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Interdigitated MgO/Au front selective contacts for enhanced photocatalytic systems based on TiO₂ as light-absorber

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Selective charge extraction is a central limitation in heterogeneous photocatalysis, where short carrier diffusion lengths and interfacial recombination strongly restrict efficiency. Here we translate the photovoltaic concept of selective contacts to photocatalytic systems by designing interdigitated front architectures on a planar TiO₂ absorber. Magnesium–magnesium oxide (Mg–MgO_x) is used as an electron-selective layer, while gold nanoparticles act simultaneously as hole-selective contacts, plasmonic enhancers, and charge-transfer mediators toward gas-phase reactants. Interdigitated Mg–MgO_x/Au patterns with controlled coverage and perimeter were fabricated on sol–gel anatase TiO₂ films and tested for hydrogen production from ethanol–water vapor mixtures under UV illumination. While Au nanoparticles alone strongly enhance activity through efficient hole extraction and plasmonic effects, the addition of Mg–MgO_x enables selective electron collection. However, performance is not governed by Mg–MgO_x coverage alone. Samples with similar Mg–MgO_x area fractions but different geometries show markedly different hydrogen production rates. To rationalize this behavior, we introduce a dimensionless geometric parameter η , defined as the normalized ratio between selective-contact perimeter and coverage. Hydrogen production follows a Langmuir–Hinshelwood-type kinetic model when expressed as a function of η , demonstrating that interfacial length, rather than area alone, controls the number of photogenerated carriers that reach adsorbed reactants before recombining. Highly interdigitated samples show up to a twofold increase in hydrogen production compared to non-patterned TiO₂/Au references, despite having comparable material composition.

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Broader context

Sustainable hydrogen production is a cornerstone of global efforts to decarbonize energy systems, enabling low-carbon fuel cycles and providing storage pathways for intermittent renewable electricity. Photocatalysis, the direct use of sunlight to drive chemical reactions, offers a scalable route to produce hydrogen without electricity or high-temperature processes, but its efficiency is fundamentally limited by rapid recombination of photogenerated charge carriers at interfaces. In this work, we adapt selective contact concepts from photovoltaic technology to photocatalytic systems by engineering interdigitated electron- and hole-selective regions on a planar titanium dioxide (TiO₂) absorber. Specifically, magnesium–magnesium oxide (Mg–MgO_x) acts as an electron extractor while gold nanoparticles serve both as hole collectors and plasmonic enhancers. Through systematic experimentation with varying contact geometries, we show that hydrogen production is governed not by material coverage alone but by the interplay between interface length and carrier extraction efficiency, captured by a new dimensionless geometric parameter. Our findings reveal that optimized interdigitated architectures can nearly double hydrogen yield compared with non-patterned references. These insights provide a generalizable design principle for enhancing photocatalytic performance and help bridge the gap between fundamental photocatalysis research and the development of practical solar-to-fuel technologies.

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1. Introduction

Photocatalysis enables the direct conversion of solar energy into chemical fuels by coupling light absorption with surface redox reactions. Among the processes explored, water splitting and the photo-reforming of simple hydrocarbons have attracted particular attention as routes for hydrogen production.¹ Hydrogen is a clean and energy-dense fuel that can act as both an energy carrier and storage medium, highlighting photocatalysis as a promising approach for solar-to-fuel technologies.²

Photocatalytic performance is fundamentally limited by non-radiative recombination, largely arising from defect-induced mid-gap states in the semiconductor. A common strategy to mitigate these losses is to increase crystallinity while reducing characteristic dimensions, thereby shortening the distance that photogenerated carriers must travel to reach the surface. When this transport length approaches the carrier diffusion length, recombination losses are reduced and photocatalytic efficiency improves.

Beyond bulk recombination, photocatalytic performance is also limited by inefficient carrier transport and extraction to active reaction sites. This is typically addressed by incorporating co-catalysts, which enhance carrier extraction and facilitate charge transfer from the solid to the surrounding medium. Metallic nanoparticles, particularly noble metals, are widely used due to their multifunctional role: they can promote interfacial charge transfer, induce band bending through their high work function, and, in some cases, enhance light absorption *via* localized surface plasmon resonance.³

An alternative approach to improve charge separation involves engineering semiconductor heterojunctions, such as Z-scheme and S-scheme configurations.⁴ These architectures exploit favorable band alignments to spatially separate electrons and holes, thereby reducing recombination. In addition, combining semiconductors with different band gaps can extend light absorption across a broader spectral range.⁵

In solar cell technology, charge separation and extraction are achieved using transport materials and selective contacts, commonly referred to as electron and hole transport layers (ETLs and HTLs). These layers selectively extract one type of carrier while blocking the other, thereby reducing interfacial recombination and enforcing spatial separation of electrons and holes. In addition, they often provide surface passivation, further suppressing recombination at the absorber interface. This combined effect has been central to the efficiency improvements achieved in modern photovoltaic devices.⁶

From this perspective, the widespread use of metallic co-catalysts and semiconductor heterojunctions in photocatalysis can be viewed as conceptually analogous to selective contacts in solar cells.³ More broadly, selective contacts describe interfacial layers that promote directional carrier extraction, enforce spatial separation of electrons and holes, and suppress recombination losses.^{7,8} While these principles have been systematically exploited in photovoltaics to achieve

record efficiencies at both laboratory^{9,10} and commercial scales,¹¹ their implementation in photocatalysis remains less controlled at the device level.

Applying the selective-contact paradigm to photocatalysis is not straightforward. Most photocatalysts exhibit highly nanostructured morphologies, which makes the controlled integration of separate electron- and hole-transport layers difficult. Although a few studies have demonstrated such architectures,^{12–14} their fabrication remains complex and has not yet become a broadly applicable strategy.

In this work, we extend the selective-contact concept to a photocatalytic device based on a planar TiO₂ absorber. Gold nanoparticles (Au NPs) are incorporated as multifunctional elements that act both as hole-selective contacts and as charge-transfer mediators between the solid-state device and gas-phase reactants. In addition, a Mg–MgO_x electron-transport layer is introduced to enhance charge separation and extraction. Within this architecture, the TiO₂/Au interface preferentially extracts photogenerated holes to drive alcohol oxidation, while the TiO₂/Mg–MgO_x interface selectively collects electrons. Au nanoparticles deposited on the Mg–MgO_x regions further facilitate electron transfer toward hydrogen evolution reaction (Fig. 1a).

To spatially organize these selective extraction pathways, we adopt the photovoltaic concept of interdigitated contacts. In solar cells, interdigitated architectures eliminate front-side metallization shading by relocating metallic contacts to the rear of the device. Their design is governed by the carrier diffusion lengths in the absorber, allocating larger collection areas to minority carriers while majority carriers can be collected over wider regions due to their longer diffusion lengths.^{15,16} In the present photocatalytic system, interdigitated contacts are likewise advantageous because oxide semiconductors typically exhibit short carrier diffusion lengths. Moreover, under continuous gas-flow operation the lifetime of reactive intermediates is limited, requiring oxidation and reduction sites to be placed in close proximity to suppress back reactions caused by local charge imbalance (Fig. 1b).

Using this approach, we fabricate and characterize photocatalytic devices with interdigitated Mg–MgO_x/Au selective contacts and evaluate their hydrogen production performance. Unlike previously reported strategies based on nanoscale separated dual cocatalyst decoration^{12–14,17} or facet-dependent redox separation,^{18–20} the interdigitated architecture is implemented at the device scale (hundreds of micrometers to millimeters), enabling controlled spatial organization of electron- and hole-extraction pathways across the absorber surface. Although a semiconductor junction is present, this architecture differs fundamentally from Z-scheme or S-scheme photocatalysts because the MgO_x layer is ultrathin and does not contribute to light absorption, acting instead purely as an electron-selective contact. By correlating photocatalytic activity with both the device electronic structure and the geometry of the interdigitated pattern, we demonstrate that device-level contact architecture can strongly influence photocatalytic performance.



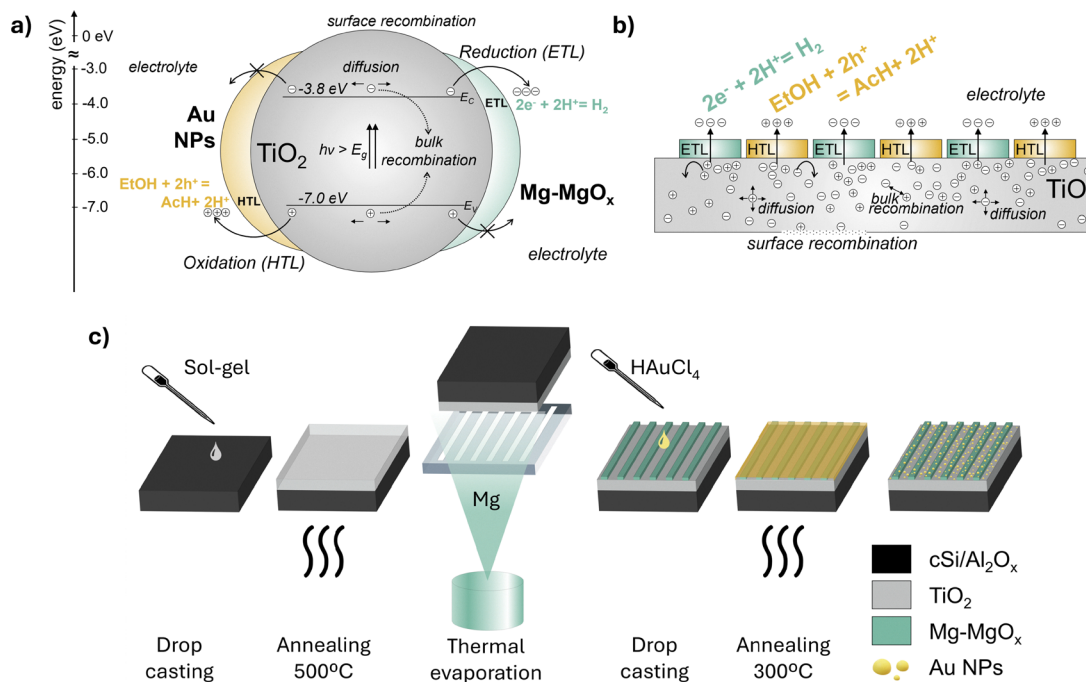


Fig. 1 (a) Energy-level schematic of the photocatalytic process in a generic nanostructured TiO_2 absorber incorporating ETL and HTL layers. (b) Schematic illustration of the electronic and photocatalytic processes occurring in a planar TiO_2 device equipped with ETL and HTL contacts. (c) Fabrication steps of the interdigitated samples investigated in this work.

2. Experimental section

2.1. Preparation of TiO_2 thin films

TiO_2 thin films were prepared by a sol-gel method using titanium(IV) propoxide as precursor. The precursor was dissolved in absolute ethanol under an argon atmosphere and hydrolyzed by the controlled addition of hydrochloric acid and water under continuous stirring. The resulting sol was diluted with ethanol to obtain a deposition solution.

Silicon wafers coated with an insulating Al_2O_x layer deposited by atomic layer deposition ($\text{cSi}/\text{Al}_2\text{O}_x$) were used as substrates. The substrates were cut into $2 \times 2 \text{ cm}^2$ pieces and coated by drop casting the TiO_2 sol, followed by drying at room temperature for 24 h. The films were calcined in air at $500 \text{ }^\circ\text{C}$ for 4 h ($5 \text{ }^\circ\text{C min}^{-1}$ ramp) to obtain anatase TiO_2 . To minimize cracking and ensure full surface coverage, three successive TiO_2 layers were deposited. The resulting TiO_2 absorber films had a typical thickness of $1.5 \pm 0.3 \text{ }\mu\text{m}$.

2.2. Fabrication of interdigitated front contacts

Magnesium electron-selective contacts were deposited by thermal evaporation in a glovebox-integrated UNIVEX 350G vacuum system at a base pressure of $\sim 10^{-5}$ mbar. Deposition was monitored using a quartz crystal microbalance, yielding Mg layers with a nominal thickness of 10 nm. Interdigitated patterns were defined using manually assembled shadow masks made from simple mechanical spacers and masking materials. After deposition, samples were stored under nitrogen atmosphere to limit uncontrolled Mg oxidation.

Gold nanoparticles were introduced by drop casting $150 \text{ }\mu\text{L}$ of a 0.1125 M HAuCl_4 solution, corresponding to a 1:100 Au: TiO_2 mass ratio. The samples were dried at $50 \text{ }^\circ\text{C}$ and annealed at $300 \text{ }^\circ\text{C}$ for 1 h in air to form and anchor Au nanoparticles on the TiO_2 surface.

2.3. Photocatalytic hydrogen production

Photocatalytic experiments were carried out in a continuous-flow glass reactor using a gaseous ethanol-water mixture (9:1 molar ratio) carried by argon (20 mL min^{-1}). Samples were illuminated using a 500 W Hg-Xe solar simulator delivering UV-A irradiance of 72 mW cm^{-2} at the sample surface. Reaction products were monitored online by micro-gas chromatography.

Further experimental details, including the detailed fabrication procedures, characterization methods and photocatalytic measurement protocols, are provided in the SI.

3. Results and discussions

3.1. Sample characterization

We fabricated several samples with different Mg layer geometries. Table S1 shows 3D sketches of the most representative samples together with the geometric characteristics of the Mg interdigitated patterns. Samples are labeled as T-MgX-Au, where T denotes the TiO_2 catalytic absorber and the increasing values of X correspond to a more interdigitated pattern of Mg that results in a larger perimeter of the Mg-MgO_x pattern.



The TiO₂ absorber layer was first examined by Raman spectroscopy. The spectra confirmed the presence of the anatase phase²¹ with no detectable traces of rutile or brookite, the other two common TiO₂ polymorphs (Fig. S2). The surface morphology of the absorber was investigated by SEM, revealing a continuous TiO₂ layer containing cracks; however, these cracks did not reach the underlying c-Si/Al₂O₃ substrate due to the deposition of three consecutive sol-gel layers (Fig. S3a and b). Owing to the ultrathin nature of the Mg films, Mg deposited onto TiO₂ can infiltrate these cracks, but it does not fill them or coat them conformally (Fig. S3c and d).

XPS analysis of the Ti 2p and O 1s core levels further verified the presence of TiO₂ films for samples containing both Mg and Au (Fig. 2a, b and Fig. S4a, b). The Mg 1s peak at 1304.6 eV²² (Fig. 2c) and the Mg 2p peak at 51.0 eV²³ (Fig. 2d) confirm that the Mg layer was fully oxidized to MgO_x during the annealing step required for Au nanoparticle formation. This is expected due to the air atmosphere used during the heat treatment. Importantly, this oxidation is beneficial for the device design: transforming metallic Mg into MgO_x converts the TiO₂/Mg interface from a Schottky junction into a semiconductor/ETL junction, since MgO_x is a well-known ETL in various photovoltaic absorbers.^{24–26} Complementary STEM and HR-EDX analysis of the T-Mg1-Au sample further support this interpretation. The oxygen signal extends over the Ti signal in regions where Mg is present, matching the spatial distribution

of Mg and providing an additional confirmation of Mg oxidation (Fig. 2g). The maps also show that although the Mg-MgO_x layer and the Au nanoparticles percolate through the surface cracks of the TiO₂, there is no significant signal from either species deeper inside the film, indicating that the cracks do not fully penetrate the TiO₂ layer.

Analysis of the Au 4f core levels in the T-Au sample (Fig. 2f) shows fully metallic gold, with the Au 4f_{7/2} and 4f_{5/2} peaks located at 84.0 eV and 87.7 eV,^{27,28} respectively. The T-Mg1-Au sample also exhibits these metallic Au peaks; however, additional Au^{δ+} components appear (Fig. 2e), with Au 4f_{7/2} and 4f_{5/2} peaks at 85.2 eV and 89.0 eV, which correspond to oxidized gold species. Such energy shifts and oxidation states are typical for Au-O-Mg interfacial environments, indicating the formation of Au-O-Mg linkages. This interfacial chemistry provides a likely explanation for the stronger adhesion of Au and the enhanced dispersion of Au nanoparticles on the Mg-MgO_x surface compared with bare TiO₂.²⁹

Fig. 3a shows that the mean Au NPs diameter on TiO₂ is approximately 30 nm, whereas NPs grown on Mg-MgO_x exhibit a larger average diameter of over 40 nm. The presence of oxidized Au species at the interface may contribute to this different growth behavior. In both cases, smaller nanoparticles are also present and appear to percolate into TiO₂ cracks and surface roughness; however, their precise size is difficult to determine from SEM images alone. For a more interdigitated

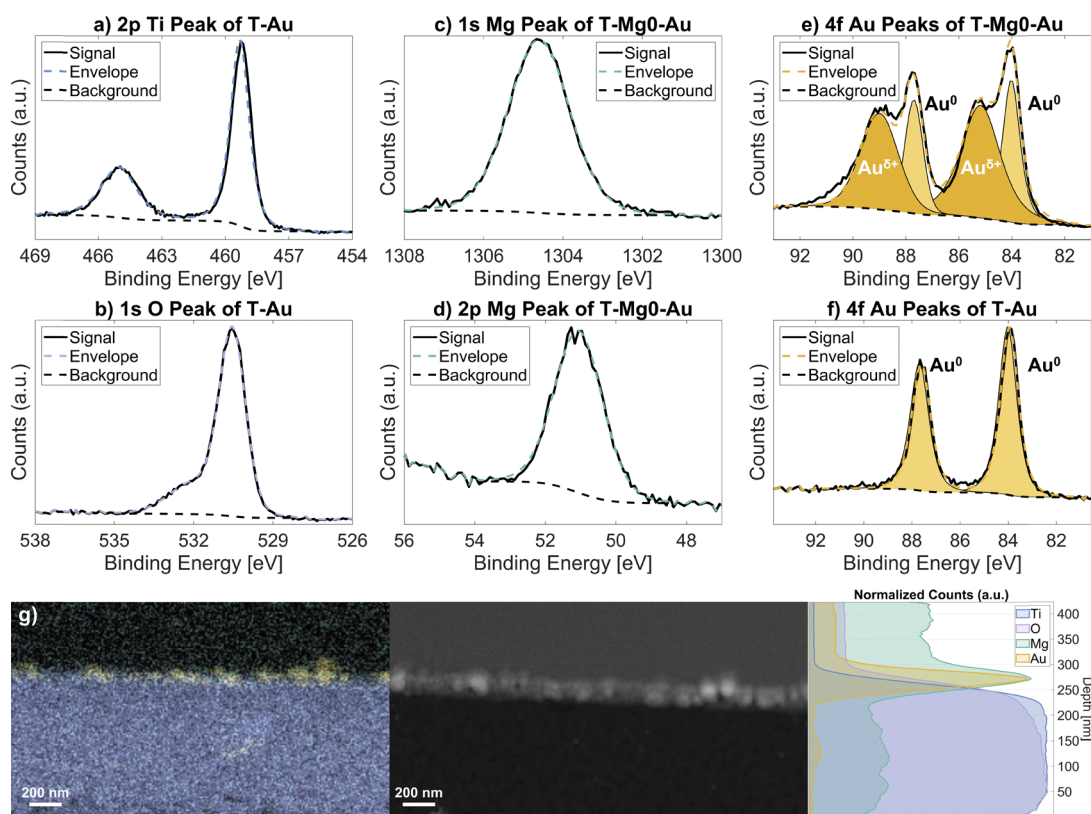


Fig. 2 (a) Ti 2p XPS peak of the T-Au (TiO₂/Au) sample. (b) O 1s XPS peak of the T-Au sample. (c) Mg 1s XPS peak of the T-Mg1-Au sample. (d) Mg 2p XPS peak of the T-Mg1-Au sample. (e) Au 4f XPS peaks of the T-Mg1-Au (TiO₂/Mg-MgO_x(full coverage)/Au) sample. (f) Au 4f XPS peaks of the T-Au sample. (g) HR-EDX map, STEM image and elemental line profile of the cross-section of the T-Mg1-Au sample.



sample, such as T-Mg4-Au, SEM-EDX mapping confirms that the Au distribution follows the Mg interdigitated geometry, with a clearly higher Au signal on the Mg-MgO_x regions than on the bare TiO₂ areas (Fig. 3c). These results collectively support the strong interaction between Au and the Mg-MgO_x layer, consistent with previous reports of Au-O-Mg bonding influencing nanoparticle size, adhesion, and dispersion.

3.2. Hydrogen production

The photocatalytic activity of the samples was evaluated, and the results are summarized in Table 1, Fig. S5, S6 and Table S2. The bare TiO₂ sample produces a measurable amount of hydrogen; however, the quantity of acetaldehyde detected is more than six times higher than the generated H₂. This indicates that a significant fraction of the produced hydrogen recombines with residual oxygen in the chamber before reaching the gas chromatograph.

Introducing Au nanoparticles dramatically enhances the photocatalytic response: the T-Au sample produces more than twenty times the hydrogen generated by bare TiO₂. This improvement arises from several synergistic effects. First, due to the much higher work function of gold ($\Phi_{\text{Au}} \approx 5.3 \text{ eV}^{30}$)

compared with TiO₂ ($\Phi_{\text{TiO}_2} \approx 4.4 \text{ eV}^{31}$), Fermi level equilibration induces charge redistribution at the TiO₂/Au interface. This creates a depletion region in TiO₂ and an upward band bending that suppresses electron transfer from TiO₂ to Au while promoting hole extraction into the metal, effectively forming a HTL.³² Incorporating an HTL is especially beneficial because the fabricated anatase is typically highly n-doped,³³ and minority carrier (hole) collection is otherwise inefficient.

Second, the nanometric Au particles exhibit localized surface plasmon resonance (LSPR), enabling strong visible-light absorption. Plasmonic excitation generates hot carriers and increases the local temperature. Hot electrons can be injected into TiO₂ and subsequently participate in the photocatalytic reaction, thereby extending photoresponse into the visible range,³⁴ whereas pristine anatase absorbs only in the UV. The modest temperature rise induced by LSPR also accelerates surface reaction kinetics *via* the Arrhenius relation. Although higher temperatures can increase charge recombination in TiO₂, the operating temperature of the samples remained below $\sim 75 \text{ }^\circ\text{C}$, ensuring that the enhancement in reaction kinetics outweighed any recombination losses.³⁵

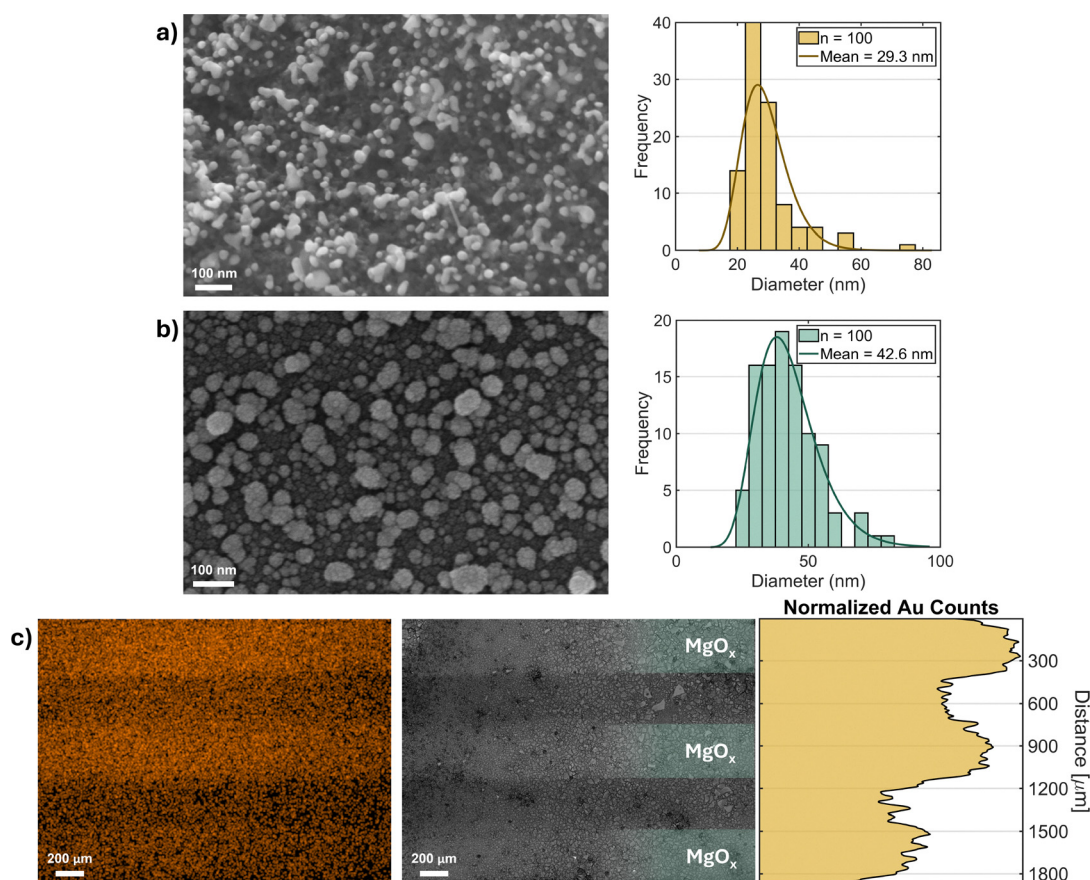


Fig. 3 (a) SEM image of the surface of the T-Au (TiO₂/Au) sample and the diameter distribution of the observed Au NPs. (b) SEM image of the surface of the T-Mg1-Au (TiO₂/Mg-MgO_x(full coverage)/Au) sample and the corresponding diameter distribution of the Au NPs. The Au NPs outlines correspond to fitted log-normal distributions. (c) EDX Au map, SEM image and Au line profile of the surface of the T-Mg4-Au (TiO₂/Mg-MgO_x(highly interdigitated)/Au) sample.



Table 1 Table summarizing the geometric parameters of the ETL patterns for all samples (eqn (8)), the amount of hydrogen produced during the first two hours, the mean H₂ production rate over that period, and the corresponding peak H₂ generation rate

Sample	Mg coverage [%]	Mg perimeter [mm]	Geometric factor [η]	H ₂ generated during 2 h [mmol g ⁻¹]	Mean H ₂ generation rate [$\mu\text{mol min}^{-1} \text{g}^{-1}$]	Maximum H ₂ generation rate [$\mu\text{mol min}^{-1} \text{g}^{-1}$]
Bare TiO ₂	—	—	—	0.3	2.9	3.6
T-Au	—	—	—	8.0	66.2	86.4
T-Mg1	~ 100	~ 8	~ 0.1	0.03	0.2	0.7
T-Mg2	~ 50	~ 28.3	~ 0.7	0.03	0.2	0.7
T-Mg1-Au	98.6	8.6	0.1	4.8	40.0	57.9
T-Mg2-Au	50.7	27.6	0.7	10.7	88.7	109.3
T-Mg3-Au	24.3	198.2	10.7	15.7	130.0	170.5
T-Mg4-Au	53.2	991.4	22.8	16.0	133.8	166.9

To further substantiate this enhancement in performance, the hydrogen production results were correlated with time-resolved photoluminescence (TRPL) measurements (Fig. 4a and Table 2). The decay curves were fitted using a biexponential model (eqn (S1)), from which the average lifetime³⁶ was calculated (eqn (S2)). For the TiO₂/Au sample, the fast decay component (τ_1) is shorter than that of bare TiO₂, while the slow decay component (τ_2) is slightly prolonged. These effects are reflected in the average lifetime (τ_{avg}), which is lower for TiO₂/Au despite its significantly higher hydrogen production. This apparent contradiction can be rationalized by considering the photoluminescence quenching induced by Au nanoparticles, as reported in similar TiO₂-based systems.^{37,38} Therefore, although the TiO₂/Au sample exhibits shorter lifetimes, this behavior is consistent with improved charge separation and enhanced photocatalytic activity.

When Mg-MgO_x is deposited without Au, either across the full surface (T-Mg1) or in partially covered geometries (T-Mg2), the photocatalytic activity decreases sharply, with hydrogen production falling to roughly one tenth of that of bare TiO₂. This behavior reflects the electronic roles of the materials: although MgO_x is an effective electron-selective layer, the anatase TiO₂ used here is strongly n-type, meaning that hole extraction, not electron extraction, is the limiting step. Extensive MgO_x coverage therefore prioritizes majority-carrier extraction at the expense of minority-carrier collection, reducing overall reaction rates. In the extreme case of full Mg coverage, only cracks and small uncovered regions remain available for hole extraction, explaining the substantial drop in catalytic activity.

The TRPL results support this interpretation. The T-Mg1 sample exhibits the longest lifetimes (τ_1 , τ_2 , and τ_{avg}), indicating reduced recombination and confirming that Mg-MgO_x effectively improves charge separation. However, this improvement does not translate into higher hydrogen production, demonstrating that efficient carrier separation alone is insufficient to drive the reaction in the absence of effective surface charge transfer pathways.

Upon incorporation of Au nanoparticles (T-Mg1-Au and T-Mg2-Au), the hydrogen production increases markedly, while the measured lifetimes decrease relative to T-Mg1 but remain higher than those of the TiO₂/Au reference in terms of τ_1 and τ_{avg} . This combination of trends indicates that Mg-MgO_x

enhances charge separation, whereas Au nanoparticles are essential to enable efficient surface reactions. In addition to acting as a hole-selective contact and promoting plasmonic carrier generation, Au nanoparticles deposited on Mg-MgO_x facilitate charge transfer by lowering overpotential barriers at solid-gas and solid-electrolyte interfaces,³⁹ thereby improving overall catalytic efficiency.

With both ETL (MgO_x) and HTL (Au) present, the system recovers performance. However, in T-Mg1-Au, the area devoted to electron extraction remains too large relative to the region available for hole transfer, limiting the improvement. Reducing the MgO_x coverage, as in T-Mg2-Au, leads to a more balanced configuration between electron and hole extraction, allowing this sample to outperform even the T-Au reference.

The next step was to explore more intricate designs to evaluate how the trade-off between the active area devoted to electron and hole extraction evolves with geometry. For this purpose, the T-Mg3-Au and T-Mg4-Au samples were fabricated and tested. Both architectures produce approximately twice the hydrogen generated by the T-Au reference. Although T-Mg3-Au exhibits the highest peak production rate, the total hydrogen yield and average production over the first two hours are higher for T-Mg4-Au.

A comparison of their geometrical parameters reveals that T-Mg3-Au has the lowest Mg-MgO_x coverage (~24%), whereas T-Mg4-Au approaches ~50%, similar to T-Mg2-Au, which nevertheless produces ~40% less hydrogen. This indicates that surface coverage alone does not govern performance. Instead, the dominant difference lies in the perimeter of the Mg-MgO_x patterns: T-Mg4-Au exhibits a perimeter approximately five times larger than that of T-Mg3-Au, while T-Mg3-Au itself has more than seven times the perimeter of T-Mg2-Au. These observations highlight the critical role of interface density, suggesting a strong interplay between active area, perimeter, and carrier extraction efficiency.

TRPL measurements further support this interpretation. The most interdigitated sample, T-Mg4-Au, exhibits slightly longer lifetimes (τ_1 , τ_2 , and τ_{avg}) compared to T-Mg1-Au and T-Mg2-Au, although all values remain within the same range. This relatively modest variation indicates that bulk recombination dynamics are not significantly altered by increasing interdigitated. Instead, the performance enhancement arises from improved spatial organization of charge extraction and reaction



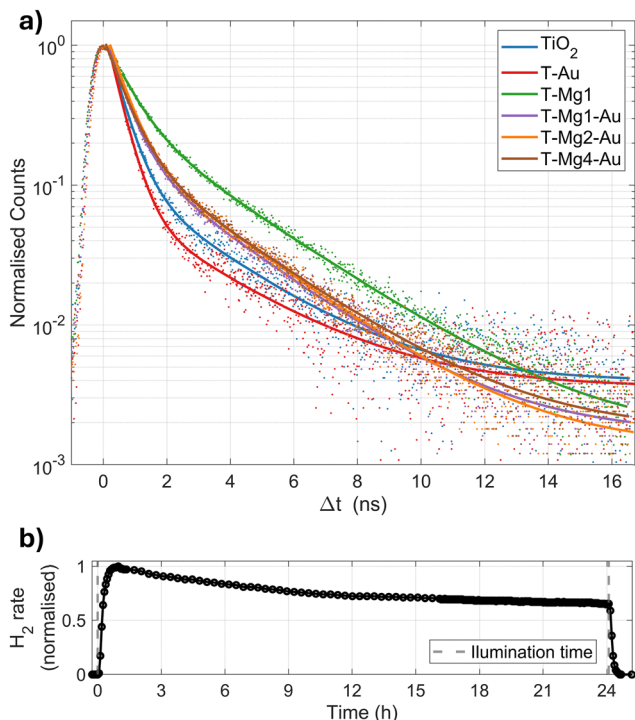


Fig. 4 (a) Time-resolved photoluminescence (TRPL) decay curves of representative samples, highlighting variations in charge carrier dynamics across different contact architectures. (b) Normalized hydrogen production rate as a function of time for the T-Mg4-Au sample during extended photocatalytic operation. The sample was remeasured several months after the initial 2 h photocatalytic test. The production rate is normalized to the peak value of each cycle to highlight the relative activity decay and stability over time.

Table 2 Bi-exponential fitting (eqn (S1)) parameters extracted from TRPL decay curves for the different samples. The table reports the reduced chi-squared (χ^2), fast and slow decay components (τ_1 and τ_2), intensity-weighted average lifetime (τ_{avg} from eqn (S2)), amplitudes (B_1 and B_2), and background offset (A) obtained from the fits of curves in Fig. 4

Sample	χ^2	τ_1 (ns)	τ_2 (ns)	τ_{avg} (ns)	B_1	B_2	A
TiO ₂	1.022	0.46	2.65	1.47	3391.8	512.5	243.8
T-Au	1.104	0.42	2.86	1.28	4046.7	325.3	251.9
T-Mg1	1.160	0.70	2.87	2.31	1864.6	1309.0	26.0
T-Mg1-Au	1.103	0.55	2.64	1.63	3972.1	871.8	60.3
T-Mg2-Au	1.096	0.54	2.65	1.64	4234.8	931.5	46.7
T-Mg4-Au	1.010	0.59	2.76	1.68	4287.4	919.2	54.7

sites. The interdigitated geometry enables electrons and holes to be extracted at distinct but closely spaced regions, facilitating efficient charge separation while maintaining short diffusion paths for surface intermediates involved in ethanol dehydrogenation. As a result, the benefits of interdigitation extend beyond what is captured by TRPL, which primarily probes bulk recombination, and include improved coupling between charge extraction and surface reaction kinetics.

Moreover, the photocatalytic stability of the best-performing sample (T-Mg4-Au) was evaluated after several months of storage under ambient conditions in the dark, followed by extended operation (Fig. 4b). The peak hydrogen production at the beginning of this new measurement ($113.3 \mu\text{mol min}^{-1} \text{g}^{-1}$) closely matches the final value recorded at the end of the initial 2 h cycle ($116.5 \mu\text{mol min}^{-1} \text{g}^{-1}$), indicating good preservation of the catalytic activity over time. During 24 h of continuous operation, the activity gradually decreases to approximately 65% of the peak value within that cycle ($74.0 \mu\text{mol min}^{-1} \text{g}^{-1}$). After this extended test, the sample was allowed to rest, exposed to air, and subsequently remeasured (full second and third cycles shown in Fig. S7). In the following 14.5 h cycle, the peak production reached $81.2 \mu\text{mol min}^{-1} \text{g}^{-1}$, with the activity stabilizing at around 70% of this peak value ($57.0 \mu\text{mol min}^{-1} \text{g}^{-1}$). Although the hydrogen production rate does not remain strictly constant over time, the system exhibits a relatively stable and resilient behavior under operating conditions, with partial recovery upon air exposure. This behavior suggests that the mild deactivation observed during operation may be related to the reducing reaction environment (absence of oxygen and presence of hydrogen), which could induce partial reduction of oxide components and the formation of excess oxygen vacancies.

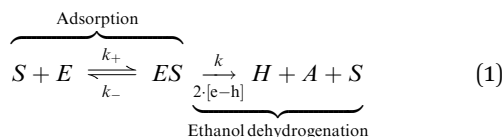
To further contextualize these results, a comparison with representative TiO₂-based photocatalytic systems from the literature is provided in Table S3. Despite the use of a planar thin-film architecture, which inherently exhibits a lower surface-to-mass ratio than nanopowder or porous systems, the hydrogen production rates obtained in this work fall within the range of state-of-the-art TiO₂ photocatalysts. This comparison highlights that the performance achieved here is competitive with similar TiO₂/Au-based systems, while relying on a geometrical strategy for carrier management rather than optimization of catalyst composition or nanostructures.

3.3. Langmuir-Hinshelwood Geometric Kinetic Model

To understand the influence of the ETL geometry on our samples, it is first necessary to consider the reaction mechanism and kinetics. As in any heterogeneous catalytic system, the reactants must initially adsorb onto the surface. Adsorbed species can also desorb if the reaction does not proceed. In photocatalysis, desorption is possible because charge carriers are required to drive the redox reaction; without sufficient electrons or holes, the adsorbed molecules may desorb before reaction occurs. Once reactants are adsorbed and appropriate charge carriers are available, the reaction can proceed. While product desorption/readsorption can be important in some cases, it is negligible in our system because the reaction is performed in a continuous gas flow that constantly supplies fresh reactants and efficiently removes products. Under these conditions, desorption of products is rapid relative to the catalytic step. Based on these considerations, we can construct a reaction flow diagram for our system, where ethanol is the reactant and hydrogen and acetaldehyde are the products, as



described in Fig. 5a and eqn (1).



In this scheme, S denotes the active sites of the solid catalyst, E is the ethanol concentration or partial pressure, and ES represents active sites occupied by adsorbed ethanol. The term $[e-h]$ refers to the concentration of photogenerated electron-hole pairs that reach the surface or the adsorbed reactants and are able to drive the photocatalytic reaction. H and A correspond to the concentrations or partial pressures of hydrogen and acetaldehyde, respectively. The kinetic constants k_{\pm} and k describe the adsorption and desorption rates of ethanol, while k is the intrinsic rate constant of the ethanol dehydrogenation step. From this eqn (1), we can write the time derivative of each species involved in the reaction as follows:

$$\frac{dE}{dt} = +k_- \cdot ES - k_+ \cdot E \cdot S \quad (2)$$

$$\frac{dH}{dt} = \frac{dA}{dt} = k \cdot ES \cdot [e-h]^2 \quad (3)$$

$$\frac{dES}{dt} = -\frac{dS}{dt} = k_+ \cdot E \cdot S - (k_- + k \cdot [e-h]^2) ES \quad (4)$$

We assume that the active sites with adsorbed ethanol rapidly reach a steady-state concentration ($d[ES]/dt = 0$), since the adsorption process is much faster than the dehydrogenation reaction, which constitutes the rate-limiting step. We also define S_0 as the total fixed number of active sites on the catalyst ($S_0 = S + ES$, with $dS_0/dt = 0$). With these assumptions and definitions, we can proceed to formulate the kinetic expressions.

$$\begin{aligned} \frac{dES}{dt} &= k_+ \cdot E \cdot (S_0 - ES) - (k_- + k \cdot [e-h]^2) ES = 0 \\ \rightarrow ES &= \frac{k_+ \cdot S_0 \cdot E}{k_- + k \cdot [e-h]^2 + k_+ \cdot E} \end{aligned} \quad (5)$$

$$\frac{dH}{dt} = k \cdot ES \cdot [e-h]^2 = \frac{k_+ \cdot S_0 \cdot k \cdot E \cdot [e-h]^2}{k_- + k \cdot [e-h]^2 + k_+ \cdot E} \quad (6)$$

$$\begin{aligned} \frac{dH}{dt} &= \frac{k_+ \cdot S_0 \cdot k \cdot E \cdot [e-h]^2}{k_- + k \cdot [e-h]^2 + k_+ \cdot E} \\ &= k_{\text{app}} \frac{K \cdot [e-h]^2}{1 + K \cdot [e-h]^2} \left\{ \begin{array}{l} k_{\text{app}} = k_+ \cdot S_0 \\ K = \frac{k}{k_- + k_+ \cdot E} \end{array} \right. \end{aligned} \quad (7)$$

As shown, this expression links the hydrogen production rate to both the ethanol concentration and the number of charge carriers available to catalyze the reaction. All photocatalytic experiments were carried out under dynamic conditions that guarantee a constant ethanol flow over the photocatalyst,

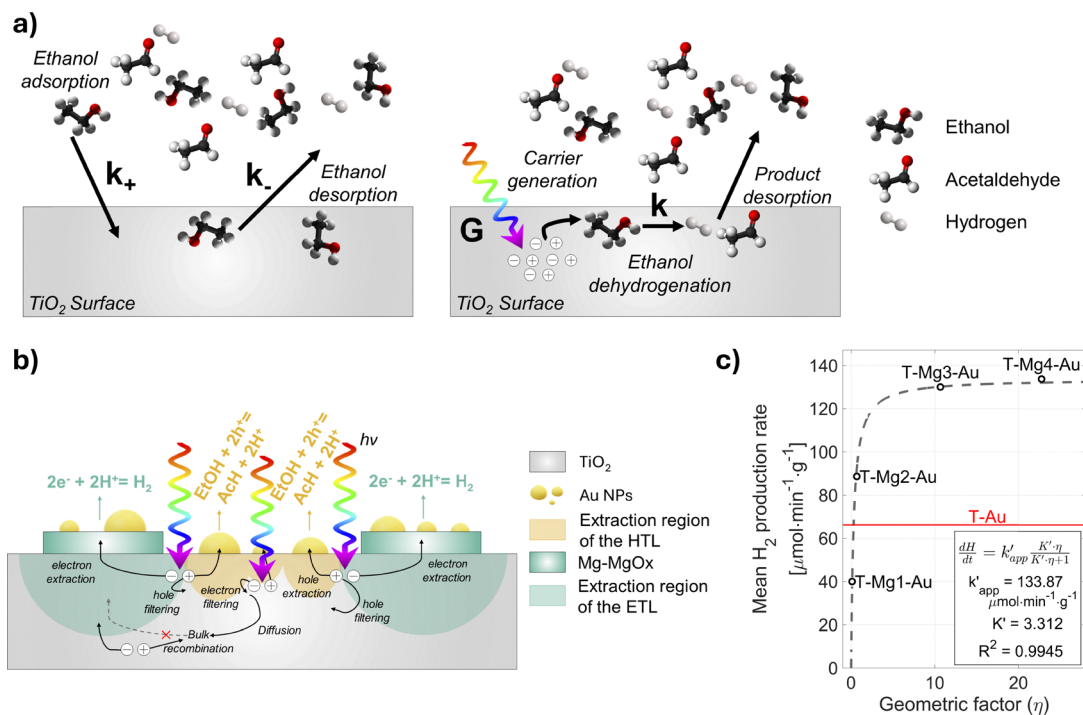


Fig. 5 (a) Schematic of the processes and reactions described by the Langmuir–Hinshelwood model for heterogeneous photocatalysis. (b) Electronic processes, charge filtering and carrier extraction in the interdigitated samples, with illustrative extraction regions associated with each selective contact. (c) Langmuir–Hinshelwood geometric kinetic model fitting of eqn (9) applied to the mean reaction rate of the interdigitated samples, compared to the T–Au(TiO₂/Au) reference.



and this amount was identical across all measurements. Once the system reaches steady state, the ethanol concentration can therefore be treated as constant ($E = \text{const} \rightarrow dE/dt = 0$). In this form, the expression essentially reduces to a conventional Langmuir–Hinshelwood model,^{40,41} but with the explicit inclusion of charge carriers as one of the reacting species under constant supply, while the other reactant remains at steady state.

In our experiment we defined a geometric factor, η , that captures the trends we observed between hydrogen production and the geometry of the Mg–MgO_x pattern:

$$\eta = \left(\frac{\text{Perimeter ETL}}{\text{Substrate Perimeter}} \right) / \left(\frac{\text{Area ETL}}{\text{Substrate Area}} \right) \quad (8)$$

As shown in eqn (8), η is obtained by normalizing the Mg–MgO_x perimeter by the substrate perimeter and dividing this by the normalized Mg–MgO_x area. In practice, the denominator corresponds to the fractional coverage. The result is a dimensionless parameter that highlights how much interfacial length is available per unit of covered area, which helps rationalize why samples with comparable coverage may nonetheless exhibit markedly different photocatalytic behavior. The physical meaning of this parameter can be interpreted as the ratio between the effective extraction interface, represented by the Mg–MgO_x perimeter, and the corresponding extraction area, *i.e.*, the Mg–MgO_x coverage. Both quantities are normalized by the substrate perimeter and area, respectively, to account for small variations between samples and to ensure that η remains a dimensionless descriptor.

If we plot the mean hydrogen production rate of each sample against the geometric factor η (Fig. 5c), we observe that the data follow eqn (9) with remarkable accuracy:

$$\left(\frac{dH}{dt} \right)_{\text{mean}} = k'_{\text{app}} \frac{K' \cdot \eta}{1 + K' \cdot \eta} \left\{ \begin{array}{l} k'_{\text{app}} = 133.87 \mu\text{mol min}^{-1} \text{g}^{-1} \\ K' = 3.312 \end{array} \right. \quad (9)$$

Eqn (9) has the same functional form as eqn (7), except that the rate is expressed as a function of the geometric parameter rather than the square charge-carrier concentration. Because the surface composition of all samples is identical, we can assume that intrinsic adsorption and desorption rates (k_+ and k_-) and the fundamental dehydrogenation rate (k) are the same. The samples also have comparable dimensions, and all rates have been normalized to the amount of photocatalytically active TiO₂. Consequently, the total number of active sites S_0 can be considered similar across the series.

Under these conditions, the parallel behavior of both expressions suggests that optimizing the ETL pattern effectively increases the number of charge carriers that reach catalytic sites and participate in the reaction. In other words, the geometric design controls how efficiently carriers avoid recombination and are extracted through the selective contacts. Patterns with a larger perimeter provide more interface length through which carriers can be collected, a feature that becomes crucial when the carrier diffusion length (or, equivalently,

lifetime) is relatively short. To minimize recombination losses, carriers generated anywhere in the absorber must quickly enter the influence region of either the hole- or electron-selective contact (Fig. 5b). This influence region corresponds to the size of the space charge region formed at the ETL-absorber and HTL-absorber junctions.

It is important to note that this Langmuir–Hinshelwood geometric–kinetic framework is primarily applicable to planar architectures, where both area and perimeter can be unambiguously defined, as in the present case. The model further relies on the assumption of sufficiently selective transport layers and on a characteristic carrier diffusion length that is comparable to or smaller than the spacing between extraction regions. Under these conditions, carrier collection is limited by the distance to the nearest selective interface, and the perimeter density becomes a meaningful descriptor of extraction efficiency. In contrast, if the diffusion length is sufficiently large, photogenerated carriers can readily reach both selective contacts regardless of their spatial arrangement, reducing the dependence on interdigitation. In the present system, this condition is satisfied: the Mg–MgO_x layer defines discrete electron-selective domains, while the Au nanoparticles form a spatially distributed hole-selective network, making the geometry of the electron-selective interface the dominant factor governing carrier extraction.

Within this framework, an effective ETL pattern is one that maximizes perimeter while using only the necessary fraction of active area to enhance electron extraction. This balance ensures that the system benefits simultaneously from rapid majority-carrier extraction and sufficient uncovered TiO₂ surface for minority-carrier transfer, which together determines the overall photocatalytic performance.

4. Conclusions

Interdigitated front selective contacts based on Mg–MgO_x and Au have been fabricated and tested for photocatalytic hydrogen generation from ethanol-containing gas mixtures. The results show that the geometry of the ETL plays a decisive role in determining the photocatalytic efficiency of the system. The combination of Mg–MgO_x as the electron-selective layer and Au as both hole extractor and plasmonic activator reaches its full potential only when both materials are arranged in patterns that balance extraction and recombination. Simply increasing the Mg–MgO_x coverage cannot account for the differences observed among samples. The geometric parameter η , which relates perimeter to coverage, provides a quantitative way to describe this effect: as η increases, the available interface length for carrier collection expands, and the reaction shifts into a more efficient regime, seen in higher initial rates and greater hydrogen output. Stability tests further show that the optimized interdigitated architectures maintain a significant fraction of their activity over extended operation times, confirming that the performance gains are not limited to short-term measurements.



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