

Harnessing Effective Electric Field Amplification and Intermetallic Hybridization via Nanoelectrode Superlattices to Boost Electrocatalytic Green Hydrogen Production

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Funding: H.K.L. thanks the funding supports from the Singapore Ministry of Education (AcRF Tier 1 RG92/24), A*STAR Singapore (MTC IRG M23M6c0098), the National University of Singapore Center of Hydrogen Innovation (CHI-P2022-05), and the Nanyang Technological University start-up grants. The research was conducted as a part of NICES (NTU-IMRE

Chemistry Lab for Eco Sustainability; REQ0275931), a joint research initiative between Nanyang Technological University (NTU) and Institute of Materials Research and Engineering (IMRE) from Agency for Science, Technology, and Research (A*STAR).

Keywords: electrocatalysis, nanoparticle superlattices, electric field amplification, intermetallic hybridization, green hydrogen

Electrocatalytic hydrogen evolution reaction (HER) offers a sustainable pathway for green hydrogen production, addressing growing energy demands while reducing fossil fuel dependence. However, existing electrocatalysts face challenges, including low current densities, excessive Pt reliance, and inefficient charge transfer. Here, we achieve ampere-level HER catalysis by introducing two-dimensional nanoelectrode superlattices that boost electrocatalytic efficiency through two key concepts: (i) Electric field amplification, where Ag nanoparticles serve as nanoelectrodes and we leverage their interparticle interactions within the superlattice to concentrate local electric fields for facilitating charge accumulation and transfer. (ii) Intermetallic Pt-Ag hybridization, which modulates electronic structure and electron distribution to enhance intrinsic catalytic activity. Notably, Ag hexagonal@Pt achieves the highest performance, delivering -15.88 A cm^{-2} at -0.9 V vs. RHE with 98% Faradaic efficiency and outperforming Ag standing@Pt and Ag disorganized@Pt by up to 8-fold. Moreover, it surpasses Pt/C by ~ 934 -fold and exhibits ~ 4 -fold reduction in overpotential at high current densities of $\geq 500 \text{ mA cm}^{-2}$ compared to other emerging electrocatalysts. Mechanistic studies reveal that optimizing spatial nanoelectrode arrangement is crucial for enhancing HER activity through synergistic electric field concentration and intermetallic hybridization. This work offers critical insights into advancing electrocatalysis for green hydrogen production and broader energy, chemical, and environmental applications.

1. Introduction

The global transition to sustainable energy is imperative to address rising energy demands and mitigate the environmental impact of fossil fuel dependency.^[1] Among the promising solutions, green hydrogen production has emerged as a cornerstone of clean energy technologies.^[2] Hydrogen, a zero-carbon energy carrier, can be sustainably produced via water splitting driven by renewable electricity or light.^[3-6] This approach offers immense potential for decarbonizing critical sectors such as transportation, industrial manufacturing, and energy storage.^[3, 7] At the heart of this process lies the hydrogen evolution reaction (HER), where water molecules are electrochemically reduced at the cathode to generate molecular hydrogen.^[8-10] The development of efficient HER electrocatalysts is therefore vital for the feasibility of green hydrogen technologies and has become a focal point in energy research.

Platinum (Pt) is widely regarded as the benchmark HER catalyst owing to its exceptional catalytic activity and stability, particularly in acidic environments.^[11-12] Its high performance is attributed to its optimal hydrogen adsorption energy (the Sabatier principle) which facilitates both proton reduction and hydrogen desorption.^[13-14] Despite its advantages, the reliance on pure Pt-based platforms presents significant economic and scalability challenges due to the high cost and scarcity of Pt.^[15-16] These limitations have driven extensive efforts to design catalytic systems that reduce Pt usage while maintaining or even enhancing catalytic performance.^[17-20] Achieving this balance is critical to enabling the widespread adoption of green hydrogen technologies and addressing global energy sustainability.

Recent advancements in Pt-based hybrid electrocatalysts have explored diverse strategies to overcome these challenges. These include alloying Pt with other metals (e.g., Ni, Ru, or Cu) to introduce synergistic effects, integrating Pt nanoparticles onto conductive substrates to maximize active site exposure, and engineering nanoscale architectures to improve charge and mass transport.^[21-27] For instance, nanoporous Pt alloys have demonstrated enhanced activity and durability by leveraging strain-induced electronic modifications that optimize the adsorption energies of HER intermediates.^[28] However, most systems still face performance bottlenecks, particularly in achieving high current densities ($\geq 500 \text{ mA cm}^{-2}$) with low overpotentials, both of which are essential for industrial-scale hydrogen production.^[29-32] These limitations often stem from intrinsic challenges, where reducing Pt content compromises catalytic activity due to suboptimal hydrogen adsorption properties.^[33] Additionally, the inefficient spatial distribution of electric fields severely hinders the effective utilization of supplied electrons, restricting the transfer of active charge carriers to reactants and their use in the chemical reaction.^[34]

Herein, we achieve efficient electrocatalytic HER by introducing a multifunctional, two-dimensional (2D) catalytic architecture that integrates ordered Ag nanoparticle superlattices functionalized with Pt nanoparticles. Our design focuses on two critical aspects to enhance HER performance. (i) Effective concentration of electric field by utilizing each Ag nanoparticle as a nanoelectrode and leveraging particle-particle interactions within the single-particle-thick superlattice. This unique structural architecture amplifies the local electric field, enabling the accumulation of charge carriers at the catalytic interface and facilitating their efficient transfer to reacting species for HER. (ii) The hybridization of Pt with Ag introduces synergistic chemical and electronic effects, altering the electronic structure of the catalyst and enhancing the intrinsic catalytic activity of Pt. These combined structural and chemical enhancements in our design represent a notable departure from conventional strategies, which primarily rely on alloying or doping to improve electrocatalytic performance.

As a proof of concept, we demonstrate the self-assembly of Ag nanoparticle superlattices functionalized with Pt nanoparticles via a wet chemical method, yielding three distinct configurations: Pt-coated Ag hexagonal superlattice (Ag hexagonal@Pt), Ag standing square superlattice (Ag standing@Pt), and Ag disorganized array (Ag disorganized@Pt). Among these, Ag hexagonal@Pt achieves superior performance, including an ultrahigh current density of -15.88 A cm^{-2} at -0.9 V vs. RHE , a low overpotential of 0.12 V at 500 mA cm^{-2} , high Faradaic efficiency (98 %), and a rapid H_2 production rate of $\sim 566 \text{ } \mu\text{mol h}^{-1} \text{ cm}^{-2}$. This performance far surpasses that of Ag standing@Pt and Ag disorganized@Pt, which possess similar chemical and electronic properties but lack the structural advantages of the hexagonal architecture. Moreover, Ag hexagonal@Pt demonstrates a ~ 934 -fold higher current density at -0.9 V vs. RHE compared to commercially available Pt/C and achieves up to 4-fold superior overpotentials at high current densities ($\geq 500 \text{ mA cm}^{-2}$) compared to other state-of-the-art electrocatalytic platforms. Mechanistic studies underscore the critical role of synergistic electric field concentration and Pt-Ag hybridization in boosting HER performance. These findings establish a promising dual-effect strategy that reduces Pt reliance while delivering a multifunctional design for efficient electrocatalysis. By enhancing both electric field intensity and catalytic activity, our work provides crucial insights for advancing electrocatalytic green hydrogen production and developing sustainable, practical energy technologies.

2. Results and discussion

Our electrocatalytic design integrates two-dimensional (2D) self-assembled Ag octahedra superlattices/arrays with a thin platinum (Pt) coating to create bimetallic platforms that enhance hydrogen evolution reaction (HER) performance (**Figure 1A**). The configuration of the Ag octahedra superlattices plays a crucial role in amplifying localized electric fields, particularly at the tips and edges of the Ag nanoparticles.^[35-38] We synthesize Ag octahedra nanoparticles using a polyol reduction method, achieving a uniform edge length of (444 ± 14) nm (**Figure S1**).^[39] Using our previously reported liquid-liquid interface self-assembly technique,^[37, 39] we organize the Ag nanoparticles into three distinct 2D arrays (**Figure S2**) by leveraging different surface capping molecules to mediate interactions between the Ag surface molecules and the liquid-liquid interface. Hydrophilic poly(vinylpyrrolidone) (PVP)-capped Ag nanoparticles form a hexagonal superlattice with tip-to-edge alignment. In contrast, hydrophobic 1-dodecanethiol ($C_{12}SH$)-capped Ag octahedra produce a standing square superlattice with edge-to-edge alignment, while 1-butanethiol (C_4SH)-capped Ag octahedra with intermediate hydrophobicity assemble into a disorganized array. We subsequently transfer the resulting (i) Ag hexagonal superlattice, (ii) Ag standing square superlattice, and (iii) Ag disorganized array onto polydimethylsiloxane (PDMS) supports to facilitate further experiments.

To create the bimetallic electrocatalytic ensemble, we deposit Pt nanoparticles (38 ± 6 nm) on the Ag superlattices via in situ reduction of Pt^{4+} precursors, forming Ag superlattice@Pt structures that retain their original spatial arrangements (**Figure 1B**; **Figure S3, S4**). The uniform Pt coating spans the entire array, ensuring consistent coverage across the superlattices. We acid-treat the as-synthesized Ag superlattice@Pt to remove all capping molecules before performing characterizations and catalytic reactions. Scanning electron microscopy energy-dispersive X-ray spectroscopy (SEM-EDX) mapping and line scan analyses confirm the successful Pt coating, as evidenced by the emergence of Pt elemental signals (**Figure 1C**; **Figure S5**). For comparison, we sputter-coat Pt films of similar thickness (36 ± 2 nm; **Figure S6**) onto acid-treated Ag hexagonal (Ag hexagonal+Pt) and Ag standing (Ag standing+Pt) arrays. X-ray photoelectron spectroscopy (XPS) further validates the presence of Pt nanoparticles in both the wet-chemistry coated Ag superlattice@Pt and the sputter-coated Ag superlattice+Pt ensembles (**Figure 1D**; **Figure S7, S8**). X-ray diffraction (XRD) analysis also affirms that the introduction of Pt does not induce alloying effect or significant lattice distortion of the intrinsic Ag crystal structure (**Figure S9**).

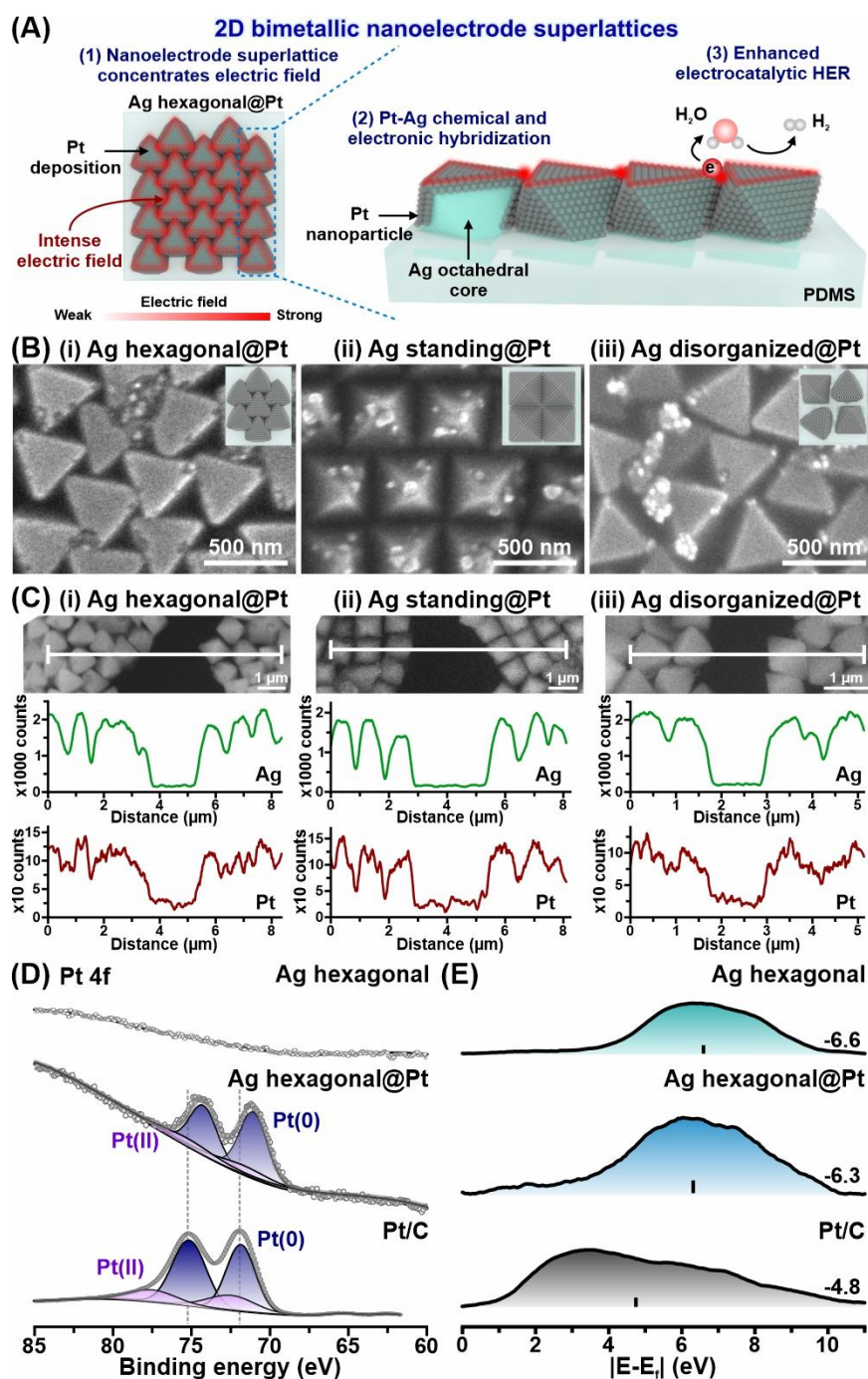


Figure 1. (A) Scheme depicting the design of two-dimensional (2D) Ag hexagonal@Pt superlattice for efficient electrocatalytic hydrogen evolution reaction (HER) under acidic conditions. (B) SEM image of various Ag superlattices/arrays coated with Pt nanoparticles (Ag superlattice@Pt) via wet chemical method. Inset, schematic illustration of respective Ag superlattice@Pt. (C) SEM images and EDX line scan analysis results for (i) Ag hexagonal@Pt, (ii) Ag standing@Pt, and (iii) Ag disorganized@Pt ensembles. (D) High-resolution Pt 4f XPS spectra and (E) d-band center analysis of Ag hexagonal superlattice, Ag hexagonal@Pt ensemble, and commercially available Pt/C.

We investigate the effects of bimetallic hybridization on the electronic properties of Ag superlattices with Pt, a critical factor for efficient electrocatalysis. High-resolution XPS analysis reveals distinct interfacial interactions between Ag superlattices and Pt in Ag superlattice@Pt and Ag superlattice+Pt films. Ag superlattice@Pt exhibits a new electron-deficient Ag 3d shoulder peak at higher binding energy, indicating modifications in the electronic environment of Ag due to hybridization with Pt during the wet chemical deposition process (**Figure S7**). Furthermore, the Pt 4f peak in Ag superlattice@Pt shifts negatively by ~ 0.9 eV compared to Pt/C, reflecting the formation of electron-rich Pt species. These changes in the Ag 3d and Pt 4f peaks collectively signify strong Pt-Ag interfacial interactions and electron migration from Ag to Pt, observed in both Ag hexagonal@Pt and Ag standing@Pt ensembles. In contrast, Ag superlattice+Pt films show Pt 4f peaks that align with Pt/C and no changes in the initial Ag 3d features, indicating the absence of electronic and chemical coupling when Pt is deposited via sputter coating (**Figure S8**). The differences in electronic properties arise from the Pt incorporation method. In Ag superlattice@Pt, the wet chemical deposition process allows Pt to grow directly on Ag surfaces, enabling effective interfacial bimetallic mixing. Conversely, sputter-coated Pt in Ag superlattice+Pt films remains physically in contact with Ag but without forming chemical interactions, resulting in no changes to the electronic properties. Notably, the strong Pt-Ag interfacial hybridization in Ag superlattice@Pt enhances the electron density of active Pt species, potentially improving its intrinsic catalytic activity through chemical effects.

Building on the insights from electronic interactions, we analyze the d-band center of various electrocatalysts, which serves as a key determinant of catalytic performance by controlling the adsorption strength of reaction species on the catalyst surface (**Figure 1E; Figure S10, S11**).^[40] Valence-band XPS measurements reveal that the Ag hexagonal superlattice has the lowest d-band center at -6.6 eV, while the control Pt/C platform exhibits the highest at -4.8 eV. Notably, Ag hexagonal@Pt shows an intermediate d-band center at -6.3 eV that is positioned between Ag hexagonal superlattice and Pt/C. A lower d-band center generally corresponds to weaker hydrogen interaction and adsorption. Pt/C, with the highest d-band center, exhibits the strongest hydrogen interaction and adsorption, which hinders H₂ desorption due to excessive binding strength and consequently slows the catalytic reaction. Ag hexagonal@Pt achieves an optimal balance with its intermediate d-band center, enabling stronger interaction with the adsorbed proton (H_{ad}) to drive HER while promoting efficient H₂ desorption. In contrast, the sputter-coated Ag hexagonal+Pt platform shows a higher d-band center at -5.8 eV and reveals two distinct features in the d-band spectrum corresponding to standalone Ag hexagonal and Pt. This result indicates a lack of electronic interaction between

Ag and Pt in Ag hexagonal+Pt, consistent with high-resolution XPS analysis (**Figure S7, S8**). Although Ag hexagonal+Pt has a lower d-band center than Pt/C, the absence of electronic coupling hinders efficient electron transfer from Ag to the H_{ad} on Pt (**Figure S10**). More importantly, Ag standing@Pt (-6.2 eV) and Ag disorganized@Pt (-6.2 eV) ensembles exhibit d-band center positions similar to Ag hexagonal@Pt (-6.3 eV). These comparable chemical and electronic properties across the three Ag superlattice@Pt ensembles are crucial for isolating potential structural effects on their ability to concentrate electric field and its resulting influence on electrocatalytic HER.

Having established their chemical and electronic interactions, we employ Ag superlattice@Pt ensembles as 2D bimetallic nanoelectrode arrays to drive electrocatalytic HER under acidic conditions. In a three-electrode system, we immerse a 1 cm $\times$ 1.5 cm portion of Ag superlattice@Pt in an acidic aqueous electrolyte (0.5 M Na_2SO_4 + 0.1 M H_2SO_4 , pH 1.47) as the working electrode, with a Pt wire as the counter electrode and Ag/AgCl (3.5 M) as the reference electrode (**Figure 2A**). We determine the electrochemical surface area (ECSA) by measuring the double-layer capacitance (C_{dl}) using cyclic voltammetry (CV) in the same acidic electrolyte solution (**Figure 2B; Figure S12, S13; Table S1**), where ECSA is directly proportional to C_{dl} . All recorded currents are normalized to the respective ECSA of each platform rather than geometric area to ensure fair comparisons. To evaluate catalytic performance, we conduct linear sweep voltammetry (LSV) measurements from 0.1 to -0.9 V (vs. RHE) at a scan rate of 10 mV s⁻¹ to determine current density, overpotentials at 500 and 1000 mA cm⁻², and Tafel slope values (**Figure 2C, 2E, 2F; Figure S14 - S16**). Efficient HER electrocatalysts are characterized by their high current density, low overpotential, and small Tafel slope. These metrics indicate the catalyst's capability to drive rapid hydrogen production, overcome kinetic activation barriers, and enable faster proton adsorption on the catalyst surface. Among the seven platforms tested, Ag hexagonal@Pt achieves an ultrahigh current density of -15.88 A cm⁻² at -0.9 V vs. RHE, notably placing it in the ampere range. This performance surpasses that of Ag hexagonal+Pt film and standalone Ag hexagonal superlattice (i.e., no Pt coating) ~8-fold and ~12-fold (**Figure S14**), respectively. These results highlight the critical role of Pt as the primary catalyst and emphasize that its effective hybridization with Ag drastically enhances catalytic activity.

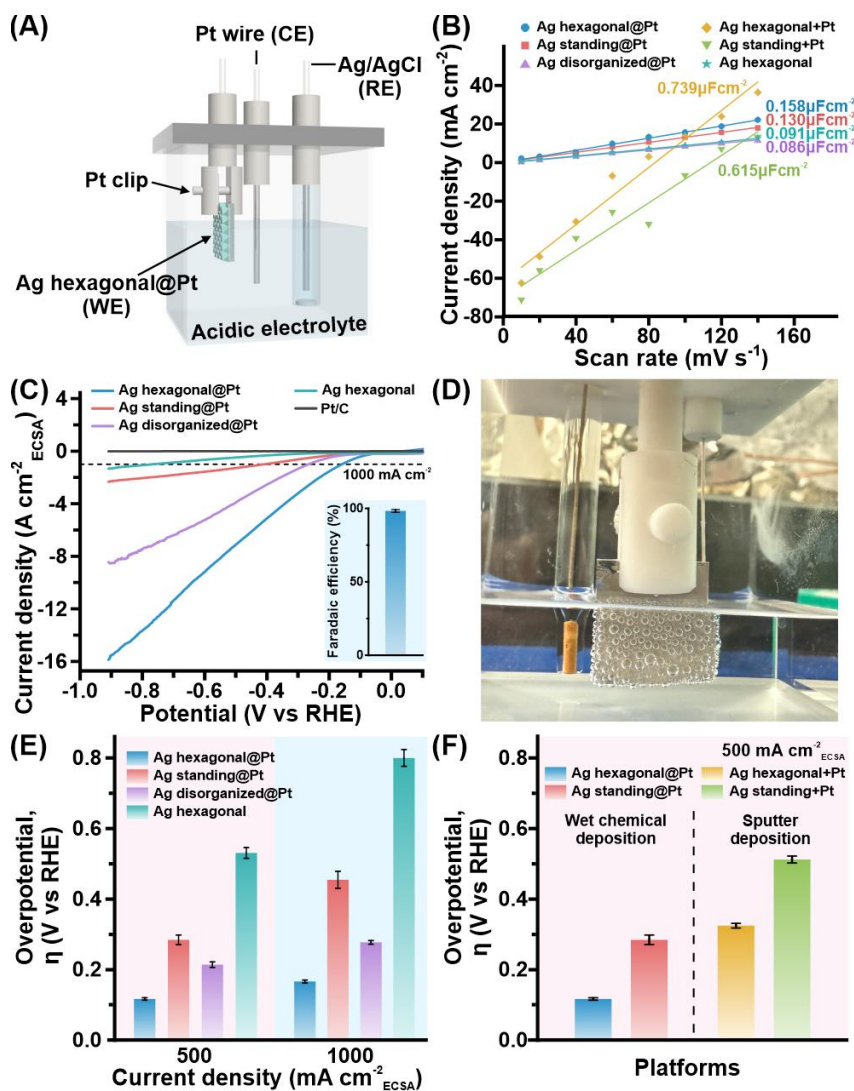


Figure 2. (A) Schematic illustration of the electrochemical experimental setup for HER using various electrocatalytic platforms. (B) Linear plots of capacitive current density versus scan rates. (C) Linear sweep voltammograms normalized to the respective ECSA of the electrocatalytic platforms. The inset plot shows the Faradaic efficiency of Ag hexagonal@Pt electrocatalyst at -0.7 V vs. RHE. (D) Optical image showing H₂ bubbles formed on Ag hexagonal@Pt electrocatalyst at an applied potential of ≤ -0.1 V vs. RHE. (E) Comparison of the overpotential for various electrocatalytic platforms at current densities of 500 mA cm⁻² and 1000 mA cm⁻². (F) Comparison of the overpotential at 500 mA cm⁻² for Ag superlattices coated with Pt nanoparticles via the wet chemical method (Ag superlattice@Pt) with those sputtered with Pt (Ag superlattice+Pt).

More importantly, Ag hexagonal@Pt outperforms Ag standing@Pt and Ag disorganized@Pt by ~8-fold and 2-fold higher current densities, respectively, despite their

similar chemical and electronic properties. This result highlights the critical role of the Ag hexagonal superlattice's structural configuration in enhancing electrocatalysis, likely by concentrating the electric field (to be discussed later). Additionally, we confirm that the high current density in Ag hexagonal@Pt directly supports electrochemical HER, as evidenced by its near-perfect Faradaic efficiency (98 %) for H₂ production and the vigorous evolution of H₂ bubbles observed even at a low applied potential of ≤ -0.1 V vs. RHE (**Figure 2C, 2D, S17**). It is noteworthy that detrimental bubble accumulation is likely mitigated in our system by the coexistence of hydrophobic (PDMS support) and hydrophilic (Pt coating) regions on the catalyst surface (**Figure S17**), which is previously reported to facilitate bubble desorption from a material surface.^[41-42] More importantly, Ag hexagonal@Pt achieves a ~934-fold higher in current density, ~28-fold higher in Pt mass activity, and ~28-fold higher in turnover frequency (TOF) at -0.9 V vs. RHE compared to commercially available Pt/C (**Figure S18, S19**). Our findings provide clear evidence that the structural configuration of the Ag superlattice and the interfacial Ag-Pt electronic interaction play critical roles in boosting electrochemical HER performance beyond the Pt/C gold standard.

We further demonstrate the superior catalytic performance of Ag superlattices@Pt by evaluating their overpotentials at high current densities (500 and 1000 mA cm⁻²) and Tafel slope values derived from polarization curves. Ag hexagonal@Pt achieves the lowest overpotentials of 0.12 V and 0.17 V at 500 and 1000 mA cm⁻², respectively, outperforming Ag disorganized@Pt (0.21 V and 0.28 V) and Ag standing@Pt (0.28 V and 0.45 V; **Figure 2E**) platforms. These findings indicate that Ag hexagonal@Pt requires the lowest kinetic activation energy for HER (**Figure S15**) compared to the other structural configurations. Additionally, Ag hexagonal@Pt surpasses Ag hexagonal+Pt film and standalone Ag hexagonal by showing ~2.8-fold and ~4.6-fold lower overpotentials at 500 mA cm⁻². A similar trend is observed in Ag standing@Pt, which achieves ~1.8-fold lower overpotentials than its sputter-coated counterpart (Ag standing+Pt) (**Figure 2F**). We also note the Tafel slope of Ag hexagonal@Pt drastically decreases to 114.55 mV dec⁻¹ after Pt deposition, compared to 580.13 mV dec⁻¹ in standalone Ag hexagonal (**Figure S16**). This observation highlights that the Volmer step is the rate-limiting step in HER and underscores the critical role of the Pt layer in facilitating proton adsorption, a key step in HER.^[43-44] Ag hexagonal@Pt also exhibits the lowest Tafel slope among the electrocatalytic platforms, outperforming Ag standing@Pt (284.41 mV dec⁻¹) and Ag disorganized@Pt (235.79 mV dec⁻¹) ensembles. Our results confirm that the unique structural configuration of Ag hexagonal@Pt effectively lowers the kinetic activation barrier and enhances proton adsorption, driving superior HER performance.

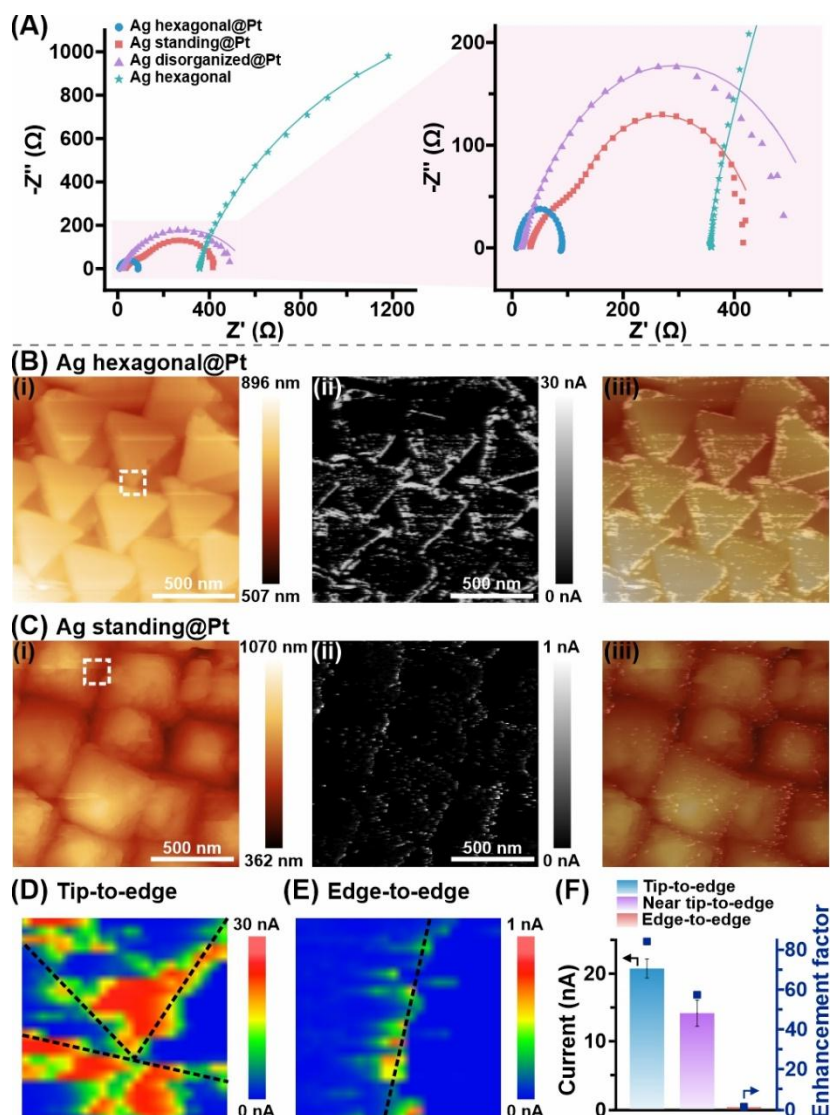


Figure 3. (A) EIS Nyquist plots of various electrocatalytic platforms at -0.1 V vs RHE. Conductive AFM (c-AFM) characterization of (B) Ag hexagonal@Pt and (C) Ag standing@Pt platforms showing (i) topographic images, (ii) current maps, and (iii) overlay of topographic images and current maps. c-AFM is conducted at an applied bias voltage of 0.27 V for both platforms. Magnified current maps highlighting the current distribution at (D) tip-to-edge and (E) edge-to-edge configurations, derived from the white dotted frame of (B) Ag hexagonal@Pt and (C) Ag standing@Pt, respectively. Black dotted lines indicate the outline of the nanoparticles. (F) Average current and corresponding enhancement factors observed at the tip-to-edge and edge-to-edge regions. Note that the color chart scales for the current maps of Ag hexagonal@Pt and Ag standing@Pt differ.

Thus far, our results demonstrate that Ag hexagonal@Pt exhibits superior electrocatalytic HER performance compared to Ag standing@Pt and Ag disorganized@Pt,

albeit their similar electronic and chemical properties. To investigate the structural origin of this enhanced activity, we analyze the electrochemical impedance spectroscopy (EIS) and spatial current maps obtained via conductive atomic force microscopy for these platforms. In EIS characterization, electrical resistance (R_s) reflects the intrinsic electrical conductivity of the electrocatalyst, while charge transfer resistance (R_{CT}) represents the resistance for transferring charge carriers from the catalyst surface to the reactants.^[45] The Nyquist plots reveal comparable R_s values for Ag hexagonal@Pt (9.25 Ω), Ag standing@Pt (31.69 Ω), and Ag disorganized@Pt (16.45 Ω ; **Figure 3A**; **Figure S20**; **Table S2**). These results confirm that the platforms exhibit similarly high electrical conductivity, ruling out intrinsic electrical conductivity as a factor contributing to the apparent differences in their HER performance. Notably, the R_{CT} of Ag hexagonal@Pt is the lowest at 83.03 Ω , which is >2-fold and >6-fold lower than that of Ag standing@Pt and Ag disorganized@Pt platforms, respectively. This drastic decrease in R_{CT} value indicates that Ag hexagonal@Pt facilitates more efficient charge transfer between the catalyst and H_{ad} , even though all platforms have comparable electrochemical surface areas. Furthermore, as the applied potential becomes more negative (0 V to -0.5 V vs. RHE; **Figure S21, S22**; **Table S3**), the diameter of the semicircular arc in the Nyquist plot decreases, reflecting a more facile charge transfer process. The peak shift towards higher frequency in the phase Bode plot indicates that HER operates in a mixed kinetic-diffusion-controlled region rather than being constrained by mass transport, consistent with the observed Tafel slope values.^[43, 46] The result signifies that generating stronger electric field at more negative applied potentials could be beneficial in facilitating charge transfer.

To uncover the influence of structural configuration on catalytic performance, we further investigate the electric field distribution of Ag superlattices using conductive atomic force microscopy (c-AFM; **Figure 3B-F**; **Figure S23**). Under an applied bias voltage of 0.27 V, both Ag hexagonal@Pt and Ag standing@Pt display current distributions visualized through electric field mapping (**Figure 3B, 3C**). The highest currents predominantly localize at the tips and edges of the Ag octahedra, as evident in the overlap of topographic images and current maps. This phenomenon highlights the ability of the Ag building blocks to amplify localized electric fields at sharp features (e.g., tips and edges) through the lightning rod effect. More importantly, Ag hexagonal@Pt exhibits up to 84-fold higher current than Ag standing@Pt, despite both platforms sharing identical electronic and chemical properties due to their similar building blocks and uniform Pt coatings (**Figure 3F**). Given that their intrinsic conductivity and chemical properties are the same, the observed differences in current distributions between Ag hexagonal@Pt and Ag standing@Pt platforms are thus attributed to variations in the strength

of the localized electric field, which is in turn controlled by their distinct structural configurations. The higher current in Ag hexagonal@Pt strongly suggests the presence of a stronger localized electric field at specific spatial positions.

The enhanced field in Ag hexagonal@Pt notably arises from its unique hexagonal close-packed arrangement, where the interaction points between the sharp tips of individual nanoelectrodes and the edges of adjacent nanoparticles drastically amplify the local electric field (**Figure 3D**). Furthermore, the enhanced electric field propagates along the edges extending away from the tip-to-edge interaction points, though the intensity diminishes as reflected by lower current in these regions. The combination of intense electric field amplification and its subsequent delocalization over a broader area is crucial for creating an extensive region of high electric field strength, which is highly beneficial for electrocatalysis. In contrast, the edge-to-edge interactions between adjacent Ag octahedra in Ag standing@Pt produce weaker electric field enhancement, confined to the immediate interaction points between nanoparticles (**Figure 3E**). This limited enhancement lacks the broader field distribution observed in Ag hexagonal@Pt. These comparisons jointly underscore the pivotal role of structural orientation in 2D superlattices in governing the spatial distribution of the electric field and local charge transport, both of which are crucial for optimizing electrocatalytic HER performance.

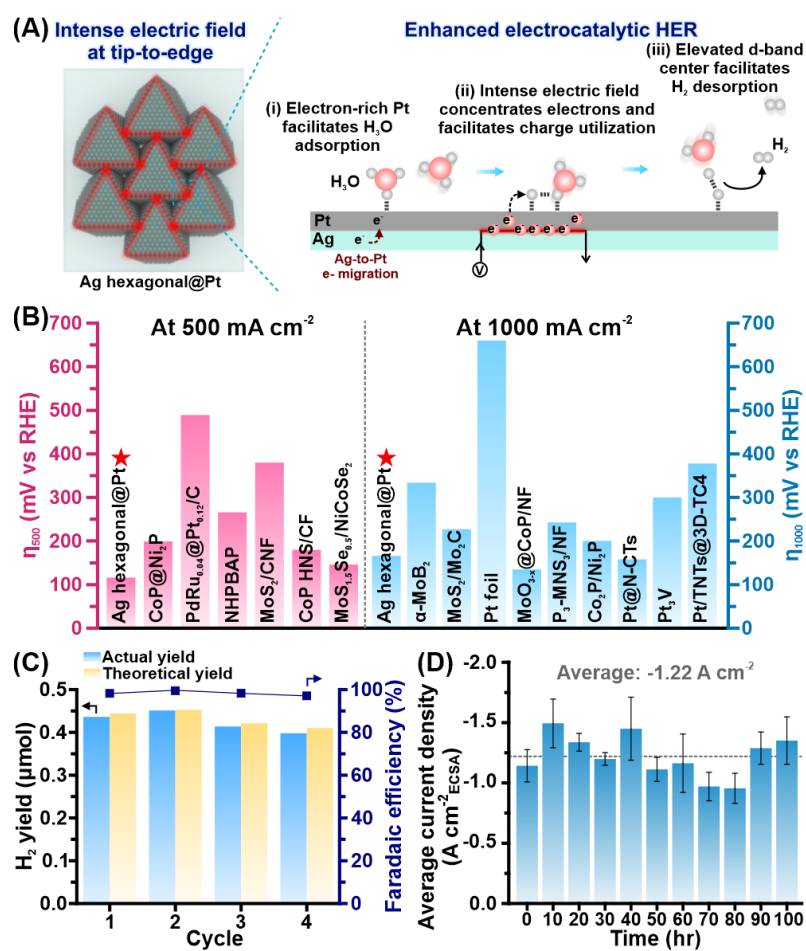


Figure 4. (A) Proposed mechanism for efficient electrocatalytic HER enabled by Ag hexagonal@Pt superlattice under acidic conditions. (B) Comparison of the overpotential of Ag hexagonal@Pt with other emerging electrocatalysts at high current densities of 500 mA cm⁻² and 1000 mA cm⁻² under similar acidic conditions. (C) Theoretical and actual H₂ generation over four successive cycles at -0.7 V vs. RHE, with the corresponding Faradaic efficiency included. (D) ECSA-normalized current density recorded from Ag hexagonal@Pt superlattice catalyst during a 105-hour chronoamperometry (CA) test at an applied potential of -0.46 V vs. RHE.

Collectively, our findings reveal two key mechanisms by which Ag hexagonal@Pt enhances electrocatalytic HER performance: (i) electric field concentration and (ii) chemical effects arising from Pt-Ag hybridization (**Figure 4A**). The unique tip-to-edge arrangement in Ag hexagonal superlattices generates localized electric field enhancement through the lightning rod effect and interparticle interactions, significantly concentrating electrical energy at the catalyst surface. This intensified electric field boosts charge accumulation and local conductivity, enabling efficient charge transfer to reactant species at the nanoelectrode-

electrolyte interface. Additionally, the strong electric field promotes proton adsorption (H_{ad}) on the catalyst surface, a critical step in HER, while simultaneously lowering the kinetic energy barrier for their subsequent reaction to produce H_2 molecules. This effect is evident from the low onset potential, even at high current densities reaching 1000 mA cm^{-2} . In addition, the chemical hybridization between Ag and Pt nanoparticles creates an electron-rich Pt layer due to electron migration from Ag to Pt. This enriched Pt surface improves its intrinsic catalytic activity, facilitating efficient H_{ad} adsorption and the hydrogen evolution process. The Pt coating also enhances charge transfer to the reactants by improving the conductivity of the Ag hexagonal superlattice and providing abundant active catalytic sites. Together, the synergistic effects of enhanced electric field concentration and optimized electronic properties through Pt-Ag hybridization enable Ag hexagonal@Pt to achieve superior catalytic performance, delivering ultrahigh current density in the ampere range and facilitating efficient hydrogen evolution under acidic conditions.

The synergistic effects in Ag hexagonal@Pt enable highly efficient electrocatalytic HER under acidic conditions, outperforming even the Pt/C gold standard. Moreover, Ag hexagonal@Pt achieves an ultrahigh current density of -15.88 A cm^{-2} at -0.9 V vs. RHE , ranking it among the top-performing HER catalysts. It exhibits competitive overpotentials of 116 mV at 500 mA cm^{-2} and 166 mV at 1000 mA cm^{-2} , offering up to a ~ 4 -fold improvement over other emerging electrocatalysts, involving Pt foil, semiconductors, and precious metals (**Figure 4B; Table S4**).^[47-60] These results highlight the platform's ability to initiate HER with lower energy requirements, produce hydrogen at lower potentials, and achieve superior energy efficiency. Ag hexagonal@Pt also demonstrates excellent electrochemical stability, maintaining a near-perfect Faradaic efficiency of 98% over four successive cycles (**Figure 4C; Figure S24**) and showing $<4\%$ deviation in current densities over 60 LSV cycles without intermediate treatments (**Figure S25**). Moreover, Ag hexagonal@Pt maintains a stable current density averaging at 1220 mA cm^{-2} over 105 hours when operated at -0.46 V vs. RHE . High-resolution XPS and SEM analyses confirm the platform's exceptional chemical and structural integrity, showcasing its resistance to catalyst poisoning and degradation during repeated use (**Figure S26 - S28**).

3. Conclusion

In conclusion, we have demonstrated 2D bimetallic nanoelectrode superlattices as a unique electrocatalytic platform that achieves efficient hydrogen evolution reaction (HER) at the ampere-level. By integrating self-assembled Ag nanoparticle superlattices with Pt nanoparticles, we strategically amplify local electric fields at nanoelectrode interfaces and leverage Pt-Ag hybridization to facilitate charge processes and enhance intrinsic catalytic activity. These synergistic effects enable Ag hexagonal@Pt to achieve an ultrahigh current density of -15.88 A cm^{-2} at -0.9 V vs. RHE with a near-perfect Faradaic efficiency of 98%. Notably, Ag hexagonal@Pt is superior over Ag standing@Pt and Ag disorganized@Pt by up to 8-fold, highlighting the critical role of spatial nanoelectrode arrangement in optimizing electrocatalysis. Our superlattice design also surpasses the benchmark Pt/C by ~ 934 -fold in current density and outperforms emerging HER electrocatalysts by up to ~ 4 -fold in overpotential reduction at high current densities ($\geq 500 \text{ mA cm}^{-2}$). Mechanistic studies confirm that electric field concentration enhances charge accumulation and transfer, while Pt-Ag hybridization modulates electronic structure to drive superior HER activity. This work establishes electric field engineering and intermetallic hybridization as promising design principles for HER electrocatalysts, paving the way for green hydrogen production and broader energy applications. Our approach also offers valuable insights for reducing Pt reliance while unlocking new possibilities in green fuel production, chemical synthesis, and environmental sustainability.

4. Experimental Section

Chemicals

Silver nitrate ($\geq 99\%$), anhydrous 1,5-pentanediol (PD, $\geq 97\%$), poly(vinylpyrrolidone) (PVP, average MW = 55000), copper(II) chloride (CuCl_2 , 97%), 1-dodecanethiol (C_{12}SH , $\geq 98\%$), 1-butanethiol (C_4SH , 99%), decane ($\geq 95\%$) L-ascorbic acid ($\geq 99\%$), chloroplatinic acid hydrate ($\geq 99.9\%$), platinum on graphitized carbon (20% Pt/C), and Nafion 117 containing solution were purchased from Sigma-Aldrich. Sodium sulfate (anhydrous, AR grade) was from UNI-Chem. KELCOGEL® gellan gum was from CP Kelco. SYLGARD™ 184 silicone elastomer kit (base and curing agent) was from Dow. Sulfuric acid (H_2SO_4 , 95-97%) and hydrochloric acid (HCl, 37%) were from Honeywell. Ethanol (EtOH , $\geq 98\%$, AR grade), acetone ($\geq 99.8\%$, AR grade), and propan-2-ol (IPA, $\geq 99.5\%$) were obtained from Fisher Scientific. Nitrogen (N_2 , ALPHAGAZ 1; 99.999%) and argon (Ar, 99.9995%) were purchased from Leeden National Oxygen Ltd. All chemicals were used without further purification. Milli-Q water ($> 18.0 \text{ M}\Omega\cdot\text{cm}$) was purified with a Sartorius Arium 611 ® UV ultrapure water system.

Synthesis and purification of silver octahedra

The preparation of Ag octahedra was carried out based on the polyol reduction method reported in the literature.^[39] Ag nanocube was first synthesized and used as seeds for subsequent growth into Ag octahedra. Briefly, 10 mL of copper (II) chloride (8 mg mL^{-1}), poly(vinylpyrrolidone) (PVP, 20 mg mL^{-1}) and silver nitrate (20 mg mL^{-1}) were separately dissolved in 1,5-pentanediol (PD). 35 μL copper (II) chloride solution was then added to the silver nitrate precursor. Then, a round-bottomed flask containing 20 mL 1,5-pentanediol was heated to 190°C for 10 min. 250 μL poly(vinylpyrrolidone) precursor was added to flask dropwise every 30 s, while 500 μL silver nitrate precursor was added in one shot every minute. The process was allowed to continue for ~ 16 min to obtain Ag nanocubes. To synthesize the Ag octahedra, the as-synthesized Ag nanocubes were subjected to the same injection procedure using 30 mL of poly(vinylpyrrolidone) precursor (20 mg mL^{-1}) and silver nitrate solution (40 mg mL^{-1} , also contained 120 μL CuCl_2).

For the purification of Ag octahedra, the final solution was centrifuged to remove 1,5-pentanediol with acetone and ethanol. The Ag octahedra solution was then dispersed in 20 mL ethanol and 100 mL aqueous poly(vinylpyrrolidone) solution (0.2 g L^{-1}). The resulting solution was vacuum filtered through Durapore® polyvinylidene fluoride filter membranes (Millipore) with pore sizes of 5000 nm and 650 nm, repeated at least 2 times for each pore size. The Ag octahedra was redispersed in AR ethanol to make up a concentration of $\sim 10 \text{ mg mL}^{-1}$. SEM

imaging was performed and the edge lengths of Ag octahedra were measured using ImageJ software.

Surface modifications of Ag octahedra

Ag octahedra solution (300 μL , 10 mg mL^{-1}) was dispersed in a mixture of 450 μL of ethanol (EtOH) and 750 μL of propan-2-ol (IPA). 150 μL of 10 mM thiol solution in ethanol (1-dodecanethiol or 1-butanethiol) was then added dropwise to this dispersion under stirring. Ligand exchange was allowed to take place for 2 h, washed with copious amount of solvent (1:1 of EtOH:IPA), and subsequently redispersed in 1.5 ml of EtOH/IPA (1:1). A fresh ethanolic solution of respective thiol (150 μL) was then added to the Ag octahedra dispersion under stirring for another 2 h. Finally, the Ag octahedra was washed with copious amount of solvent (1:1 of IPA:H₂O) and re-dispersed in 750 μL of IPA/H₂O (1:1) for subsequent use.

Interfacial self-assembly and gel-trapping of Ag octahedra at water-decane interface

The gel-trapping experiment was carried out following the method described in literature.^[39] Aqueous gellan gum solution (2 mL, 2 wt%) was used as the water phase and decane was used as the oil phase to create an immiscible liquid-liquid interface. The gellan gum solution was first heated to $\sim 80^\circ\text{C}$ in an oil bath to ensure that the gel was fully hydrated, and the hydrogel solution was subjected to vacuum for several times (at least twice) to remove air bubbles trapped within the solution. Subsequently, pre-heated decane ($\sim 80^\circ\text{C}$) was added on top of the gellan gum solution. PVP-, C₁₂SH-, or C₄SH-capped Ag octahedra in IPA/H₂O (1:1; $\sim 300 \mu\text{L}$) solution was then added onto the water-oil interface and the entire mixture was left at 80°C for ~ 10 min before allowing it to cool to room temperature. Once the gel had set in the aqueous phase, the oil phase was then decanted gently. The substrates were kept in fridge before use.

Preparation of Ag superlattice/PDMS

A thin layer of premixed polydimethylsiloxane (PDMS) precursor mixture (5:1 of elastomer base : curing agent) was poured over the Ag superlattice on gellan gum and left to cure at $\sim 30^\circ\text{C}$ in the oven for overnight. The curing of the PDMS layer enabled the transfer of the assembled Ag array onto the hardened PDMS support for subsequent characterization and electrocatalytic experiments.

Synthesis of Pt-coated Ag superlattice (Ag superlattice@Pt) platform

A mixture of 3 mL of ethanol, 3 mL of PVP (1 mg mL^{-1}), 4 mL of ascorbic acid (32 mM), 600 μL of HCl (1 M), and a Ag superlattice/PDMS substrate ($1.5 \times 1.5 \text{ cm}$) was added to a small petri dish. Then, 2 mL of chloroplatinic acid hydrate (20 mM) was added to the mixture while stirring at 750 rpm stirring at room temperature. The reaction solution was stirred for at least 3 minutes to complete the Pt coating process. The resulting Ag superlattice@Pt platform was then washed thoroughly with ethanol, dried with a stream of N_2 gas, and stored in a dry box for subsequent experiments.

Acid treatment of Ag superlattice@Pt prior to electrocatalytic hydrogen evolution reaction (HER)

The Ag superlattice@Pt ($1.5 \times 1.5 \text{ cm}$) platform was immersed in 10 mL of 1 M HCl prepared in a 1:1 EtOH:H₂O solution for 5 min to remove surface thiols or capping agents used during the self-assembly process. The platforms were then washed with ample 1:1 EtOH:H₂O solution, dried with a stream of N_2 gas, and stored in a dry box for subsequent experiments.

Preparation of Pt-sputtered Ag superlattice (Ag superlattice+Pt) platform

The Ag superlattice was treated with acid following the same protocol before Pt coating. Platinum metal was then deposited through sputtering using a fully automated JOEL JFC-1600 Auto Fine Coater. A $\sim 36 \text{ nm}$ thick Pt film was sputtered onto the acid-treated Ag superlattice/PDMS ($1.5 \times 1.5 \text{ cm}$) at a current of 20 mA for 120 s.

Preparation of Pt/carbon (Pt/C) electrode

A 6 μL aliquot of ethanolic Pt/C solution (0.05 M) was deposited onto a pre-polished L-shaped glassy carbon working electrode (diameter, 4 mm) and dried under ambient conditions. Subsequently, 5 μL of 5% Nafion 117 solution was drop-cast onto the prepared electrode prior to electrochemical measurements.

Electrochemical measurements

All electrochemical measurements were conducted at room temperature using a three-electrode electrochemical setup. The working electrode (WE) consisted of either a Pt clip with Ag superlattice substrates or a L-shaped electrode deposited with Pt/C. A Pt wire was used as the counter electrode (CE), and an Ag/AgCl (3.5 M KCl) electrode served as the reference electrode (RE). The electrolyte solution was acidic (pH1.47) and composed of 30 mL of H₂SO₄ (0.1 M) and Na₂SO₄ (0.5 M).

Before measurements, the Ag superlattice substrates were cleaned via cyclic voltammetry (CV) at a scan rate of 100 mV s⁻¹. Linear sweep voltammetry (LSV) measurements were performed between 0.2 V and -1.2 V vs. Ag/AgCl with a scan rate of 10 mV s⁻¹. For the stability test, LSV measurements were repeated under identical conditions for 60 cycles. All polarization curves were normalized by the respective electrochemical surface area (ECSA) to ensure fair comparison. Electrochemical impedance spectroscopy (EIS) was carried out with a 10 mV_{RMS} amplitude in a single sine mode, sweeping frequencies from 10⁶ Hz to 0.1 Hz at 10 points per decade. The impedance spectra were fitted using the electrochemical circle fit function in Nova 2.1.7 software from Metrohm.

The applied potential vs. Ag/AgCl was converted to the reversible hydrogen electrode (RHE) scale using the equation:

$$E(RHE) = E(Ag/AgCl) + E^0(Ag/AgCl) + (0.059 \times pH)$$

where $E(Ag/AgCl)$ is the applied potential, $E^0(Ag/AgCl)$ is the standard potential for the 3.5 M Ag/AgCl electrode (0.205V), and pH is the electrolyte's pH.

The Tafel slope value was calculated by fitting the polarization curve to the Tafel equation:

$$\eta = b \log|j| + \alpha$$

where η , b , j , and α are the overpotential, Tafel slope, current density, and a constant, respectively.

Electrochemical surface area (ECSA) measurements

The electrochemical surface area (ECSA) was determined using a widely adopted method based on the electrochemical double-layer capacitance (C_{dl}), measured via cyclic voltammetry (CV). An acidic electrolyte (pH 0.17) composed of 30 mL H₂SO₄ (1 M) and Na₂SO₄ (0.5 M) was used for the ECSA measurements. CV curves were recorded over the potential range of 0.1 V to 0.45 V (vs. RHE) for all Ag superlattice substrates or 0.2 V to 0.55 V (vs. RHE) for Pt/C, where no Faradaic current was present. The measurements were performed at scan rates of 10, 20, 40, 60, 80, 100, 120, and 140 mV s⁻¹.

The double-layer capacitance was calculated using the formula:

$$C_{dl} = \frac{j}{r}$$

where j is the current density and r is the scan rate.

ECSA can be calculated as:

$$ECSA = \frac{C_{dl}}{C_s}$$

where C_s is the specific capacitance value for a flat standard with 1 cm² of real surface area.

The average specific capacitance of 0.035 mF cm^{-2} in $1 \text{ M H}_2\text{SO}_4$ was used to calculate the ECSA.^[61] This value was based on reported capacitances of various metallic surfaces (including Pt, Ni, Cu, Carbon, Mo, and CuAu) in H_2SO_4 solutions.^[62-71]

Faradaic efficiency (FE) calculation and hydrogen gas (H_2) quantification

Hydrogen gas was quantified through chronoamperometry (CA) performed over a fixed duration with an applied potential at -0.7 V vs. RHE. The total charge (Q) passed during the experiment was calculated from the resulting current over the specific time period.

The Faradaic efficiency was calculated using the following equation:

$$FE = \frac{n(\text{H}_2)_{\text{actual}}}{\frac{Q}{2F}}$$

where $n(\text{H}_2)_{\text{actual}}$ is the actual amount of hydrogen gas (in mol) generated (quantified using gas chromatography), Q is the total charge (in C) passed during the reaction, and F is the Faraday constant (96485 C mol^{-1}).

Turnover frequency (TOF) calculation

The TOF values ($\text{H}_2 \text{ s}^{-1}$) are calculated with the following method that was previously reported in the literature^[72]:

$$TOF = \frac{I}{2nF}$$

where I is the current density extracted from linear sweep voltammetry curve (in A), n is the number of active sites, and F is the Faraday constant (96485 C mol^{-1}).

We estimate n from cyclic voltammetry (CV) measurements carried out in $0.5 \text{ M Na}_2\text{SO}_4 + 0.1 \text{ M H}_2\text{SO}_4$ (pH 1.47) between -0.6 V and 1 V vs. RHE at 50 mV s^{-1} . We integrate the voltammetric charge (Q) over one CV cycle and calculate the upper limit of active site density using:

$$n = \frac{Q}{2F}$$

Material characterization

Scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX) characterizations were performed with JEOL-JSM-7600F microscope equipped with Oxford Instruments X-Max 50 mm^2 EDS detector and AZtec v.5.1 software. Pt film was sputter-coated with JOEL JFC-1600 Auto Fine Coater. X-ray photoelectron spectroscopy (XPS)

characterizations were measured using a Phoibos 100 spectrometer with a monochromatic Al X-ray radiation source. All XPS spectra were calibrated against high resolution C 1s peak at 284.5 eV. X-ray diffraction (XRD) patterns were recorded using Rigaku Miniflex 600C with Cu K α irradiation. Electrochemical measurements were conducted with Metrohm Autolab potentiostat fitted with the FRA32M impedance analyzer. Contact angles were measured on a Theta Lite tensiometer equipped with a Firewire digital camera. Static contact angle was measured with a 4- μ l ultrapure sessile water droplet. Elemental composition analysis was conducted using a Thermo Scientific iCAP 6500 model ICP-OES. Conductive atomic force microscopy (C-AFM) characterizations were performed using Bruker Dimension Icon XR fitted with PeakForce TunaTM module and current sensitivity of 20 nA V⁻¹. NCS19/Cr-Au tip was used in AFM characterizations. The generated hydrogen gas was analyzed by injecting 0.8 mL of the reactor's headspace gas into a gas chromatograph (SRI Multiple Gas Analyzer #5) equipped with a thermal conductivity detector (GC-TCD) and argon as carrier gas.

Acknowledgements

H.K.L. thanks the funding supports from the Singapore Ministry of Education (AcRF Tier 1 RG92/24), A*STAR Singapore (MTC IRG M23M6c0098), the National University of Singapore Center of Hydrogen Innovation (CHI-P2022-05), and the Nanyang Technological University start-up grants. The research was conducted as a part of NICES (NTU-IMRE Chemistry Lab for Eco Sustainability; REQ0275931), a joint research initiative between Nanyang Technological University (NTU) and Institute of Materials Research and Engineering (IMRE) from Agency for Science, Technology, and Research (A*STAR).

Data Availability Statement

Data will be made available on request.

Received: ((will be filled in by the editorial staff))

Revised: ((will be filled in by the editorial staff))

Published online: ((will be filled in by the editorial staff))

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