results to a probed depth expressed in nanometre would not be attempted. The presence of Cu atoms in the outer shells of the MSI-Cu/TiO₂ sample was evidenced. However, the signal of Ti was dominant to the ones of Cu and Si, indicating the low quantity of Cu and Si atoms on the surface. In general, LEIS measurements directly confirm the existence of

a Cu enrichment in the outer shells of the photocatalyst. It demonstrates that the TiO₂ overlayer partially covers CuO₂ nanoparticles or the thin layer is discontinuous.

Defective surface structure and electronic states

We employed electron paramagnetic resonance spectroscopy (EPR) to analyze the nature of Cu species and hence get information about the oxidation state and coordination of EPR active copper sites (**Fig. 2A**); the EPR spectrum of SiO₂@TiO₂ as a reference was illustrated in **Fig. S4A**. In detail, Cu²⁺ (*d*⁹) species contain an odd number of electrons assigned to a spin $s = 1/2$, resulting in an EPR transition. The two principal isotopes of copper (⁶³Cu and ⁶⁵Cu) have similar nuclear spins of 3/2, leading to the splitting of Zeeman line into four lines ($m_I = 3/2, 1/2, (-1)/2, (-3)/2$).³⁶⁻³⁸ However, only the splitting in the z-direction is large enough to be visualized. The Jahn–Teller distortion is most encountered in octahedral complexes, especially six-coordinate copper(II) species surrounded by oxygen atoms.³⁹ **Fig. 2A** compared EPR spectra of MSI-Cu/TiO₂ and TiO₂/Cu. In particular, MSI-Cu/TiO₂ photocatalyst exhibited an axial EPR spectrum involving typical parallel and perpendicular edges, revealing two different Cu sites, in agreement with previous studies.^{40,41} The hyperfine splitting A_{\parallel} of 122 G at g_{\parallel} -factor of 2.402 can be attributed to the charge of donor atoms coordinating to Cu. The splitting by four unveils the presence of Cu²⁺ sites coordinated with four oxygen atoms that attest to the existence of CuO₂ revealed by HRTEM. The partial coverage of TiO₂ onto cuprate nanoparticles could create heterobimetallic sites *via* metal-oxygen-metal support bonding, particularly Ti-O-Cu, leading to the extraordinarily abnormal coordination of Cu²⁺ (crystal structure⁴² in **Fig. 2B**). Copper-deposited on TiO₂ observed an

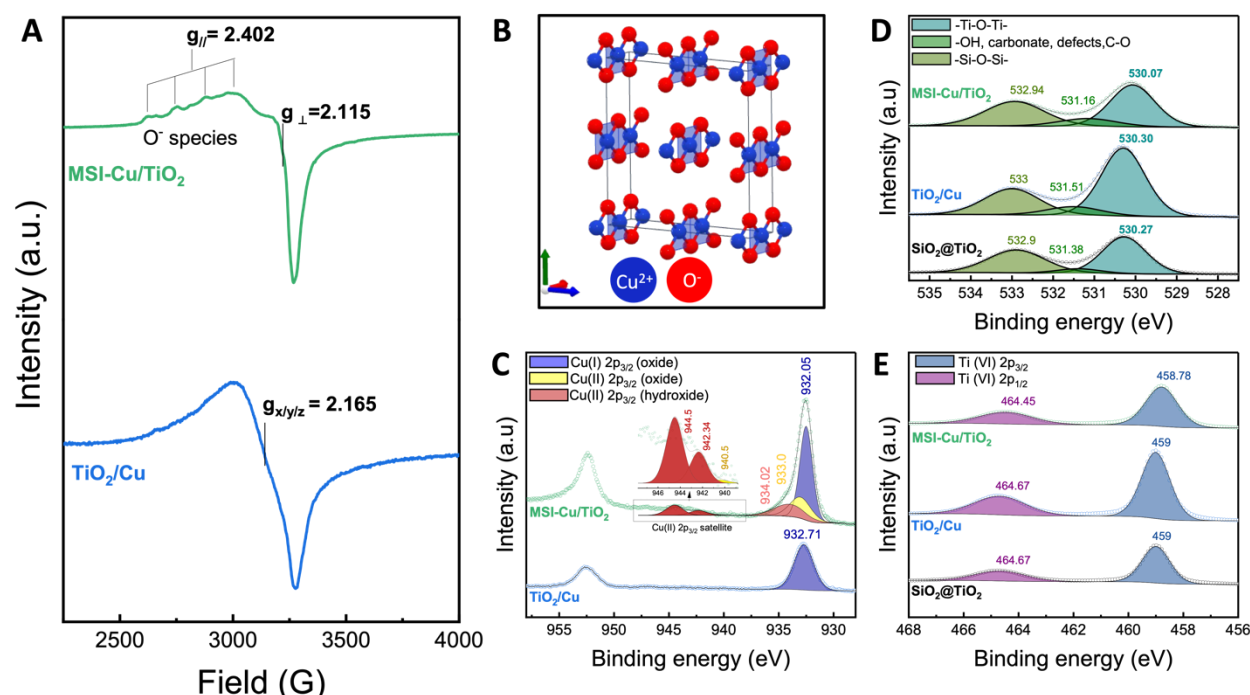


Fig. 2 | Characterization of surface electronic properties and catalytic active sites. (A) EPR spectra of MSI-Cu/TiO₂ and TiO₂/Cu. (B) Crystal structure of cuprate CuO₂. XPS spectra: (C) Cu 2p, (D) O 1s, and (E) Ti 2p.



isotropic spectrum. The outermost copper species on TiO_2/Cu are generally bound to polar water molecules, which are most likely to coordinate to Cu^{2+} . As a result, EPR spectrum of these hydrated Cu species typically displayed isotropic pattern, which is similar to EPR spectra of aqueous copper complexes such as $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ or $[\text{Cu}(\text{H}_2\text{O})_5(\text{OH})]^+$.^{43,44} Besides, g-factor of 2.165 estimated from EPR spectrum of TiO_2/Cu is fully consistent with those, at around 2.16–2.17, of copper on hydrated zeolite.^{45,46} In the case of TiO_2/Cu , no such bond between cuprate and titania was detected.

Surface analysis of the photocatalysts was further carried out by X-ray photoelectron spectroscopy (XPS) (Fig. S4B), recording signals of core levels Cu 2p, O 1s, and Ti 2p. In Fig. 2C, the high-resolution XPS spectra of Cu 2p show the characteristic peaks assigned to Cu 2p_{3/2} and Cu 2p_{1/2} transitions with satellite peaks. This indicates the existence of Cu(II) state within the MSI-Cu/TiO₂ sample.^{47,48} The Cu 2p_{3/2} can be deconvoluted into three peaks centered at 932.05 eV, 933 eV, and 934.01 eV. The peak at 932.05 eV corresponds to Cu^(II) oxide, while these peaks at 933 eV and 934.01 eV are indicative of Cu^(III) oxide and Cu^(III) hydroxide, respectively.⁴⁹ The corresponding shake-up satellite peak at 940.5 eV gives rise to Cu^(III) oxide, while the others at 942.34 eV and 944.5 eV evidence Cu^(III) hydroxide. These Cu^(III) 2p transitions shifted toward lower binding energy, and the satellite was much weaker than previous reports.^{47,49} In addition, the XPS Cu 2p spectrum of the TiO₂/Cu sample surprisingly revealed a single peak of Cu 2p_{3/2} without any shake-up satellite, commonly assigned to the Cu^(II) state. The oxidation state change of Cu in TiO₂/Cu and the shift towards lower binding energy of Cu^(III) in MSI-Cu/TiO₂ can be attributed to the impact of electron bombardment in a high vacuum environment.^{50,51} In fact, the electron bombardment can reduce copper species dispersed on the photocatalyst surface from Cu^(III) to Cu^(II). This effect becomes evident in the case of TiO₂/Cu, where the TiO₂ overlayer did not protect Cu species and were directly exposed to the electron beam. In general, even though copper species in both MSI and conventional nanostructures were found to exist in Cu^(II) state, the MSI-encapsulated one observed an apparent discrepancy. The combinatory features of Cu(OH)₂ and CuO reflect an abnormal coordination of Cu^(III) species in MSI-Cu/TiO₂, resulting in the coexistence of CuO₂ planes, in agreement with the results obtained from HRTEM and EPR.

In the high-resolution XPS spectra of O 1s (Fig. 2D, Fig. S4C), the peaks of lattice oxygen show a shift from -530.3 eV for TiO₂/Cu and SiO₂@TiO₂ to 530.07 eV for MSI-Cu/TiO₂. In fact, the Ti-O-Cu formation creates oxygen vacancies in the interface that negatively charge the surface, and hence causing the shift. Moreover, Cu atoms link to electronegative O atoms in Ti-O-Ti to construct Ti-O-Cu. Consequently, the remaining Ti atoms (Ti⁴⁺) are reduced to Ti³⁺ which can be noticed by the intensity of Ti 2p_{3/2} shoulder peak at around 457.6 eV (Fig. S4D).⁵³ The high intensity was detected for MSI-Cu/TiO₂ (Fig. S4D). This demonstrates the generation of Ti³⁺ due to the SMSI construction.

We investigated chemical bonds within our photocatalysts through Fourier-transform infrared spectra, and the results are shown in Fig. S4E. The broad bands from 3247 cm⁻¹ to 3400 cm⁻¹ are attributed to the stretching vibration of hydroxyl groups in silanol (Si-OH) moiety and adsorbed water molecules.⁵⁴ The deformation vibration mode of O-H bonds is assigned to the band at 1626 cm⁻¹.⁵⁴

The bands around 1109 cm⁻¹ and 806 cm⁻¹ represent the symmetric and asymmetric stretching vibration mode of Si-O-Si bonds, while the band at 953 cm⁻¹ can be due to stretching vibration of Si-O-Ti bonds. FTIR spectroscopy is not sensitive enough to discriminate between interfacial Ti-O-Cu and Ti-O-Si.

Optical properties and photoelectrochemical photon-to-current conversion

The optical properties are evaluated using UV-Vis diffuse reflectance spectroscopy (Fig. S5-A, B). The reference (SiO₂@TiO₂) exhibited strong absorption at the wavelength of below 400 nm. The absorption bands for MSI-Cu/TiO₂ and TiO₂/Cu shift toward the visible region. The Cu-mediated photocatalysts absorbed wavelength from 400 nm to 500 nm, wherein the absorption of MSI-Cu/TiO₂ showed a larger extent. This is due to the charge transfer from O 2p of TiO₂ to the d-orbitals of Cu.⁵⁵ The TiO₂/Cu samples showed a weak absorption band in the range 500–600 nm and much more slightly from 600 nm toward IR, whereas we observed a reverse pattern for MSI-Cu/TiO₂. In fact, the band from 500 to 600 nm could be assigned to the interband absorption of Cu₂O, while the d-d transition of a single electron among 3d⁹ states of Cu²⁺ species is attributed to the broadband from 600 nm toward IR.^{51,56} This clearly evidences that Cu²⁺ species exist in MSI-Cu/TiO₂, while a mixed state with a small amount of Cu¹⁺ might be found in TiO₂/Cu. We used the Tauc method to estimate the bandgap energy of 3.19 eV, 3.23 eV, and 3.24 eV for MSI-Cu/TiO₂, TiO₂/Cu, and SiO₂@TiO₂, respectively.⁵⁷ The 3.24 eV bandgap energy of SiO₂@TiO₂ corresponds to the anatase phase of TiO₂, which is in agreement with HRTEM results and previous studies. A narrower bandgap of the remaining samples can be explained by bandgap alignment between TiO₂ and CuO_x semiconductor composites, which generates the so-called semiconductor heterojunction. In Fig. S6, Mott-Schottky plots of SiO₂@TiO₂, TiO₂/Cu, and MSI-Cu/TiO₂ with positive slope intrinsically demonstrated *n-type* TiO₂. Because Cu content is very low and highly dispersed on the surface of nanostructures, we could not witness any effect of *p-type* CuO_x in these Mott-Schottky plots. We then estimated the flat-band potential, which is Fermi level as no band bending, of our photocatalyst samples. Under UV-Vis irradiation, electrons are excited from valance bands to conduction bands within both semiconductors. These photogenerated electrons are injected among TiO₂ and cuprate clusters through photo-induced interfacial charge transfer (IFCT). This resulted in the rising of the Fermi level, from -0.683 V vs. RHE for pure TiO₂ to -0.725 V vs. RHE and -0.875 V vs. RHE for TiO₂/Cu and MSI-Cu/TiO₂ (Fig. S6). Obviously, the metal oxide-support interaction could favor interfacial charge transfer between cuprate and TiO₂, evidenced by the largest anodic shift of flat-band potential. The shift also demonstrates the increasing extent of interfacial band bending, which optimizes charge carrier separation.⁶⁰ To examine the effect of encapsulation of CuO₂ nanoparticles on the photocatalytic hydrogen evolution reaction (HER), we carried out the electrochemical performance of the HER and OER in K₂SO₄ electrolyte buffered at pH 7 in the presence of argon bubbles. Fig. 3A shows that the current density is markedly improved by



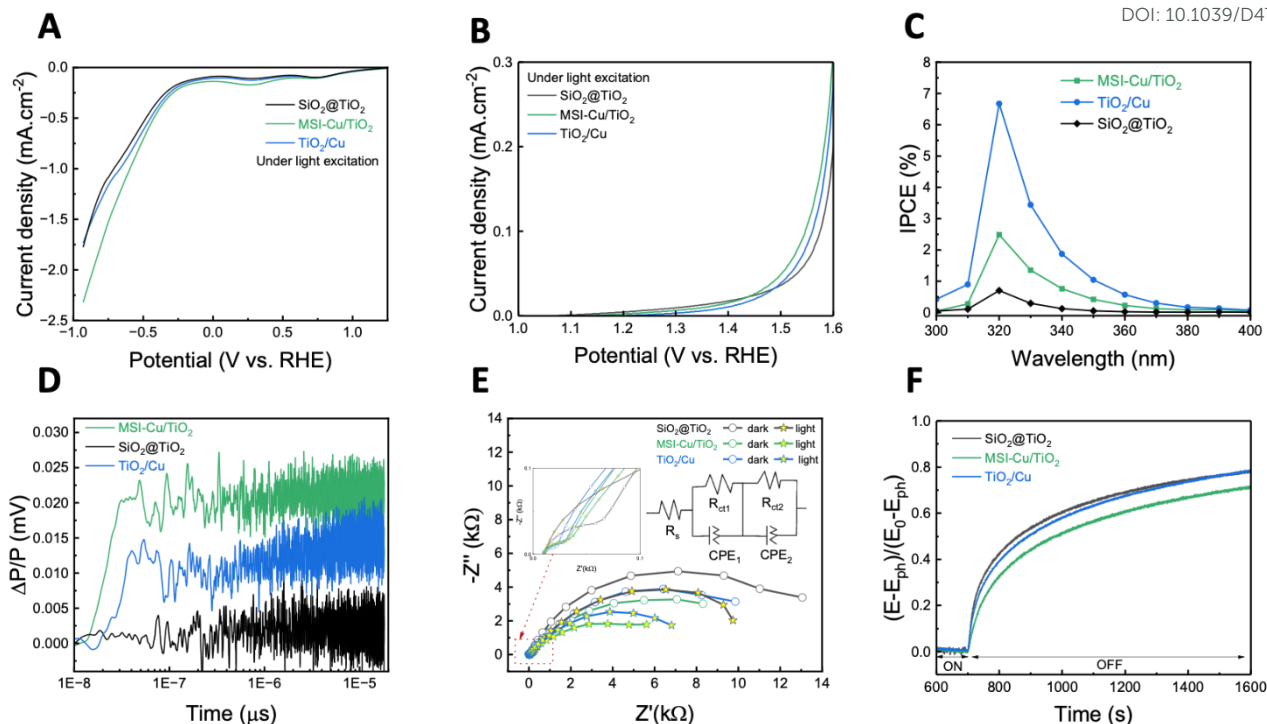


Fig. 3 | Photoelectrochemical, and charge carrier dynamics properties of $\text{SiO}_2@\text{TiO}_2$, $\text{MSI-Cu}/\text{TiO}_2$, and TiO_2/Cu : (A) (B) Electrochemical activity tests on different photocatalysts in phosphate-buffered K_2SO_4 0.5M electrolyte (pH 7) for the (A) HER and (B) OER through linear sweep voltammetry at scan rate of $0.05\text{ V}\cdot\text{s}^{-1}$. (C) Incident photon-to-current efficiency (IPCE) spectra in ultraviolet range ran at a fixed bias voltage of 0.6 V vs. Ag/AgCl 3M ($\sim 1.23\text{ V}$ vs. RHE) in Na_2SO_3 0.1 M buffered at pH = 7 under intermittent illumination triggered from a solar simulator AM 1.5G. (D) Time-resolved Microwave Conductivity (TRMC) signals of the samples triggered by laser irradiation ($I_{\text{ex}} = 6.623\text{ mJ}\cdot\text{cm}^{-2}$ at $\lambda = 420\text{ nm}$). (E) Electrochemical Impedance Spectroscopy (EIS) Nyquist plots of the front-contact photoelectrodes recorded in dark and AM 1.5G illumination in K_2SO_4 0.5M in the range from 10^2 Hz to 100 kHz . (F) Normalized open-circuit potential (OCP) decay curves after switching off AM 1.5G solar irradiation.

the encapsulation of Cu and its abnormal coordination. More interestingly, the encapsulation of Cu increases the current density not only in HER but also in oxygen evolution reaction (OER) that $\text{MSI-Cu}/\text{TiO}_2$ could be utilized as a photoanode in photoelectrochemical water splitting cell (Fig. 3B). The results demonstrate that the intrinsic HER activity can be significantly improved by covering copper by TiO_2 overlayer.

Amperometric photocurrent measurement provided valuable insights into charge carrier mobilities and their trapping within the photocatalysts by examining photocurrent responses (current rise, current decay, etc.). After the light was switched on, photogenerated electron-hole pairs were separated rapidly, charging space charge capacitance. Typically, photocurrent instantaneously rises to a peak value before decaying to a steady state due to electron-hole recombination, accumulation of electrons in bulk or holes on the surface, and trapping of electrons or holes at surface defects.⁶¹ We employed sulfite (SO_3^{2-}) in electrolyte solution to optimize light capture and charge transport. In our case, holding accumulation can be ruled out as a main recombination mechanism thanks to adding sulfite ions as hole scavengers. The higher photocurrent response of TiO_2/Cu reveals the superior separation of photogenerated charge carriers to those in $\text{MSI-Cu}/\text{TiO}_2$ and $\text{SiO}_2@\text{TiO}_2$ (Fig. S5C). While $\text{SiO}_2@\text{TiO}_2$ outputted a relatively steady-state photocurrent response, $\text{MSI-Cu}/\text{TiO}_2$ and TiO_2/Cu exhibited gradually rising photocurrent curves with no spike. This could be explained by larger depletion layers near the

surface or interface of semiconductor-liquid, leading to effective charge carrier separation.

Photocurrent action spectra, including IPCE and APCE under UV and visible illumination (Fig. 3C and Fig. S5-D,E,F), further examine the photocurrent as a function of the wavelength at an applied bias of 1.23 V vs. RHE. Around 1% of the incident photon at $\lambda = 320\text{ nm}$ was absorbed by $\text{SiO}_2@\text{TiO}_2$ photoelectrode to contribute to the photocurrent on the outer circuit. The other 99% was lost due to charge carrier recombination within the material. The external quantum efficiency (IPCE, Fig. 3C) was much greater at 2.5 % for $\text{MSI-Cu}/\text{TiO}_2$ and nearly 7% for TiO_2/Cu . When considering only charge carrier recombination as a main effect on photocurrent response, we estimated the internal quantum efficiency (APCE, Fig. S5E) at over 5% for $\text{MSI-Cu}/\text{TiO}_2$ and 9% for TiO_2/Cu . Cu-modified photocatalysts converted visible photons to current despite a negligible extent, while $\text{SiO}_2@\text{TiO}_2$ was unactive in the visible range (Fig. S5-D,F). These experimental outputs are consistent with the one of UV-vis DRS and amperometric photocurrent response measurements.

We investigated charge carrier dynamics at microsecond and nanosecond timescales by time-resolved microwave conductivity spectroscopy (TRMC) and time-resolved photoluminescence spectroscopy (TRPL). Fig. S7A displays TRMC spectra of three photocatalysts triggered by an ultraviolet laser at 360 nm, where TiO_2 is activated only. In detail, the signal of $\text{SiO}_2@\text{TiO}_2$ observed the highest maximum intensity and a



Table 1 | Parameters obtained from EIS, Mott-Schottky, and OCP decay measurements.

Samples		^a R _{ct2} (Ω)	^b E _{fb} (V _{RHE})	^c k _r (s ⁻¹)
SiO ₂ @TiO ₂	light	11722	-0.683	1 × 10 ⁻⁶
	dark	14510		
TiO ₂ /Cu	light	8465.8	-0.725	2.5 × 10 ⁻⁷
	dark	13022		
MSI-Cu/TiO ₂	light	6826.6	-0.875	1.9 × 10 ⁻⁸
	dark	11175		

^aR_s, R_{int}, R_{ct} were estimated by EIS plot fitting. ^bE_{fb} values were determined from Fig. S6. ^ck_r was obtained by fitting OCP curves in Fig. S7C.

sharp decay, while MSI-Cu/TiO₂ outputted two times smaller maximum intensity but a long-lasting signal. In fact, electrons, the primary mobile charge carriers in TMRC,⁶¹ were generated in bulk and then transferred to the surface of TiO₂. The sharp TRMC decay of SiO₂@TiO₂ reflects the disappearance of electrons, which could be attributed to electron-hole recombination or surface trapping. Coupling TiO₂ with cuprate nanoparticles induces surface defects, including oxygen vacancies and Ti³⁺, which are trapping sites.⁶¹ Although the trapping hinders electron transport within the crystalline structure, it precludes electron-hole recombination, leading to a longer charge carrier lifetime. Surprisingly, we recorded the TMRC signal of TiO₂/Cu at a much lower maximum intensity. These results suggested that less surface defects are created in this system. We recorded the TRMC signal under visible laser excitation (λ_{ex}=420 nm), activating only cuprate oxide. As a result, in Fig. 3D, the TRMC signal of SiO₂@TiO₂ displayed flat fluctuation at 0 mV, while those of the composites showed higher charge density and an unexpectedly longer lifetime. The visible laser generates charge carriers, mainly electrons, within the CuO₂ band structure. These electrons are injected into the conduction band of TiO₂, while holes are accumulated into the valence band of CuO₂. This inhibits charge carrier recombination and thus prolongs charge carrier lifetime, as evidenced by non-decayed TRMC signals. TRPL spectroscopy further elucidated charge carrier dynamics at nanosecond timescale *via* inspecting photons released from the relaxation of photogenerated charges. Time-resolved photoluminescence (TRPL) in Fig. S7B exhibited the sharpest decay with respect to MSI-Cu/TiO₂, followed in order by the one of TiO₂/Cu and SiO₂@TiO₂. The high probability of electron-hole recombination within SiO₂@TiO₂ would be responsible for its slighter TRPL decay. In the case of TiO₂/Cu and MSI-Cu/TiO₂, non-irradiated relaxation of electrons, such as electron trapping and transfer, are more favorable, leading to sharper TRPL decay. These experimental results are consistent with the TRMC analysis.

The charge transport capability in the CuO₂/TiO₂ interface was studied by electrochemical impedance spectroscopy (EIS). The data was fitted to an equivalent circuit model (inset Fig. 3E) involving two parallel branches (R_{ct1} and CPE₁) derived from the interfacial contact between FTO and semiconductive materials. R_{ct2} and CPE₂ represent charge transfer resistance and double-layer capacitance, respectively, at the electrode and electrolyte interface, and R_s stands for Ohmic resistance. To address electrochemical phenomena on a non-uniform surface, it is

essential to incorporate constant phase elements (CPE) with an ideality factor (n) to characterize double-layer capacitance and/or coating capacitance rather than relying on ideal capacitors. Nyquist plots were obtained from electrochemical impedance spectroscopy (EIS) measurements in both dark and under UV-visible irradiation, employing a K₂SO₄ 0.5M electrolyte solution. The first compact semicircles (inset Fig. 3E) might be due to the interfacial contact between FTO glass electrode and our photocatalysts. The second larger semicircle typically translates the charge transfer impedance between photoelectrode and electrolyte. SiO₂@TiO₂ registered the largest values of charge transfer resistance, followed by TiO₂/Cu, and the smallest values belong to MSI-Cu/TiO₂ (Table 1). The result reveals that charge transport is more favorable for CuO₂/TiO₂ composites. Moreover, the low value of charge transfer resistance on MSI-Cu/TiO₂ demonstrates that strong metal oxide-support interaction efficiently contributes to the charge carriers' transfer and separation. Upon illumination condition, the composites became more inductive, evidenced by the smaller diameter of Nyquist semi-circles. This can be ascribed to the abnormal Cu coordination that facilitates charge transfer.

Open-circuit potential (OCP) decay analysis offers information about surface recombination between trapped electrons and reaction intermediates. In fact, the charge carrier recombination occurs at nanoseconds or microseconds timescale, while OCP decay takes several minutes. Open-circuit voltage (V_{oc}) is the difference in Fermi level between a photoelectrode and a counter electrode. Upon illumination, photogenerated electrons fill up the Fermi region and shift the Fermi level toward anodic potentials. Following this, the recombination of photogenerated charge carriers occurs and maintains equilibrium with their accumulation at the interface, resulting in a steady state of V_{oc}. When switching the light off, V_{oc} decays upon recombination process due to a lack of charge carrier generation. The normalized transient decay profiles of OCP are illustrated in Fig. 3F. The results demonstrate that MSI-Cu/TiO₂ exhibited the most gradual OCP decay, indicating low surface recombination of charge. An average recombination rate constant k_r can be estimated by fitting the OCP decay profile with a pseudo-first-order kinetic model equation⁶²:

$$\frac{E - E_{ph}}{E_0 - E_{ph}} = 1 - e^{-k_r t}$$



where E is OCP at any time (V), E_0 is the stationary OCP in dark, E_{ph} is the stationary OCP under illumination, k_r is pseudo first-order recombination rate constant (s^{-1}). In this study, we performed fitting decay curves in Matlab (Fig. S7C); the corresponding value of the recombination rate constant was listed in Table 1. In detail, the recombination rate of MSI-Cu/TiO₂ is around 50 times and 13 times smaller than that of SiO₂@TiO₂ and TiO₂/Cu, respectively. This outcome evidences the role of abnormal Cu coordination induced by strong metal oxide-support interaction in enhancing charge carrier separation within the photocatalyst.

Photocatalytic hydrogen production

The photocatalytic activity of photocatalysts was evaluated following the accumulated hydrogen produced under UV-visible light illumination from methanol/water solution (1:3 v/v). We employed X-ray Fluorescence spectrophotometry (XRF) to quantify the mass percentage of either elements (Si, Ti, O, Cu)

or oxides (SiO₂, TiO₂, CuO_x) in our powder samples. Notably, the insulating SiO₂ occupies approximately 85 wt.% while the remaining active phase (TiO₂ and CuO_x), which is involved in photocatalytic reactions, accounts for 15% wt. As a result, we refined the photocatalytic H₂ evolution rate based on the mass percentage of the active phase. As shown in Fig. 4A, MSI-Cu/TiO₂ exhibited the highest yield of photocatalytic hydrogen production, reaching nearly 60 mmol.g⁻¹ after 5 hours of UV-Vis irradiation. The amount of H₂ generated was approximately twice lower (35 mmol.g⁻¹) for TiO₂/Cu, and only a negligible amount of H₂ was obtained in the sample without CuO₂. Undoubtedly, the synergistic combination of TiO₂ and CuO₂ significantly enhanced the photocatalytic activity for the H₂ generation reaction. This is in line with the enhancement of charge carrier separation and lifetime, as corroborated by PEC results, and despite TiO₂/Cu demonstrating superior absorbed photon-to-current efficiency, evidenced by IPCE and APCE, MSI-Cu/TiO₂ outperformed others in terms of overall photocatalytic

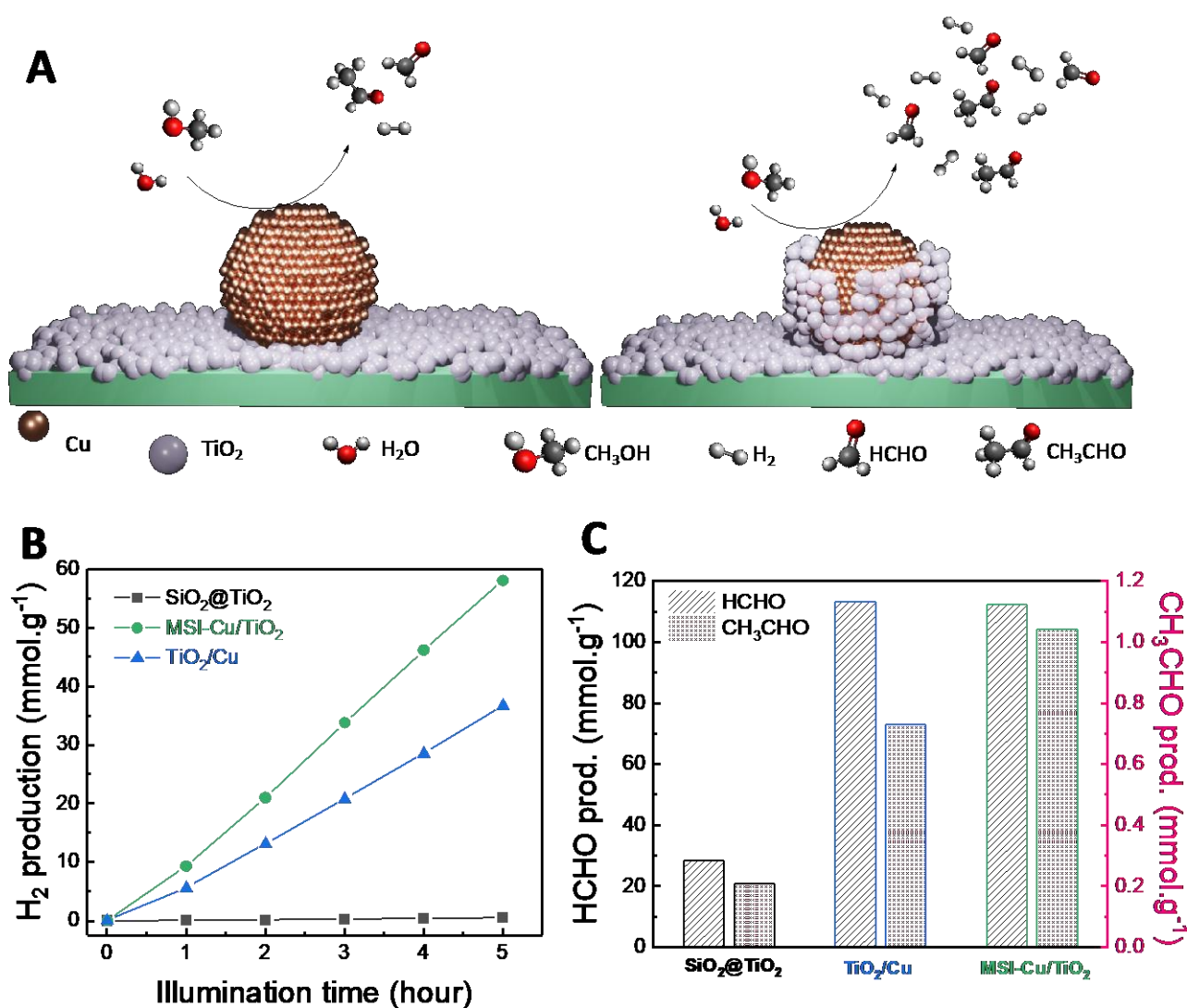


Fig. 4 | Photocatalytic activity of SiO₂@TiO₂, MSI-Cu/TiO₂, and TiO₂/Cu: (A) Graphic illustration of photocatalytic reactions occurring on TiO₂/Cu and MSI-Cu/TiO₂ photocatalysts. (B) Hydrogen production investigated by gas chromatography. (C) Formaldehyde and acetaldehyde production investigated by high performance liquid chromatography. Reaction conditions: 10 mg/10 mL photocatalyst, 25°C, H₂O:CH₃OH = 3:1 v/v, UV-Visible irradiation Mercury lamp 150W.



efficiency. This superiority is closely linked to the charge carrier dynamics within the nanostructures, which are pivotal in improving photocatalytic activity. The observed color change during the photocatalytic reaction of MSI-Cu/TiO₂ from greenish to dark red testifies to a change in the oxidation state of Cu (Fig. S8B). Indeed, some photogenerated electrons could be promoted from TiO₂ to unoccupied d⁹ orbitals of Cu^{II}, resulting in a fulfilled d¹⁰ state of Cu^I. More interestingly, the MSI-Cu/TiO₂ turned back to its original greenish color, without air exposure, when illumination was cut off, reflecting the release of the photoelectrons from cuprate to TiO₂. However, TiO₂/Cu displayed no color change, demonstrating a less effective change in the oxidation state of Cu. The partial coverage of TiO₂ onto CuO₂, practicing strong metal oxide-support interaction, generates a significant number of active sites for photocatalytic reactions, thereby enhancing the overall reaction yield. A 20-hour photocatalytic cycling experiment was performed to evaluate the stability of the MSI encapsulation layer and TiO₂/Cu sample. As shown in Fig. S8A, a decrease in the amount of H₂ produced is observed for both samples. The H₂ generation decreased by 15% for both systems in the second cycle. The decrease is mainly due to the loss of part of the sample during the recovery by centrifugation. Indeed, after the second cycle, a decrease in H₂ generation is still observed for SMSI (~10%), while TiO₂/Cu shows relatively good stability. After the third cycle, the SMSI system shows relatively good stability and remains more efficient in H₂ generation than TiO₂/Cu (Fig. S8A).

The photoactivation mechanism and H₂ generation over the MSI-Cu/TiO₂ sample is depicted in Fig. 5. Under light excitation, electrons, and holes are generated in the conduction and valence bands of TiO₂, respectively. Photogenerated electrons are transferred to copper, resulting in the reduction of Cu(II) to

Cu(I), as evidenced by the change of the sample's color from green to rust color (dark red) (Fig. S8B). The protonation at TiO₂ overlayer active sites consumes electrons and induces a building field that induces the diffusion of scavenged electrons at d-orbitals of Cu back to the TiO₂ conduction band. When UV-visible illumination was cut off, the electrons at Cu sites were released back to ensure charge balance within the band structure; this was observed by the reversion to the original sample color as well as the oxidation of Cu(I) to Cu(II). In the case of holes, they are scavenged by the sacrificial electron donor molecules (methanol).

To explore the photocatalytic H₂ generation pathway, we extended our investigation to trace intermediates produced during illumination in the liquid phase. Following five hours of illumination, reaction solutions were extracted and injected into a high-performance liquid chromatography (HPLC) – ultraviolet-visible spectroscopy detector. Formaldehyde (HCHO) and acetaldehyde (CH₃CHO) were detected in the liquid phase; HCHO was identified as a primary product from photocatalytic methanol reforming reactions. The production yields of these intermediates were visualized in Fig. 4C, where SiO₂@TiO₂ exhibited the smallest production yield of HCHO compared to the cuprate-mediated samples. This result points out the low kinetic conversion of CH₃OH to HCHO. TiO₂/Cu exhibited a slightly greater extent of the HCHO/CH₃CHO ratio than MSI-Cu/TiO₂. The dissociative adsorption of MeOH, right after the e⁻/h⁺ generation, leads to the formation of HCHO, followed by the release of H⁺. In particular, CH₃OH molecules convert to methyl hydroxyl radicals ([•]CH₂OH) through C-H activation. Then, radicals react with oxidative holes and produce formaldehyde (HCHO). Hydrogen ions generated during reactive transformation would capture photogenerated electrons and combine to release H₂ molecules. MSI-Cu/TiO₂

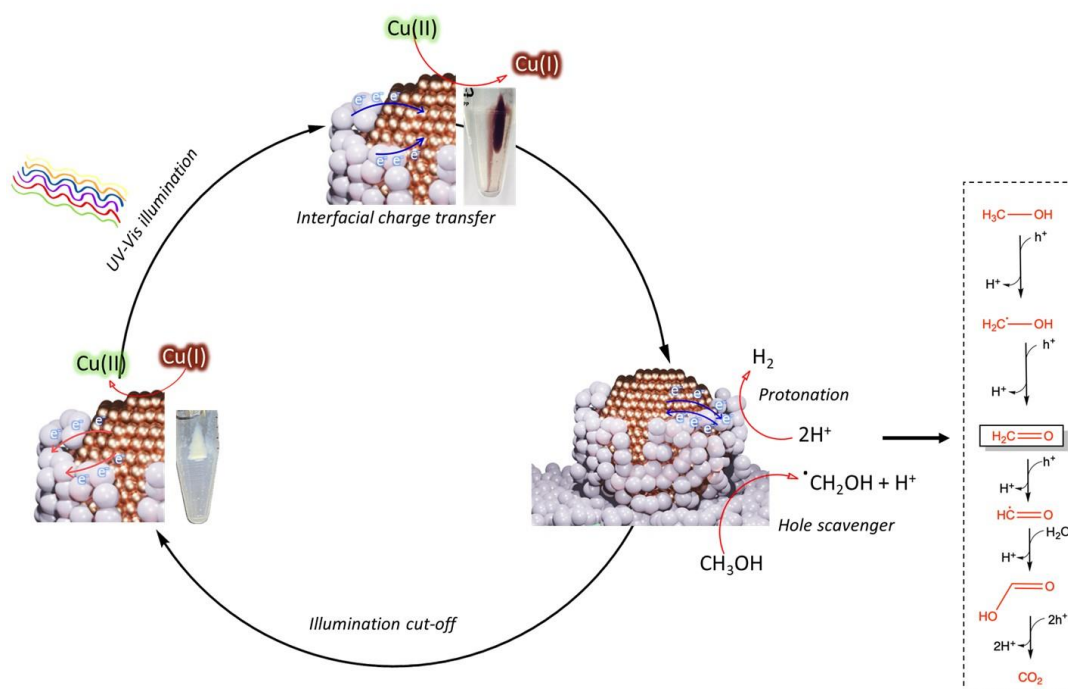


Fig. 5 | A schematic illustration of the photocatalytic hydrogen production mechanism with electron transfer pathways and the change in valence state of copper on MSI-Cu/TiO₂



generated higher production of CH₃CHO than TiO₂/Cu, probably due to more likely accessibility of O_{vac} and Ti³⁺ on the surface in the TiO₂ surface facilitated by the abnormal Cu coordination that fastened the photocharges transfer. Although converting CH₃OH to HCHO is more efficient for TiO₂/Cu than MSI-Cu/TiO₂, the H₂ evolution yield for MSI-Cu/TiO₂ was remarkably greater. In the case of TiO₂/Cu, the active sites are likely in the vicinity of the CuO₂-TiO₂ interface, which is typically associated with steric hindrance and low charge transfer. To address this limitation and enhance the kinetic of HCHO oxidation reactions, the position of CuO₂ and TiO₂ could be switched, promoting strong oxide-support interaction through partial encapsulation.

Conclusions

In this study, we present a soft-chemistry approach to construct composite photocatalysts, wherein a TiO_x shell encapsulates highly dispersed CuO₂ nanoclusters on a SiO₂ core. The fine structure was characterized by transmission electron microscopy (TEM, HRTEM, STEM), in combination with EELS chemical mapping and LEIS, which confirmed the partial coverage of TiO₂ onto copper metallic species. Surface analysis through EPR and XPS highlighted the existence of Cu sites coordinated with four oxygen in the case of MSI-Cu/TiO₂. Compared to conventional TiO₂/Cu, it exhibited a superior photocatalytic yield in the hydrogen evolution reaction. We demonstrated optimal charge carrier dynamics and photon-to-current conversion efficiencies within the SMSI-like nanostructure MSI-Cu/TiO₂ using photoelectrochemical measurements and time-resolved spectroscopy techniques. In addition, the results underscore the dominance of charge carrier dynamics in driving photocatalytic enhancement.

Experimental

Photocatalyst preparation

Synthesis of monodispersed SiO₂ microspheres. Silica microspheres with a 150-200 nm diameter were synthesized following the Stöber method⁶³. A mixture of 42 mL of EtOH and 35 mL of distilled water was stirred in a borosilicate bottle for 10 minutes at room temperature before adding 15 mL of NH₄OH 28% to adjust pH. Once the temperature had been raised to 40°C, 4 mL of TEOS was pipetted to the bottle; the mixture remained stirring for 1h. After that, the white precipitate was centrifuged, washed 3 times with distilled water, and dried at 70°C overnight.

APTMS functionalization. To deposit metal nanoparticles onto the SiO₂ surface, we employed APTMS as a coating agent; 300 mg of SiO₂ beads were then dispersed in 10 mL of EtOH. Next, 0.1 mL of APTMS was added to the mixture under stirring. After six hours of stirring, the APTMS-functionalized SiO₂ was centrifuged and washed with EtOH. The functionalization process was repeated for SiO₂@Cu and SiO₂@TiO₂ before coating with a TiO₂ shell and metallic nanoparticles.

Synthesis of Cu nanoparticles to obtain SiO₂@Cu or SiO₂@TiO₂@Cu. APTMS-functionalized SiO₂ or SiO₂@TiO₂ was

dispersed in a solution containing the desired amount of CuCl₂·2H₂O in a round-bottom flask. The volume of the mixture was adjusted to achieve a Cu²⁺ concentration of 0.1M. After sonication for 1 hour, the mixture was purged with Ar for one additional hour and heated to 80°C. Then, 0.82 M of ascorbic acid was added dropwise to the flask at 2 drops per second while vigorously stirring, ensuring a final concentration of 0.4M. The system was heated for an additional 30 minutes after all the ascorbic acid was added. The mixture was cooled to room temperature, and the pH was adjusted to 8 using tetramethylammonium hydroxide. After overnight stirring, the resulting solid was centrifuged, washed thoroughly with H₂O, and dried at 70°C overnight.

Coating cores with TiO₂ thin shell. SiO₂@Cu and SiO₂ cores were coated with a TiO₂ shell through the hydrolysis of TTIP in basic media. In detail, the core nanoparticles were firstly dispersed in 20 mL of EtOH and 0.5 mL of H₂O. Next, this pH was adjusted at 12.4 by adding 0.3 mL of NH₄OH 28%, followed by stirring for 20 minutes. Concurrently, 1.5 mL of TTIP was dissolved in 50 mL of absolute EtOH. This mixture was dropped slowly to the basic solution containing core nanoparticles under stirring at room temperature. After two hours of aging, final core-shell nanocomposites were obtained by centrifugation, then washed carefully with absolute EtOH, and finally dried at 70°C overnight. The photocatalysts need to be calcinated at 500°C for 2 hours at a temperature elevation speed of 2°C/minute.

(Photo)electrochemical measurements

Photoelectrochemical measurements and electrochemical impedance analysis, including amperometry transient photocurrent (TPC), electrochemical impedance spectroscopy (EIS), Mott-Schottky, and open-circuit voltage decay, were carried out in a three-electrode electrochemical cell with/without illuminating by AM 1.5G solar simulator. Photoelectrodes were fabricated by drop-casting 100 μL of an ultrasonicated solution (2mg·mL⁻¹) of our samples on fluorine-doped tin oxide-coated glass slides of 2.5 cm² (FTO glass) before drying overnight at room temperature. The electrochemical setup involved a platinum disk counter electrode and an Ag/AgCl (saturated KCl) reference electrode. The values of potential vs. Ag/AgCl were converted to those vs. RHE through the following equation:

$$E_{RHE} = E_{Ag/AgCl} + 0.197 + 0.059 \times pH$$

Experiments were manipulated by potentiostat PGSTAT101 Metrohm Autolab. An open-circuit voltage decay fitting was executed using the inverse method on Matlab. When the numeric and experimental curves show superimposition, the fitting is reliable for estimating important parameters such as the recombination rate constant.

Photocatalytic hydrogen evolution tests

The photocatalytic activity of our photocatalyst was evaluated *via* a hydrogen evolution reaction. Reaction conditions remained identical: the amount of photocatalyst at 10 mg/10 mL, room temperature, and testing duration of five hours under



UV-visible irradiation triggered by a Mercury lamp (150W). Reactors were degassed by argon for 20 min to remove dissolved oxygen completely before illumination. Gaseous products were quantified by the Agilent 990 micro gas chromatography (GC) system facilitated with a thermal conductive detector (TCD). Liquid phase products were detected by high-performance liquid chromatography (HPLC) on Agilent 1260 Infinity with a UV-Vis detector.

Author Contributions

V. D. Quach carried out and set up the design of the experiments and investigation process, data curation, wrote the initial draft, and reviewed and edited the final manuscript. M. C. Spadaro, M. Botifoll, and J. Arbiol performed the electron microscopy analyses and discussed their results. D. Dragoe performed XPS measurements and discussed the results. R. Wojcieszak, H. Vezin, and F. Dumeignil carried out LEIS and EPR; R. Wojcieszak discussed the LEIS result. C. Colbeau-Justin instructed V.D.Quach in TRMC. M. N. Ghazzal conceptualized and conceived the idea, acquired financing, supervised the work, contributed to the manuscript skeleton, and reviewed and edited the final manuscript. The manuscript was written with the help of all the co-authors.

Conflicts of interest

There are no conflicts to declare.

Acknowledgments

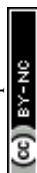
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